The American Ceramic Society

40th International Conference & Exposition on Advanced Ceramics and Composites

ABSTRACT BOOK

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Introduction

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How to Use the Abstract Book

Refer to the Table of Contents to determine page numbers on which specific session abstracts begin. At the beginning of each session are headings that list session title, location and session chair. Starting times for presentations and paper numbers precede each paper title. The Author Index lists each author and the page number on which their abstract can be found.

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Monday, January 25, 2016

Plenary Session

Plenary Session

Room: Coquina Salon D
Session Chairs: Soshu Kirihara, Osaka University; Andrew Gyekenyesi, Ohio Aerospace Institute

9:00 AM

(ICACC-PL-001-2016) Challenges and Opportunitites for 21st Century Research & Development

J. Wadsworth*[1]; 1. Battelle Memorial Institute, USA

Over the course of time, advances in materials and their manufacture have paced the rate of economic well-being and national security. The case can readily be made that those countries that have excelled in advancing materials science have been rewarded. As we contemplate the future there are several areas that will drive the need for continued innovation. World population growth, coupled with increased standard of living expectations and urbanization, will drive energy, food, and water demand to unprecedented levels. Meeting these demands will be accompanied by environmental impacts, health concerns, and conflicts. It is instructive to understand these areas of concern and to anticipate how developments in materials will be used to alleviate them. The evolution of R&D investment worldwide also sheds a light on where these developments will likely take place. Many countries are aggressively investing in R&D and challenging America's long-standing scientific leadership. In order to maintain its position, the U.S. needs to develop a comprehensive strategy that combines increased and diversified funding, continued investment in world-leading analytical and computational tools, and a focus on educating the future workforce.

9:40 AM

(ICACC-PL-002-2016) From Idea to Product: Sustainable Cycle

H. Kim*[1]; 1. Korea Institute of Materials Science, The Republic of Korea

Ceramic materials seem to be the key to the convenience of daily life of the public and even the key to the economic development of the country. Most researchers try to prove their ideas by experiments and submit the results for publication in journal and/or filing the patent. The idea must be transformed to the real product in order to bring the convenience of daily life of the public. When the idea is sold by industry to generate products, which benefits the daily life of the public, who provides the research fund to national labs by paying tax; this is a real sustainable cycle. Korean ceramic industries has a strong end users such as semiconductor industry, display industry, cellular phone manufacturers, automotive industry and so on. Some statistics on the relationship between suppliers and end users will be reviewed and some examples on the sustainable cycle will be introduced.

10:40 AM

(ICACC-PL-003-2016) Function through Defects: from ceramics to electrochemistry

J. Maier*[1]; 1. Max Planck Institute for Solid State Research, Germany

Electrochemistry is concerned with the conversion of chemical (electrical) into electrical (chemical) energy or information, and hence deals with applications such as batteries, fuel cells and sensors. Solid electrolytes and electrodes are prototype examples of functional ceramics. The first part of the lecture addresses the role of point defects as the active particles (charge carriers, acid-base- or, redox-active centers), and systematically sets out the adjusting screws to tune ionic and electronic conductivities (solid state ionics). The second part emphasizes the special role of higher-dimensional defects, in particular interfaces, in setting boundary conditions for charge carrier redistribution, transport and transfer. Nature and spacing of interfaces, and hence size, are additional powerful control parameters (nano-ionics). Such "heterogeneous doping" relying on the purposeful introduction of higher dimensional defects, is - often more powerfully than the classical homogeneous doping – able to turn insulators into conductors, electronic conductors into ionic conductors or vice versa. The third part stresses that - beyond the sheer tuning of particles' properties, and of their size and shape - also the topology of particle and phase distribution within the functional material is of high significance (electrochemical integrated circuits). Here taking advantage of the various nano-scale dimensionalities as realized in nanodots, nanowires and nanosheets, is key. It is shown at various examples, chiefly in the context of batteries, how these ceramic strategies can be employed to optimize electrochemical functions or to even generate novel properties.

11:20 AM

(ICACC-PL-004-2016) SiC-SiC Ceramic Matrix Composites in Jet Engines

S. M. Correa*[1]; 1. GE Aviation, USA

SiC-SiC Ceramic Matrix Composites (CMCs) have moved out of research laboratories into the commercial mainstream over the last five years. Currently over 10,000 jet engines incorporating CMCs in the "hot section" are on order, with the first entering airline service later this year. Why CMCs? Gas-turbines operate more efficiently at higher temperatures and pressures but, after 75 years of evolution, the industry has run into the temperature limits of even the most advanced metal superalloys. CMCs provide much higher temperature capability, weigh about a third as much, and survive better in dusty/sandy regions of the world – all of which significantly expand the usage envelope. We will cover the state-of-the art in design and the large amount of testing under way - at the level of coupons for materials data bases, components in rig tests, and engines in ground-based and flight tests. We will describe the associated high-volume manufacturing processes including Silicon Carbide Fiber, Tow Coating, Unilateral Tape, furnace operations including Melt Infiltration, and Environmental Barrier Coatings. We will conclude by summarizing requirements for the next generation of CMC systems, aimed at additional temperature capability.

40th Jubilee Symposium: Engineered Ceramics: Current Status and Future Prospects

Engineered Ceramics I

Room: Coquina Salon C
Session Chairs: Michael Halbig, NASA Glenn Research Center; Tatsuki Ohji, National Institute of Advanced Industrial Science and Technology (AIST)

1:30 PM

(ICACC-JUB-001-2016) A Retrospective and a Path Forward for Advanced Engineered Ceramics (Invited)

J. W. McCauley*[1]; 1. Army Research Laboratory/Johns Hopkins University, USA

In 1988 I gave the second James I. Mueller Memorial Lecture presenting the factors I believed were important for the successful commercialization of advanced structural ceramics: cost of final products, reliability and reproducibility. Examples presented included Self-propagating High-temperature Synthesis (SHS) for cost reduction, using a materials by design approach for increased toughness ceramic matrix composites and increased emphasis on quality control in a "Materials Information Technology" framework using a unique signature concept. These general ideas are still sound, but what has exponentially changed is the ability for materials design using modeling and simulation at multiple scales,

materials characterization tools and data storage capabilities. One example is the new Army Research Laboratory Enterprise for Multiscale Research in Materials Collaborative Research Alliance program "Materials in Extreme Dynamic Environments (MEDE)" conducted at ARL and at a University consortium managed by Johns Hopkins University. This program contains the following five critical cross-cutting core elements focusing on magnesium, boron carbide, UHMWPE (Ultra-High Molecular Weight PolyEthylene), and S-glass/epoxy: advanced experimental techniques, modeling and simulation, bridging the scales, material characteristics and properties at multiple scales, and synthesis and processing.

2:00 PM

(ICACC-JUB-002-2016) Materials by Design: The Example of Metal-Organic Frameworks (Invited)

J. J. Petrovic*[1]; 1. Petrovic and Associates, USA

Metal-organic frameworks are a new class of nanoporous crystalline materials that are chemically constructed by linking inorganic "lattice points" with organic linker struts. A wide variety of such materials may be designed and synthesized with targeted functional properties. Some current materials of this type will be described and their use discussed for the storage of gases such as hydrogen and carbon dioxide. Metal-organic framework materials may serve as an inspiration to develop designed advanced ceramic materials composed of ceramic-like "lattice points" and/or ceramic-type linkages.

2:30 PM

(ICACC-JUB-003-2016) Failure of Ion Conducting Materials by Internal Precipitation (Invited)

A. V. Virkar*[1]; 1. University of Utah, USA

Most of the fracture mechanics literature discusses fracture under remote load which is applicable to numerous practical situations. Under such conditions, the size of the crack is much smaller than the region of nearly uniform stress-field the crack experiences. When the condition of criticality is reached, catastrophic fracture usually occurs. There are some technological applications involving electrochemical systems, such as fuel cells and batteries, in which cracking occurs in a stable manner and without the presence of a remote stress-field. This cracking occurs due the precipitation of gas or a metal inside the electrolyte. The corresponding fracture mechanical problems involve fracture under local load. This type of fracture is not catastrophic but occurs in a stable manner. Also, such fracture cannot be prevented or suppressed by the conventional notion of increasing strength or toughness. In order to prevent or suppress failure under electrolytic conditions, it is necessary to design materials with suitable ion and electron transport properties. This talk is on fracture under internal load. Also, the usual approaches of increasing fracture toughness or strength does little to improve reliability. Rather, fundamentals ionic and electronic transport determine whether or not failure will occur. Examples of both anion and cation conductors will be described.

3:20 PM

(ICACC-JUB-004-2016) Smart Advanced Ceramic Materials for energy and environmental technology (Invited)

A. Michaelis*[1]; 1. Fraunhofer IKTS, Germany

Advanced ceramic materials offer enormous potential for innovations in the fields of efficient energy conversion and storage, propulsion systems, smart structures, sensor technology as well as environmental technology. The joint application of structural and functional ceramic technology allows for unique combination of electronic, ionic (electrochemical) and mechanical properties enabling the development of new, highly integrated systems in the above mentioned fields. However, due to the specific brittle failure mechanism of ceramic materials (Griffith behavior) the production of ceramic components requires new approaches for non destructive in-line testing. This is illustrated with specific examples for smart systems development for Fuel Cell, batteries and ceramic membranes. As first example, high temperature fuel cell systems development for both mobile and stationary applications are presented. Since the load following capability of fuel cells is limited, we also develop new ceramic based storage systems. Examples for development of Li-Ion batteries as well as high temperature NaNiCl batteries are presented. As an example for the potential of ceramic materials in the field of environmental technology, ceramic membranes are discussed. Such membranes can be used for micro-, ultra- or nano- filtration of liquids and gases. For this, a control and reduction of pore sizes below the 1 nm range is required.

3:50 PM

(ICACC-JUB-005-2016) Custom Mechanical Strength Test Specimens for Brittle Materials and Their Components (Invited)

A. Wereszczak*[1]; 1. Oak Ridge National Laboratory, USA

When conventional or standardized test methods cannot be used, it becomes necessary to develop customized test methods to evaluate the mechanical properties of brittle materials used in structural applications. This presentation presents several examples of customized and unconventional test methods used successfully to evaluate the tensile strength of brittle materials. These test methods include: the C-sphere, sectored flexural, serpentine bending, anticlastic bending, miniature bend bar, concurrent electric field ball-on-ring, and laser shock tests. Each of the tests is briefly overviewed in context to the application that motivated their development and the sought applied tensile stress state. *This manuscript has been authored by UT-Battelle, LLC, under Contract No. DE-AC05-00OR22725 with the U.S. Department of Energy.*

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(ICACC-JUB-006-2016) Thermal Protection Materials and Systems: Past and Future (Invited)

S. M. Johnson*[1]; 1. NASA-Ames Research Center, USA

Thermal protection materials and systems (TPS) have been critical to fulfilling humankind's desire to explore space. Composite and ceramic materials have enabled the early missions to orbit, the moon, the space station, Mars with robots, and sample return. Crewed missions to Mars are being considered, and this places even more demands on TPS materials. This talk will give some history on the materials used for earth and planetary entry and the demands placed upon such materials. TPs needs for future missions, especially to Mars, will be identified and potential solutions discussed.

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(ICACC-JUB-007-2016) Environmental Barrier Coating Development for SiC-SiC Ceramic Matrix Composites: Recent Advances and Future Directions (Invited)

D. Zhu*[1]; 1. NASA Glenn Research Center, USA

This presentation reviews the SiC/SiC major environmental and environment-fatigue degradations in simulated turbine combustion environments, and NASA environmental barrier coating system evolution for protecting the SiC/SiC Ceramic Matrix Composites for meeting the engine performance requirements. The presentation will review NASA EBC systems, EBC-CMC component system technologies for SiC/SiC ceramic matrix composite combustors and turbine airfoils, highlighting the temperature capability and durability improvements in simulated engine enviornment conditions. This paper will also focus on the performance requirements and design considerations of environmental barrier coatings for next generation turbine engine applications. The development emphasis is placed on advanced candidate environmental barrier coating systems for SiC/SiC CMCs, their performance benefits and design limitations in long-term operation and combustion environments. The efforts have been also directed to developing prime-reliant, self-healing 2700F EBC bond coat; and high stability, lower thermal

conductivity, and durable EBC top coats. Major technical barriers in developing environmental barrier coating systems, the coating integrations with next generation composites having the improved environmental stability long-term fatigue-environment system durability will be described.

S1: Mechanical Behavior and Performance of Ceramics & Composites

Mechanics and Characterization

Room: Coquina Salon D

Session Chairs: Jonathan Salem, NASA Glenn Research Center; Gregory Morscher, The University of Akron

1:30 PM

(ICACC-S1-001-2016) Shape Memory and Superelasticity in Zirconia Ceramics (Invited)

C. A. Schuh*[1]; 1. Massachusetts Institute of Technology, USA

The monoclinic to tetragonal transition in zirconia has been widely studied because of its associated large shape and volume changes, and the mismatch stresses they can induce in polycrystals. However, when the sample size is reduced relative to the grain size, the effect is to reduce the constraints leading to transformation mismatch. In small samples that are oligocrystalline (i.e., having more free surface area than grain boundary area) or single crystalline, the full shape change of the transformation is realized across the specimen, opening the door to classical shape memory and superelasticity properties. This talk will review the concept of oligocrystalline shape memory materials, with special emphasis on zirconia ceramics. As a class of smart materials, shape memory ceramics offer a number of unique features that are worthy of pursuit in a technological sense.

2:00 PM

(ICACC-S1-002-2016) Adventures and Misadventures in Applying ASTM Standard C 1421 to Measurements of the Fracture Toughness, K_{Ic}, of Glasses

G. D. Quinn*[2]; J. Swab[1]; 1. Army Research Laboratory, USA; 2. NIST, USA

ASTM Standard C 1421 for fracture toughness was originally prepared in 1997 for advanced structural ceramics. In principle, it may be used with other ceramics, glass ceramics, and brittle filled-resin composite materials. This presentation will show new surface crack in flexure (SCF) and single-edged precracked beam (SEPB) data for six glasses. The results address questions that have lingered for many years: Just what is the K_{Ic} of glass? How do the bend bars specimens compare to larger traditional configurations such as double cantilever beam or double torsion? Does testing have to be done in an inert environment? Does testing have to be done at a fast rate? Does crack healing complicate matters?

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(ICACC-S1-003-2016) A Review of Hydrostatically Pressurized Tube Test for Hoop Tensile Strength from Ambient to Elevated Temperatures at UDRI

L. Chuck*[1]; S. M. Goodrich[1]; C. D. Barklay[1]; 1. University of Dayton, USA

In 1992, the University of Dayton Research Institute developed a method to hydrostatically pressurize a ceramic tube to measure the high temperature hoop tensile strength at 1000 °C in vacuum. The high temperature tube test was hydrostatically pressurized with molten glass. Since then, this method has been used successful for both monolithic and composite ceramic tubes at elevated temperatures, as high as 1500 °C. High temperatures hoop tensile strength has been measured for many ceramics, such as SiC, Al_2O_3, Ox/Ox, SiC/SiC, SiC/C, C/SiC, etc. At room temperature, hoop tensile strength testing of tubes was pressurized using a visco-elastic material, such as modeling clay, initially, and then oil based putty. The pressurized tube test to obtain the hoop tensile strength will be reviewed that describes tube specifications, test fixtures, and test procedure. Benefits realized has been the reduced safety risk from catastrophic tube rupture, minimal specimen fabrication, and ease of Weibull size scaling testing, elimination of specimen alignment, and efficient test gage volume to specimen volume.

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(ICACC-S1-004-2016) Characterization of Deformation and Damage in Porous Bulk and Film SOFC Components via Spherical Indentation and Simulation

Z. Chen*[1]; A. Atkinson[1]; N. Brandon[1]; 1. Imperial College, United Kingdom

The aim of this work is to present the methodology to characterize deformation and contact damage initiation and evolution in porous bulk and film components used in solid oxide fuel cells, based on indentation and simulation. Spherical indentation tests at a broad range of loads (0-12000 mN) were carried out on porous bulk and film electrodes with different levels of porosity, and on multilayer cell systems. An axisymmetric model based on the Gurson model used for porous materials was developed to simulate the indentation processes. Elasticity and hardness of each component were reliably determined via both experiments and modeling. Inverse analysis via comparison of experimental indentation response curves and simulation-generated curves shows a very different relation between hardness and yield stress, compared with dense materials. Cracking behavior was examined and appropriately explained by FEM results. Further insight of the deformation and damage behavior was also obtained based on microstructural study using FIB-SEM slice and view. Fracture toughness determined by numerical method shows excellent agreement with the results measured using other conventional methods. Overall, the study shows that the model developed in this work is highly applicable for the description the deformation and damage characteristics in porous bulk and film ceramics.

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(ICACC-S1-005-2016) Stable fracture testing of brittle materials

C. Baudin*[1]; A. Garcia-Prieto[1]; 1. Instituto de Cerámica y Vidrio, CSIC, Spain

Stable fracture is necessary to get reliable and accurate fracture toughness data. The unstable crack growth is avoided by adaption of the testing machine and the specimen geometry to the material to be tested. Stable fracture testing of brittle materials is not usually performed because it is considered as extremely difficult to realize. Displacement controlled bending test of parallelepiped specimens with straight trough notches (SENB) is one of the simplest ways of testing and is widely used for ceramics. However, the analysis of the Griffith locus of SENB specimens in three points bending demonstrates that extremely stiff equipment and very deep notches are necessary to reach stability. Contrary to displacement, parameters that increase during the whole fracture test such as the crack mouth opening displacement (CMOD) are suitable as control parameters to reach stable fracture. In our laboratory, a special set up for the routine stable fracture testing of brittle ceramics using SENB in three points bending and CMOD as control parameter has been developed. The theoretical analysis as well as the developed equipment and results for materials with a wide spectrum of fracture characteristics -extremely brittle fine grain Mg-Al spinel and alumina, mullite presenting slow crack growth, porous TCP materials, refractories and nanocomposites- are presented and the effect of experimental parameters on the obtained properties is discussed.

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(ICACC-S1-006-2016) Shear tests on joined materials: a comparison between torsion and ISO 13124

M. Ferraris*[2]; L. Goglio[2]; M. Salvo[2]; F. Smeacetto[2]; S. Delapierre[2]; V. Casalegno[2]; S. Gonczy[3]; C. Henager[5]; T. Hinoki[4]; Y. Katoh[1]; 1. Oak Ridge National Laboratory, USA; 2. Politecnico di Torino, Italy; 3. Gateway Materials Technology, USA; 4. Kyoto University, Japan; 5. Pacific Northwest National Lab, USA

Results of an experimental investigation on adhesive and glass ceramic joined SiC and steel tested in torsion will be presented and compared to one recent standard (ISO 13124) which has been proposed for testing the shear bond strength of ceramic-ceramic, ceramic-metal, and ceramic-glass joints at ambient temperature by shear tests on cross-bonded test pieces. Advantages and disadvantages of these tests are discussed and compared with models, with particular focus on the measurement of pure or apparent shear strength. Modelling results help understanding the failure mode and therefore the meaning of the measured strength.

4:10 PM

(ICACC-S1-008-2016) A Test Method to Measure the Tensile Strain of Ceramic Multi-Filament Fiber Tow from Ambient to Elevated Temperatures Using Fraunhofer Laser Diffraction

L. Chuck*[1]; S. M. Goodrich[1]; C. D. Barklay[1]; 1. University of Dayton, USA

In 1990, the University of Dayton Research Institute developed a method to measure the tensile creep strain on cylindrical and flat panel tensile specimens based on Fraunhofer diffraction. The optical extensometer, made from SiC, attaches mechanically using friction without specimen damage. In 2011, this method was modified to eliminate the original clip-on feature to accommodate the delicate multifilament ceramic fiber tow, while retaining the attachment method via friction without tow damage. The metal prototype extensometer for multi-filament fiber tow was evaluated where the measured elastic moduli compared very well with published values for nylon monofilament, single strand copper, nichrome, and tantalum wires, and multi-filament carbon fiber at room temperature. After prototype evaluation, SiC extensometer was made and used successfully since 2012 without attachment damage to measure the elastic modulus of multi-filament SiC from room to over 1300 ºC in air with excellent auto-temperature compensation. The technique will be presented and select results will be present with excellent elastic modulus reproducibility.

4:30 PM

(ICACC-S1-009-2016) Modeling analysis of the four point bending test of V SiC Interfacial Joints for Fusion Applications

Y. H. Abdelmoaty*[1]; G. Vasudevamurthy[1]; 1. Virginia Commonwealth University, USA

Graded transition joining technique based on coating vanadium metal on SiC surface, and the sample will be heat treated for appropriate time and temperature in order to form interlayers of both metal silicide and carbides with gradient in thermal expansion, which called 'Graded Transition Zone'. From chemical point of view, Vanadium is a reactive metal with SiC which perform stable phases of silicide and carbides. The advantage of using coating rather than powder are forming a less porous joint with better mechanical properties. In this paper, A study for the mechanical properties of formed interlayers at different time and temperature and decide the most suitable condition to form the best mechanical properties for the joint and optimal gradient in thermal properties through the interlayers. Identifying the interlayer by use X-ray diffraction and analysis for concentration gradient data obtained by EDX studying the ternary phase diagram Si-C-V. AFM image for the surface has been taken. Next step includes hot pressing two SiC base materials within Graded Transition zone with a thin layer of vanadium in between them. Using appropriate pressure, temperature and time based on previous published works. As a final point; using the previous data collected from hot pressing the joints such as formed phases and thicknesses to simulate the joint using FEM (ANSYS®).

4:50 PM

(ICACC-S1-010-2016) Prediction of Residual Deformation in Thermosetting Composites Due to Cure

O. Kravchenko*[1]; S. Kravchenko[2]; R. Pipes[2]; 1. Case Western Reserve University, USA; 2. Purdue University, USA

Deformations induced by chemical and thermal shrinkage in thermoset carbon fiber composite during the cure cycle were studied. Chemical shrinkage is produced by the cross-linking reaction in the thermosetting polymer resin, whereas thermal shrinkage is a result of temperature change. Polymer material model included cure kinetics, unconstrained chemical shrinkage, glass transition temperature and modulus development. Homogenized composite properties were calculated using a self-consistent field micromechanics model that yielded composite properties as a function of cure state and temperature. The material model was employed to study the thermo/chemical response of a bi-lamina strip consisting of $[0/90_4]$ laminate. The sample developed curvature due to the differential expansion/shrinkage in the 0 and 90-degree layers. Fixed-free boundary conditions were used to expose constrained shrinkage soon after polymer gelation. Comparison of the end deflection and strip deflection profiles during the cure cycle of model predictions and experimental results agreed closely. It was shown that the residual deformation in the bi-lamina strip due to chemical shrinkage contributed up to 40% of the overall residual deformation. The material model was also used to predict the associated residual stresses at the microscale in a composite material and to investigate the cure history dependence of the residual deformation.

5:10 PM

(ICACC-S1-011-2016) An Experimental Study on Fabrication, Mechanical Behavior Characterization and Microstructural Evolution in Glass-Metal Joints

R. Joshi*[1]; R. Chhibber[2]; 1. IIT Jodhpur, India; 2. Indian Institute of Technology Jodhpur, India

The Glass-Metal Joints play an indispensible role in many applications such as, concentrating solar power, nuclear and electronics industry. The aim of the present work is the fabrication of glass-metal joints using borosilicate glass with stainless steel and copper. The joints were fabricated using resistance heating and mechanical behavior of these fabricated joints was determined. Single lap joint between glass and metal was used in order to measure the strength of glass-metal joint. The hardness evaluation of these fabricated joints was also carried out. Further oxidation studies were carried out to examine the role of oxide formation in the joints using X- Ray Diffraction measurements. The mechanical behavior and microstructure evolution of the stainless steel to borosilicate glass joint and copper to borosilicate glass joint was analysed and compared.

S2: Advanced Ceramic Coatings for Structural, Environmental, and Functional Applications

Thermal Barrier Coatings I

Room: Coquina Salon H
Session Chairs: Douglas Wolfe, Pennsylvania State University; Nadin Schlegel

1:30 PM

(ICACC-S2-001-2016) Development of Advanced Thermal Barrier Coatings with Improved Temperature Capability (Invited)

G. Witz*[1]; H. Bossmann[1]; J. Sopka[1]; M. Schaudinn[1]; S. Mihm[1]; T. Buecklers[1]; C. Kunz[1]; 1. Alstom, Switzerland

Continuously increasing hot gas temperatures in heavy duty gas turbines, lead to an increased surface thermal loading of the hot gas path materials. Thermal barrier coatings are used to reduce the superalloys temperature and the cooling needs. Until now 6-8 wt% yttria stabilized zirconia has been the first choice material for such applications, but it is slowly reaching its maximum temperature capability due to the phase transformation at high temperature and possibly to sintering. In Alstom new TBC materials have been developed thorough a multi-stage selection process, starting from a pre-selection of more than 30 materials. After carefully reviewing these material properties either through literature or laboratory tests, five materials have been selected for coating manufacturing and laboratory testing. Based on the laboratory test results, two materials have been selected for engine testing, in a first step in Alstom Birr test engine and afterwards in a customer engine. For such tests the coating thickness has been increased such to achieve coating surface temperature ~100K higher than with a standard thermal barrier coating system. Both coating performed as expected both in Birr and in the customer engine. One of these coating has been released for product development and is currently used for some of the part having the highest thermal load in the most recent Alstom gas turbine rating.

2:00 PM

(ICACC-S2-002-2016) Advanced Thermal Barrier Coating (TBC) Design Architectures and Compositions with Improved Durability and Performance

D. E. Wolfe*[3]; M. Schmitt[1]; M. D. Hill[2]; A. K. Rai[4]; D. Zhu[5]; 1. Pennsylvania State University, USA; 2. Trans-Tech, Inc., USA; 3. The Applied Research Laboratory, USA; 4. UES, Inc, USA; 5. NASA Glenn Research Center, USA

Electron Beam-Physical Vapor Deposition (EB-PVD) and Air Plasma Spray (APS) composite thermal barrier coatings (TBCs) have been deposited as an alternative to state of the art 7YSZ. These composites are primarily composed of a high rare earth cubic phase zirconate which is capable of elevated temperature operation beyond the ~1200°C thermal stability limitation of current 7YSZ coatings while exhibiting lower thermal conductivity. Due to the inherent low toughness of these cubic phase materials, a toughening phase has been added to improve the durability of these coatings. This study investigates the composites in terms of erosion durability, thermal cyclic durability, and thermal conductivity. It is shown that modifying the low toughness cubic matrix phase with a toughening tetragonal phase can increase erosion durability while maintaining sufficiently low thermal conductivity. Coatings were also investigated after heat treatment and similar behavior was observed. This observation is discussed in terms of microstructure and phase fraction evolution. To further investigate the erosion resistance mechanisms and the effects of porosity, additional tests were performed on coated samples as well as fully dense pellets to investigate the effects of density and microstructure.

2:20 PM

(ICACC-S2-003-2016) High Temperature Thermal Barrier Coatings (TBCs) With Enhanced Durability

M. Schmitt*[1]; A. K. Rai[3]; D. Zhu[2]; B. J. Harder[2]; D. E. Wolfe[4]; 1. Pennsylvania State University, USA; 2. NASA Glenn Research Center, USA; 3. UES Inc., USA; 4. The Applied Research Laboratory, USA

The rare earth zirconate pyrochlores ($RE_2Zr_2O_7$) continue to receive attention as an alternative to standard 7YSZ due to their higher phase stability limits (GZO: >1500°C, YSZ: ~1200°C) and lower thermal conductivities. Furthermore, their high rare earth content provides additional CMAS resistance which results in a high overall operating temperature regime. However, pyrochlores exhibit relatively low toughness values compared to 7YSZ, which results in poor erosion durability and therefore reduces their performance benefits. This work focuses on the development of advanced high temperature TBC materials which possess thermal conductivities much lower than 7YSZ but with a goal of improved durability over current rare earth pyrochlore replacement candidates. To achieve this goal, several toughening mechanisms are explored including intrinsic toughening methods such as expansion of the tetragonal field and strain field modification, as well as extrinsic methods focusing on microstructural modifications such as composites (layered and mixed phase), incorporation of secondary phases, and novel microstructures deposited via plasma spray – physical vapor deposition. These materials and coatings are characterized in terms of their erosion and thermal cyclic durability as well as thermal conductivity and compared to standard 7YSZ and $Gd_2Zr_2O_7$ coatings.

2:40 PM

(ICACC-S2-004-2016) Properties of Yttrium Aluminum Garnet (YAG) Thermal Barriewr Coatings Made by the Solution Precursor Plasma Spray Process

M. Gell*[1]; E. Jordan[1]; J. Roth[1]; B. Nair[2]; R. Kumar[1]; J. Wang[2]; C. Jiang[2]; 1. University of Connecticut, USA; 2. HiFunda LLC, USA

Yttrium aluminum garnet (YAG) coatings have been evaluated for many years as potential high temperature thermal barrier coatings (TBCs). The coatings have been made by air plasma spray (APS) and electron-beam physical vapor deposition processes. This past work has demonstrated that it is difficult to produce TBCs that have the stoichiometric YAG composition and with adequate thermal cyclic durability. The poor thermal cyclic durability is associated with the greater thermal expansion mismatch between the YAG TBC and the superalloy substrate, compared to standared yttria stabilized zirconia (YSZ). A relatively new process, Solution Precursor Plasma Spray (SPPS), has been used to successfully fabricate SPPS YAG TBCs. The SPPS YAG TBCs are stoichiometric and show superior thermal cyclic durability to APS YSZ TBCs. The favorable thermal cyclic properties are attributed the the strain-tolerant microstructure of SPPS TBCs provided by through-coating-thickness microcracks. The SPPS YAG TBCs are phase stable to 1900oC, the melting point of YAG. The elevated temperature thermal conductivity of SPPS YAG TBCs is less than that of APS YSZ and sintering studies have shown that SPPS YAG TBCs sinter at a much lower rate than APS YSZ. These properties and others that will be presented suggest that SPPS YAG TBCs have a 200oC temperature advantage compared to APS YSZ.

3:20 PM

(ICACC-S2-005-2016) Temperature Mapping of Air Film-Cooled Thermal Barrier Coated Surfaces Using Cr-Doped $GdAlO_3$ Phosphor Thermometry (Invited)

J. I. Eldridge*[1]; V. Shyam[1]; A. C. Wroblewski[1]; D. Zhu[1]; M. D. Cuy[2]; D. E. Wolfe[3]; 1. NASA Glenn Research Center, USA; 2. Vantage Partners, USA; 3. Pennsylvania State University, USA

It has been recently shown that the high luminescence intensity from a Cr-doped $GdAlO_3$ (Cr:$GdAlO_3$) thermographic phosphor enables non-rastered full-field temperature mapping of thermal barrier

coating (TBC) surfaces to temperatures above 1000°C. A major area of interest where this new capability can be applied advantageously is temperature mapping of air film-cooled TBC-coated surfaces. While infrared thermography has been typically applied to study air film cooling effectiveness, temperature accuracy depends on knowing surface emissivity (which may change) and correcting for effects of reflected radiation. Because decay time-based full-field phosphor thermometry is relatively immune to these effects, it can be utilized either instead of or as a calibration benchmark for infrared thermography. In this presentation, temperature mapping of air film-cooled TBC-coated surfaces is demonstrated for both scaled-up cooling hole geometries as well as for actual components in a burner rig test environment. The effects of thermal background radiation and flame chemiluminescence on the measurements are investigated, and the strengths and limitations of this method for studying air film cooling are discussed.

3:50 PM

(ICACC-S2-006-2016) Mechanical properties of Gd2Zr2O7 layers deposited by atmospheric plasma spraying

R. Vassen[1]; E. Bakan[1]; N. Schlegel*[1]; R. Muecke[1]; D. Mack[1];
1. Forschungszentrum Juelich, Germany

Gd2Zr2O7 is an attractive new thermal barrier coating material with improved temperature capability and reduced thermal conductivity compared to the standard material yttria partially stabilized zirconia (YSZ). Due to its rather low fracture toughness the material is typically applied as a double layer with an YSZ layer on the bond coat and on top a Gd2Zr2O7 layer. Such systems could demonstrate outstanding thermal cyclic performance especially in thermal gradient rigs. In the present investigation the mechanical behavior of free-standing Gd2Zr2O7 layers with different microstructures have be analyzed in the as-sprayed state and after annealing at 1400°C for different durations. The results of Young's modulus and viscosity determinations from 3 point bending tests are discussed with respect to the coating microstructure and are compared to data of YSZ coatings. The outcome of this comparison gives a first explanation for the improved performance of the double layer systems.

4:10 PM

(ICACC-S2-007-2016) Non-equilibrium Phases via Plasma Spray – Physical Vapor Deposition

G. Koszegi[1]; B. J. Harder[2]; M. Johnson*[1]; K. Faber[1]; 1. California Institute of Technology, USA; 2. NASA Glenn Research Center, USA

It is well recognized that thermal spray processes produce amorphous, partially amorphous or non-equilibrium crystalline coatings due to the rapid cooling of molten particles. In recent advances where plasma spray has been coupled with physical vapor deposition (PS-PVD), coatings are deposited from molten particles as well as from the vapor phase. The resultant coatings have microstructures that are columnar but also retain a significant fraction of non-equilibrium phases. In the current work, we describe PS-PVD-derived yttria-stabilized zirconia (YSZ) coatings, which include significant proportions of ZrO. The fractions of ZrO and highly defective YSZ are analyzed as a function of spray parameters using X-ray diffraction and Rietveld analysis. Stabilization kinetics through heat treatments in the range 350 to 700°C in air and inert environments are examined with thermogravimetric analysis and X-ray diffraction.

4:30 PM

(ICACC-S2-008-2016) Study of effect of Hafnium Addition on Oxidation Resistance of βNiAl Coatings Prepared by an In-situ Chemical Vapour Deposition Method

A. D. Chandio*[1]; P. Xiao[1]; 1. University of Manchester, United Kingdom

In this study, Hf was incorporated into βNiAl matrix on CMSX-4 superalloy by in-situ chemical vapour deposition (CVD) method. The Hf-doped βNiAl coating was oxidized isothermally at 1150°C for 100 hours in laboratory air. The coating formation, characterization and subsequent oxidation resistance were studied. Results demonstrated the successful preparation of Hf-βNiAl coatings using $HfCl_4$ by in-situ CVD method in two-steps. The coatings showed excellent repeatability and addition of Hf were found to minimise the substrate elemental migration. Oxidation tests showed improved adhesion of thermally grown oxide (TGO) in contrast to undoped reference βNiAl coating. The TGO morphologies and phases were significantly influenced by doping. Additionally, the TGO growth rate and residual stresses on Hf-βNiAl were observed to be lower in comparison to undoped βNiAl matrix.

4:50 PM

(ICACC-S2-009-2016) Phase Formation and Thermal Conductivity of Oxides in ZrO_2-La_2O_3-Gd_2O_3 Systems for TBC Application

S. Kim*[1]; S. Lee[1]; Y. Oh[1]; S. Lee[1]; H. Kim[1]; B. Jang[2]; 1. Korea Institute of Ceramic Engineering and Technology (KICET), The Republic of Korea; 2. National Institute of Materials Science, Japan

Rare-earth zirconate with $RE_2Zr_2O_7$ chemical formula has been one of the most candidate materials for future TBCs to replace YSZ. These zirconates have analogous cubic structures of pyrochlore and fluorite with a space group of Fd3(-)m for the former and Fm3(-)m for the latter. The low thermal conductivities of rare-earth zirconate oxides with these structures are attributed to the phonon scattering by point defects in the crystallographic structures. In this study, phase structures of selected oxide compositions in ZrO_2-La_2O_3-Gd_2O_3 systems, are investigated. Phase formation, microstructures, and thermal conductivities are examined with the densified samples among selected compositions. The possibilities of these oxides for TBC application are also discussed.

S3: 13th International Symposium on Solid Oxide Fuel Cells (SOFC): Materials, Science and Technology

Demonstration / SOFC-Systems

Room: Crystal
Session Chairs: Narottam Bansal, NASA Glenn Research Center; Shailesh Vora, U.S. Department of Energy

1:30 PM

(ICACC-S3-001-2016) Overview of DOE Office of Fossil Energy's Solid Oxide Fuel Cells Program (Invited)

S. D. Vora*[1]; 1. U.S. Department of Energy, USA

The overall objective of U.S. Department of Energy's Office of Fossil Energy Solid Oxide Fuel Cells Program, coordinated and managed by the National Energy Technology Laboratory, is the development of advanced power generation system technology. Specifically, the systems being developed, for central-station (>100 MWe) application, and based on solid oxide fuel cell (SOFC) technology, are to be cost-effective and operate with high electric efficiency. Historically, the fuel basis for this development has been coal. This continues to be the focus. However, the program is cognizant that the SOFC technology developed to meet design objectives could be adapted for implementation in advanced power generation systems fueled with natural gas. Thus, there could be strong synergy between efforts to develop advanced coal-fueled power generation and any parallel effort by the program participants to develop natural gas-fueled distributed-generation SOFC power systems. A natural gas-fueled distributed power generation system would provide early manufacturing and operational experience on large commercial scale that would benefit SOFC power system developments with both fuels. Solid Oxide Fuel Cells Program's status will be reviewed.

2:00 PM

(ICACC-S3-002-2016) Engineered Ceramics for Solid Oxide Fuel Cells (Invited)

N. Q. Minh*[1]; 1. University of California, San Diego, USA

Solid oxide fuel cells (SOFCs) have been developed as a clean and efficient technology to produce electricity from a variety of fuels. The SOFC has been considered for a broad spectrum of power generation applications with systems ranging from watt-sized devices to multi-megawatt power plants. At present, many of the applications have progressed to hardware demonstration and prototype/pre-commercial stages. The SOFC operating at high temperatures and incorporating a number of ceramic materials requires extensive engineering of the materials to develop an efficent, reliable and cost-effective technology. Key advances in engineering the ceramics have been made during 1976-2016, serving as the basis to improve the commercial viability of the technology, especially in three areas: (i) developing cost-effective and scalable manufacture techniques and processes for multilayered ceramics, (ii) engineering electrode porous microstructures to improve performance and develop certain transformational properties (e.g., direct fuel utilization), and (iii) tailoring ceramic/ceramic and ceramic/metal interfaces to minimize deleterious interactions, thus improving reliability for the SOFC. This paper reviews the advancements in fabrication process development, microstructure engineering, and interface optimization and discusses challenges and prospects for SOFC technology as a clean and efficient energy conversion technology in the future.

2:30 PM

(ICACC-S3-003-2016) Devlopment of SOFC Technology at Taiwan Institute of Nuclar Energy Research (Invited)

R. Lee*[1]; Y. Cheng[1]; T. Lin[1]; C. Hwang[1]; N. Hsu[1]; W. Hong[1]; C. Liu[1]; 1. Institute of Nuclear Energy Research, Taiwan

Taiwan Institute of Nuclear Energy Research (INER) has committed to developing the SOFC technology since 2003. Since then, substantial progress has been made on cell, sealant, stack, reforming catalyst, balance of plant (BOP) components as well as system integration. To date, fabrication processes for both planar anode-supported-cell (ASC) by conventional methods and metal-supported-cell (MSC) by atmospheric plasma spraying have been well established. Numerous stack tests were carried out with consistent and repeatable results. Several thousand hours performance tests were executed to evaluate the reliability and durability of system components. Recently, a compact INER-III SOFC power system has been demonstrated with an electric efficiency higher than 40%. Additionally, successive investigations are being conducted to extend its applications to the SOEC and biogas with satisfactory results.

3:00 PM

(ICACC-S3-004-2016) Solid Oxide Fuel Cell Technology Development at FCE

J. M. Barton*[2]; A. Torabi[2]; C. Willman[2]; H. Ghezel-Ayagh[2]; E. Tang[1]; 1. Versa Power Systems Ltd., Canada; 2. FuelCell Energy, Inc., USA

Fuel Cell Energy, inc (FCE) and its wholly-owned subsidiary Versa Power Systems (VPS) are advancing the current state of Solid Oxide Fuel Cell (SOFC) technology towards commercial deployment for efficient and nonpolluting generation of electric power from natural gas and other fuels such as coal. SOFC technology represents an important opportunity to utilize fossil fuels in an efficient and environmentally-friendly manner. SOFCs are scalable, efficient (not subject to Carnot cycle limitations), and produce low emissions compared to combustion-based electrical power generation technologies. SOFC power systems have the potential to achieve greater than 60 percent efficiency (based on higher heating value of fuel) and more than 97 percent carbon capture at a cost-of-electricity that is projected to be approximately 40 percent below that presently available through integrated gasification fuel cell (IGFC) systems with carbon capture. An attractive pathway to deployment of either IGFC or natural gas-fueled fuel cell (NGFC) systems is through near-term market opportunities in natural gas fueled distributed generation (DG) applications. The recent advancements in the base technology include: Demonstration of steady-state cell operation at 500 mA/cm^2 for over 2 years with less than 0.35% per 1000 hour degradation rate Demonstration of stable cell operation in high cathode gas humidity environment

3:40 PM

(ICACC-S3-005-2016) Advances towards direct ethanol solid oxide fuel cells (Invited)

F. C. Fonseca*[1]; M. C. Steil[2]; S. Georges[2]; F. B. Noronha[3]; P. Gélin[4]; 1. IPEN, Brazil; 2. CNRS LEPMI, France; 3. INT, Brazil; 4. IRCELYON, France

Direct ethanol solid oxide fuel cells (SOFC's) can play an important role in different applications due to relevant properties of such biofuel. Ethanol sums up the advantages of storage and distribution of liquid fuels with no significant composition variations or sulphur contamination. Moreover, it can be efficiently obtained from different biomasses and in some countries, such as Brazil and USA, bioethanol is readily available and widely distributed. However SOFC's still lack of a high-performance and durable anode for operation on carbon-containing fuels. Therefore, we have chosen adding an active layer to the standard Ni-cermet anode to ensure internal steam reforming, considering the gas phase reactions of ethanol at typical SOFC operating temperatures (~850°C). Such a catalyst is based on gadolinia-doped ceria with 0.1 wt% Ir (CGO-Ir). The initial results showing electrolyte-supported SOFC's using CGO-Ir layer running on ethanol for over one hundred hours were further confirmed by studying the durability of high-performance anode-supported samples. Such fuel cells were tested for more than 600 hours under dry ethanol, with current output similar to that on H_2, and without significant degradation due to carbon deposits, as inferred by post-test analyses. Recent results of fuel cells with CGO-based catalysts substituting Ni for Ir have shown promising results towards cost-competitive and durable direct ethanol SOFC's.

4:10 PM

(ICACC-S3-006-2016) Developing low-intermediate temperature fuel cells for direct conversion of methane to methanol fuel

A. Torabi*[1]; J. M. Barton[1]; C. Willman[1]; H. Ghezel-Ayagh[1]; 1. FuelCell Energy Inc, USA

The direct conversion of methane to liquid fuels and chemicals is highly sought, especially at low-scale to more effectively utilize remote natural gas resources. The objective of this project is development of a durable, low-cost, and high performance Low Temperature Solid Oxide Fuel Cell (LT-SOFC) for direct conversion of methane to methanol and other liquids, characterized by: a) Operating temperature < 500°C, b) Current density of > 300 mA/cm^2, in fuel cell mode and > 100 mA/cm^2 in liquid hydrocarbon production mode, c) Continuous operation of > 100 h, d) Cell area > 100 cm^2, e) Cell cost per rate of product output < 100,000/bpd, f) Process intensity of > 0.1 bpd/ft^3, g) Product yield and carbon efficiency > 50%, and h) Volumetric output per cell > 30 L/day

4:30 PM

(ICACC-S3-007-2016) Development of Materials for High Efficient Ceramic Electrochemical Hydrogen Compressor

H. Shimada*[1]; T. Yamaguchi[1]; H. Sumi[1]; K. Hamamoto[1]; T. Suzuki[1]; Y. Fujishiro[1]; S. Suzuki[2]; Y. Takahashi[2]; 1. National Institute of Advanced Industrial Science and Technology (AIST), Japan; 2. NORITAKE CO.,LIMITED, Japan

A hydrogen compressor consisting of electrochemical cells is considered to be one of ideal forms for compressing hydrogen because it can realize isothermal compression that is a very efficient way compared to conventional, mechanical compression technology. To realize high efficient ceramic compressor, it is necessary to develop materials such as high temperature and high pressure sealing

materials, and high performance proton conducting materials for the electrochemical cells. In this presentation, we will show the recent progress on the development of sealing materials and utilization technology of Ba (Ce, Zr)O_3 for the electrolyte of the electrochemical cells. The fabrication and performance of the cells are also discussed.

4:50 PM

(ICACC-S3-008-2016) Development of a hybrid SOFC-TE system

D. Rabin[1]; G. Shekel[1]; I. Azuelus[1]; D. Dadon[1]; Y. Gelbstein*[1]; 1. Ben-Gurion University of the Negev, Israel

The current research deals with the conversion of chemical and thermal energies into electricity. The conversion system will include a solid oxide fuel cell (SOFC), composed of a solid electrolyte based on dense Yttria Stabilized Zirconia (YSZ), enabling an effective O^- ionic conduction, in which temperatures in the 600-1000ºC range are developed, and a thermoelectric (TE) generator, converting some of the evolved thermal energy into electricity. A detailed description of the hybrid SOFC-thermoelectric concept, capable of achieving up to 90% total efficiency will be given. A presentation of the first stage of the electrolyte research will be given: a synthesis of YSZ compositions based on a ZrO_2 matrix doped by 3at% and 8at% of Y_2O_3 (e.g. 3YSZ and 8YSZ, respectively), in an arc-melting furnace followed by spark plasma sintering (SPS). While the first is known to obtain a tetragonal crystallographic structure, which is mechanically preferable compared to the cubic structure of the 8YSZ, its ionic conduction is known to be inferior. We will present a metallurgical route for stabilizing a tetragonal 8YSZ phase, which is expected to achieve a clear advantage in both the mechanical properties and the ionic conduction aspects.

S4: Armor Ceramics

Developments in Transparent and Glass Research

Room: Coquina Salon E

Session Chairs: Jerry LaSalvia, Army Research Laboratory; Steve Kilczewski, Army Research Laboratory

1:30 PM

(ICACC-S4-001-2016) Understanding Structure and Fracture Behavior of Glass from Its Elastic Response (Invited)

L. Huang*[1]; 1. Rensselaer Polytechnic Institute, USA

Elastic constants including the Poisson's ratio of glass are simple to define and easy to measure, and directly related to the interatomic forces and potentials, embodying its local structure and bonding information. Our *in-situ* light scattering studies show that changes in elastic moduli of glass in response to external stimuli can be used as a probe to gain insights into the atomic level structure of glass. We use elastic moduli and their dependence on temperature, pressure, and strain as critical inputs for developing and validating computer models of glasses with accurate short- and long-range interactions. These reliable computer models allow us to complement experiments to obtain detailed structure-property relationships, and to study the large-scale deformation of glasses. Our molecular dynamics simulations show that the failure mode of glass correlates strongly with the Poisson's ratio. A brittle-to-ductile transition was observed with increasing Poisson's ratio in all three families of glasses (silica, amorphous silicon and model metallic glasses) we studied. Therefore, the far-from-equilibrium fracture behavior of glass may be understood from its near-equilibrium elastic response.

2:00 PM

(ICACC-S4-002-2016) Nano-Ductility in Silicate Glasses is Driven by Topological Heterogeneity (Invited)

B. Wang[1]; Y. Yu[1]; M. Wang[1]; J. C. Mauro[2]; M. Bauchy*[1]; 1. University of California, Los Angeles, USA; 2. Corning Incorporated, USA

The existence of nanoscale ductility during the fracture of silicate glasses remains controversial. Here, based on molecular dynamics simulations coupled with topological constraint theory, we show that nano-ductility arises from the spatial heterogeneity of the atomic network's rigidity. Specifically, we report that localized floppy modes of deformation in under-constrained regions of the glass enable plastic deformations of the network, resulting in permanent change in bond configurations. Ultimately, these heterogeneous plastic events percolate, thereby resulting in a non-brittle mode of fracture. This suggests that nano-ductility is intrinsic to multi-component silicate glasses having nanoscale heterogeneities. Tuning the extent of heterogeneity would allow one to design tougher glasses fron the atomic scale.

2:30 PM

(ICACC-S4-003-2016) Gelcasting of transparent ceramics (Invited)

J. Klimke*[1]; 1. IKTS Fraunhofer Institute, Germany

Transparent polycrystalline ceramics have found various applications as transparent armors, infrared domes and laser hosts. Highly dense sintered ceramics by minimizing the defect concentration in the microstructure of the ceramics is a multi-stage optimization process, beginning with the selection and preparation of suitable starting materials and their preparation, compaction and sintering. Development progress on this path is particularly evident at transparent ceramics because major defects are immediately visible and even smallest pores reduce the measurable transmission through their contribution to light scattering. For the high demands of such ceramics, standard ceramic processes reach their limits because of remaining defects after pressing. On the other hand, liquid molding processes offer specific advantages in the preparation of the suspensions and the achievable homogeneity of the green body. In recent years, gelcasting received more and more attention in addition to the classic slipcasting processes. The paper focus on the relation between quality of the green bodies and transmission of transparent $MgAl_2O_4$ and Al_2O_3 ceramics prepared by gelcasting.

Developments in Synthesis and Processing I

Room: Coquina Salon E

Session Chair: Lionel Vargas, ARL

3:20 PM

(ICACC-S4-004-2016) Additive Manufacturing of ceramic-based composites (Invited)

N. Travitzky*[1]; P. Greil[1]; 1. University of Erlangen-Nuremberg, Germany

The wide-use of advanced ceramic-based materials depends on the availability of industrial processing routes to fabricate parts with required geometries. Owing to the inability of current technology related methods to produce complex-shaped ceramic parts with the desired microstructures and properties, Additive Manufacturing (AM) is becoming increasingly important approach. The mechanical properties of the materials fabricated by AM techniques in many cases are similar to the corresponding properties for commercially available ceramic-based materials fabricated by other methods. AM technologies can create parts using advanced materials superior to traditional ones. Layer-wise fabrication of the parts by AM techniques, however, can lead to unsatisfactory surface roughness. In order to improve the surface finish different methods have been studied. Dense ceramic-based composites with complex geometry have been fabricated via different AM processing routes.

Microstructure and mechanical properties of the fabricated composites have been investigated.

3:50 PM

(ICACC-S4-005-2016) Additive Manufacturing of Advanced Ceramic Components: What is possible today and what are the trends? (Invited)

T. Moritz*[1]; H. Richter[1]; U. Scheithauer[1]; M. Ahlhelm[1]; E. Schwarzer[1]; A. Michaelis[1]; 1. Fraunhofer IKTS, Germany

In the field of polymers and metals additive manufacturing (AM) methods are already used for manifold applications. Also for ceramic materials AM is gaining more and more importance, especially as resource efficient manufacturing method. Nevertheless, for ceramics AM methods are right at the beginning of technological development. AM offers the possibility to produce components of extremely complex geometry which cannot be obtained by conventional shaping routes. A main advantage of AM techniques can be seen in the tool-free shaping methodology. The range of possible applications is enormous ranging from medical, patient-specific instruments or implants to special tools or customized jewelry and luxury goods. The trend in AM in the field of ceramic materials goes to increasing the material portfolio, enlarging the dimensions of the manufactured products by increasing the building area of the AM machines and improving the properties of the manufactured components. For an increasing multifunctionality of ceramic components multi material applications for the combination of different properties will play a growing role. The presentation will give an overview of existing powder and suspension based AM methods including their strengths and drawbacks for attaining porous or dense material structures and their suitability for certain advanced ceramic materials.

4:20 PM

(ICACC-S4-006-2016) Optimization of Boron Carbide Ceramic Suspension Gels (CeraSGels) for Room Temperature Robocasting

W. J. Costakis*[1]; A. Diaz Cano[1]; L. Rueschhoff[1]; A. McEachen[1]; R. Trice[1]; J. Youngblood[1]; 1. Purdue University, USA

Robocasting is an additive manufacturing technique that can yield near-net complex ceramic structures at room temperature. It is proposed that this direct writing technology can be used to deposit boron carbide ceramic suspension gels (CeraSGel) in a layer by layer fashion to produce components for armor applications. Rheological properties can be tailored for optimal printing conditions through varying polymer molecular weight and boron carbide solid loadings. Formed green body pieces can be machined then sintered to achieve desirable mechanical properties making this method a cost effective alternative for producing complex shapes. The rheological behavior of suspensions along with microstructural and mechanical properties of robocast specimens was studied. Pattern generation for desired architectural control and other programing optimizations will be discussed. Powder content and polymer molecular weight were varied to determine the optimal composition for forming. The combination of the physical properties of boron carbide and the cost effective nature of robocasting make this method ideal for armor applications.

4:40 PM

(ICACC-S4-007-2016) Room-temperature injection molding of boron carbide suspensions

A. Diaz Cano*[1]; J. Youngblood[1]; R. Trice[1]; 1. Purdue University, USA

Room-temperature injection molding of rheologically designed ceramic suspension gels(CeraSGel) is proposed as an advanced processing technique to produce complex-shaped boron carbide components for armor applications via injection molding or casting. The rheology of CeraSGels was tailored by varying the proportions of the constituents to include water, polyethelenemine (PEI) and B4C powder. Common dispersants used for ceramics systems were tested via zeta potential and rheometry/rheology measuremnts in order to evaluate their electrostatic and steric effects. Ceramicolymer mass ratio was optimized to achieve the desired viscosity for forming. Different types and amounts of sintering aids were evaluated with attrition milled B4C powders to maximize density after sintering to 2000C for 1 hr and will be reported.

5:00 PM

(ICACC-S4-008-2016) Further Results on the Densification and Microstructure of Boron Carbide Utilizing Al- and Si-Based Additives

K. D. Behler*[1]; J. LaSalvia[1]; P. E. O'Shannessy[1]; K. A. Kuwelkar[2]; S. D. Walck[1]; 1. TKC Global and US Army Research Laboratory, USA; 2. Rutgers University, USA

The effects of Al- and Si-based additive compounds on the densification and microstructure of boron carbide has been investigated. Alumina powder and precursors (aluminum nitrate nonahydrate), silica (TEOS), boron oxide (boric acid) and their mixtures were added to H.C. Starck HS Grade boron carbide powder through a wet-chemistry process in an effort to improve mixing, particle coating and densification. Mixed powders were densified by hot-pressing between 1900°C – 2000°C using a ram pressure of 20 MPa for 1 – 3 hrs. Densification behavior was derived from monitoring the ram displacement using an LVDT and data acquisition system. Densities >99% were obtained in samples containing additives as measured by Archimedes's method. The resulting microstructures were characterized using scanning and transmission electron microscopy. Rietveld refinement was performed on XRD data to identify phases, such as SiC present in samples using TEOS as a precursor, and to determine the chemical composition of the pre- and post-densified powders. EDS was used to identify and map the Al- and Si-based phases within the microstructures. Experimental procedures and results are presented.

5:20 PM

(ICACC-S4-009-2016) Effect of Boron to Carbon Ratio on the Properties of Boron Carbide

T. L. Munhollon*[1]; K. Xie[2]; L. Farbaniec[2]; V. Domnich[1]; R. A. Haber[1]; 1. Rutgers University, USA; 2. Johns Hopkins University, USA

It is well known that boron carbide undergoes a large reduction in shear strength when subjected to pressures in excess of the Hugoniot elastic limit. Interest in boron rich boron carbide has grown in recent years as a high strength/low density material that maintains its strength at high pressures. Therefore, understanding the effect of the carbon concentration on the properties of boron carbide becomes critical. This work will focus on examining the chemistry, microstructure and select mechanical properties of boron rich boron carbide produced by boron additions during pressure assisted densification. A variety of experimental techniques have been employed including Raman microscopy, electron microscopy (both transmission and scanning) and micro and nano indentation. Electron microscopy is used to examine microstructures as well as chemistry variations (EELS) within the boron rich boron carbide. Raman spectroscopy examines whether stoichiometric variations exists from grain to grain as well as the existence of amorphous bands around indents produced using micro and nano indentation. Indentation results are used to estimate the transition velocities of the each boron rich boron carbide material.

5:40 PM

(ICACC-S4-010-2016) Size and Morphology Control of Nanocrystalline Boron Carbide Ceramic Powders via Study of Kinetics and Mechanism for CTR Reaction

P. Foroughi*[1]; Z. Cheng[1]; 1. Florida International University, USA

Boron carbide (B_4C) powders are synthesized by solution processing of boric acid and sucrose followed by pyrolysis and carbothermal reduction (CTR) reaction of the yielded molecular-scale mixed

boron trioxide (B_2O_3) and carbon. Previous efforts on synthesis of B_4C via CTR show noticeable morphology and particle size non-uniformity. Consequently, a profound understanding of critical factors to get uniform B_4C particles is essential. These factors are: CTR conditions (temperature, holding time, and heating/cooling rate), moisture absorption of pyrolyzed powders due to the aging and inert gas flow rate/vacuum level. The effects of all aforementioned factors on product yield, morphology and crystallite size in B_4C synthesis are studied. The products are characterized using techniques including X-ray diffraction (XRD) for phase analysis, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) for microstructure study. In addition, reaction kinetics of B_4C formation via CTR is studied in detail using quantitative X-ray diffraction (QXRD) combined with weight loss analysis, which helps determine the best reaction mechanism models (e.g., nucleation & growth versus just nucleation and no growth) that may lead to improved control of particle size and morphology for synthesized B_4C powders.

S6: Advanced Materials and Technologies for Direct Thermal Energy Conversion and Rechargeable Energy Storage

Sodium Batteries and Thermoelectrics

Room: Tomoka A

Session Chairs: Palani Balaya, National University of Singapore; Shigeto Okada, Kyushu University

1:30 PM

(ICACC-S6-001-2016) An overview of P2-sodium layered oxides in Na-Batteries (Invited)

C. Delmas*[1]; B. Mortemard[1]; J. Yoshida[1]; M. Guignard[1]; D. Carlier[1]; A. Wattiaux[1]; 1. ICMCB -CNRS, France

In the perspective of the development at very large scale of renewable energy systems that require stationary batteries, the prevailing parameters are the lifetime, the price and the material availability. From these points of view, sodium based batteries have to be investigated. For several years a lot of studies were carried out on P2 type layered oxides. One of the main interests of this structure is the existence of an ion conduction plane made of face sharing trigonal prims which exhibits a high ionic diffusivity. This structure is able to accommodate a lot of transition metal cations, allowing the optimization of the properties by cationic substitution. The electrochemical intercalation(de) of material with only one 3d cation (Co, V) shows the existence of a huge number of order/disorder transition; while in material with several 3d elements in the MO_2 slab most of them have disappeared thank to the 3d statistical distribution. The shape of the electrochemical curves gives also a map of the various redox processes occurring during charge and discharge. A general overview of the structural and electrochemical behaviour of this material family will be presented with a special focus on our recent results.

2:00 PM

(ICACC-S6-002-2016) Materials Trend Development in Sodium Batteries from Oxides to Phosphates (Invited)

I. Belharouak*[2]; R. Essehli[2]; H. Ben Yahia[2]; Y. Sun[1]; 1. Hanyang University, The Republic of Korea; 2. Qatar Foundation, Qatar

The Lithium ion batteries have attracted, during the last four decades, the attention of researchers from different fields, due to their use in practical applications such as Laptops, cellphones, toys, etc. This attention has been renewed recently, since LIBs are promising for large scale energy storage applications such as electric vehicles and grid storage applications. Indeed, the olivine $LiFePO_4$ (170 mAh/g), which is used in the new generation of LIBs, is a particularly promising example due to its advantages of being environmentally benign and safe. However, with lithium based cathode materials, there are concerns with regard to the abundance of lithium in the earth crust. Recent reports have pointed out sodium ion batteries, as energy storage systems, worthy of intensive investigation for large battery applications, since the sodium reserves are easily accessible. Provided that appropriate electrode materials can be discovered, substituting Na for Li should be accelerated due to the similar chemistries between Li and Na systems because Na is substantially less expensive than Li. This paper will discuss new results obtained on radially aligned hierarchical columnar P2 and O3 type structures as cathode materials for high energy density sodium-ion batteries. The paper will also introduce α-$Na_2M_2Fe(PO_4)_3$ as dual positive/negative electrode material for sodium ion batteries.

2:30 PM

(ICACC-S6-003-2016) Alluaudite family of high-voltage sodium battery cathodes (Invited)

P. Barpanda*[1]; 1. Indian Institute of Science, India

Sodium ion batteries have emerged as an alternative platform to realize large-scale electrochemical energy storage. Similar to the Li-ion batteries, the sodium-ion batteries put emphasis on high voltage cathode materials for better energy density. Putting SO4-based polyanionic systems on anvil, recently Na-Fe-S-O alluaudite class has been reported offering the highest Fe-redox voltage known till date. Extending the alluaudite systems to other 3d metal homolgoues, some new alluaudite compounds have been recently discovered. In the current work, we will describe the low temperature synthesis (T < 350 C), structural, magnetic and electrochemical performance of these alluaudites to update their status in the sodium battery scenario.

3:20 PM

(ICACC-S6-004-2016) Development of MXene nanosheets for negative electrode materials of sodium-ion battery (Invited)

M. Okubo*[1]; A. Yamada[1]; 1. The University of Tokyo, Japan

Sodium-ion batteries hold much promise for inexpensive and efficient energy storage in power grid. A high energy and high power negative electrode material is a key to improve the performance of sodium-ion batteries, however, the present set of the negative electrode materials mainly consists of the intercalation materials, where slow ion diffusion limits the power density. Here, we report pseudo capacitance of nanosheet compound MXene Ti_2CT_x for the negative electrode in advanced sodium-ion batteries.

3:50 PM

(ICACC-S6-005-2016) Redox behaviors of diimide compounds as high capacity negative electrode materials for sodium aqueous batteries (Invited)

J. Gaubicher*[1]; P. Jimenez-Manero[1]; P. Poizot[1]; K. Antonia[1]; B. Lestriez[1]; D. Guyomard[1]; 1. INSTITUT DES MATERIAUX JEAN ROUXEL, France

The increasing importance of renewable energy sources like sunlight and wind power connected to the electrical grid has trigged the necessity of low cost energy storage systems. In this context, sodium aqueous electrolyte ion-batteries constitute a new promising technology. Today, the performances of these batteries are limited however, by low capacity negative electrodes. To address this issue, the electrochemical and physical behavior of several diimide derivatives have been investigated in neutral Li, Na, K and Mg aqueous supporting electrolytes. The long term reversibility of redox processes involves close to one electron leading to high capacity values (approx. 90-100 mAh/g) at low voltage. Very interestingly, electrochemical activity shows singular features that unraveled a solid state disproportional mechanism favors by the unstability of the radical anion. Conversely, the extent of this reaction can be modulated according to the polarisability of the counter cation or the extent of the conjugated backbone. Results also enable to rationalize the capacity retention and the self discharge mechanisms of these materials based on both morphological and side reaction

considerations. Appropriate electrode chemistry and molecular engineering allows achieving remarkable cyclability with minimum conducting additives.

4:20 PM

(ICACC-S6-006-2016) Revisiting $Na_2Ti_3O_7$ as a Promising Anode for Sodium-ion Battery Application

A. Rudola*[1]; P. Balaya[1]; 1. National University of Singapore, Singapore

Over the past two decades, lithium-ion batteries have firmly established themselves as the dominant battery technology in the world for diverse applications. However, lithium reserves may be inadequate to meet the expected huge future demand. A battery technology relying on sodium would be desirable due to its globally abundant reserves. Over the past five years, there has been immense research in the field of sodium-ion batteries (NIBs) and these widespread efforts have already identified a few suitable cathodes. With the aim to develop an equally capable anode, we have uncovered a new sodium storage mechanism for the previously known anode $Na_2Ti_3O_7$, which relates with the existence of an intermediate phase discovered in this work through galvanostatic cycling studies. In this presentation, we will discuss the conditions required to isolate this intermediate phase and also discuss its sodium storage mechanism with the help of *ex-situ* X-ray diffraction studies. We will demonstrate its impressive sodium storage performance highlighted by an extremely low voltage activity at 0.2 V *vs* Na/Na^+. We believe that this anode could be very attractive not only for grid storage NIB application, but also perhaps in electric vehicles, if paired with an appropriate cathode.

4:40 PM

(ICACC-S6-007-2016) Cathode properties on sodium iron phosphate glass for sodium ion batteries

T. Honma*[1]; S. Nakata[1]; K. Shinozaki[1]; T. Komatsu[1]; 1. Nagaoka Univeristy of Technology, Japan

Sodium ion batteries are considered to be alternative high energy density batteries because of their low cost resources. In 2012, sodium iron pyrophosphate $Na_2FeP_2O_7$ was found by our group, which exhibits good cathode properties (2.9V, 89mAh/g). To increase discharge capacity sodium and iron content must be high in cathode matrix. However when we focus on crystalline materials, there are only two material $Na_2FeP_2O_7$ and $Na_4Fe_3(PO_4)_2P_2O_7$ are known for good cathode in sodium iron phosphate system. On the other hand glass formation region is widely exist hence; we can easily fabricate glassy material in higher sodium iron oxide composition. In this study we examined cathode properties on glass powders in the system of sodium iron phosphate. All glass sample with composition of $xFeO\text{-}(100\text{-}x)[Na_2O\text{-}P_2O_5]$ examined in this study was prepared by conventional melt quenching method in N_2 flow. Glassy sample was obtained at x= 20 to 45. The sample composition of x=45 is corresponds that of intermediate composition between $Na_4Fe_3(PO_4)_2P_2O_7$ and $NaFePO_4$. We obtained good reversible charge-discharge capacity in the x= 20, 27.5, 33.3 and 40. In x=40 exhibits higher reversible discharge capacity 115mAh/g which is much higher than that of $Na_2FeP_2O_7$ glass-ceramics after. We can expect to realize ceramic-based monolithic batteries by using glass and glass-ceramics.

5:00 PM

(ICACC-S6-008-2016) Multifunctional perovskite-type thermoelectric ceramics (Invited)

A. Weidenkaff*[1]; W. Xie[1]; X. Xiao[1]; M. Widenmeyer[1]; T. Zou[1]; A. Veziridis[1]; 1. University of Stuttgart, Germany

New materials and engineering research fields, including that of thermoelectricity will enable radically new and better future energy technologies. Herein we present our latest progress of various multifunctional thermoelectric materials and their implementation into devices. Perovskite-type ceramics as well as their nanocomposites are prospective candidates for high temperature thermoelectric energy conversion processes in exhaust gas catalysts and solid oxide fuel cells. Here they are combining their catalytic activity with the thermoelectric conversion. Their good performance can be explained based on their suitable band structures, adjusted charge carrier density, hindered phonon transport, and strongly correlated electronic systems. These properties are tuneable by changing the composition, structure, crystallites size, interfaces and materials combinations with tailor-made scalable synthesis procedures.

S7: 10th International Symposium on Nanostructured Materials: Functional Nanomaterials and Thin Films for Sustainable Energy Harvesting, Environmental and Health Applications

Nanomaterials for Energy Harvesting Applications I

Room: Coquina Salon A

Session Chair: Sanjay Mathur, University of Cologne

1:30 PM

(ICACC-S7-001-2016) Boron-based nitride nano-ceramics for energy applications (Invited)

P. Miele*[1]; M. Bechelany[1]; S. Bernard[1]; U. B. Demirci[1]; 1. Université de Montpellier, France

The development of new materials for near-future technological challenges in energy or environment issues is strongly dependent on the elaboration of ceramics with suitable morphologies, shapes and properties. This ambitious goal can be achieved by both the utilization of non-conventional chemical methods and the related preparation of tailored precursors. In the case of non oxide ceramics, the pyrolysis of preceramic precurors is a suitable process for preparing various inorganic materials with controlled chemical composition and complex shapes. The general strategy to produce such materials is a molecule-to-ceramic conversion, involving a complex sequence of physical and chemical modifications. This process can be divided into two sub-processes both starting from a molecular precursor. The first route lies on the creation of polymeric intermediates, allowing a subsequent shaping step whereas the second method is related to a one-step access to specific shapes. In this talk, several examples of Polymer Derived *nano*-Ceramics will illustrate this elegant method as well as their use in energy applications, particularly for hydrogen storage. We will focus on boron- and silicon-based PDCs displaying various forms and sizes. On the other hand, graphen-like BN nanocomposites will also be described for the fabrication of gas barriers as well as preliminary results of the ALD preparation of nitrides for energy applications.

2:00 PM

(ICACC-S7-002-2016) Advanced SiOC-Based Nanocomposites for Energy Storage Applications (Invited)

R. Riedel*[1]; 1. TU Darmstadt, Germany

Silicon oxycarbide/metal nanocomposites (SiOC/M) are prepared by chemical modification of polysilsesquioxane Wacker-Belsil PMS MK (SiOCMK) and polysiloxane Polyramic RD-684a (SiOCRD) with molecular metal compounds and subsequent pyrolysis at 1000 °C. The obtained samples consist of an amorphous SiOC matrix and in-situ generated metal-containing precipitates and are studied for their application as anode materials in Li ion batteries. The samples were characterized for their electrochemical performance in detail. The SiOC/M nanocomposites show excellent reversible capacity values and cycling stability as well as rate capability as compared to graphite based anodes. Incremental capacity measurements outline different final Li-M alloy stages upon Li-uptake, dependent on the embedding polymer-derived SiOC matrix. The presentation will

discuss the synthesis of a variety of novel in situ generated metal containg nanoparticles embeded in an amorphous SiOC host matrix. The electrochemical behavior of the nanocomposites including the contribution of the SiOC matrix to the total capacity performance of the anode material will be addressed in detail.

2:30 PM

(ICACC-S7-003-2016) Nano-composite materials and their applications in energy harvesting (Invited)

S. Christiansen*[1]; 1. Helmholtz-Zentrum für Materialien und Energie Berlin (HZB), Germany

We will report on novel nano-patterned composite materials for energy harvesting and their characterization based on correlated microscopies / spectroscopies. We rely on a wealth of nano-composites composed of silicon (Si) as well as GaN nanowires (NWs) or nanocones (NCs), complex gold and silver plasmonic nano-particles, few layer graphene and transparent conductive oxide layers all realized by a combination of wet chemical solution processing and vapor phase deposition methods. NWs and particles show a large surface area that can chemically be functionalized to account for surface passivation or functionality. Examples of how nano-composites will be formed and utilized in energy harvesting applications will be provided. The backbone of our devices are Si and GaN NWs and NCs for which optical modes can be controlled and efficient absorption of solar light can as much be tuned as light emission in light emitting diodes (LEDs) or laser devices. The integration of NWs or NCs in thin film solarcell concepts and LEDs will be demonstrated together with novel graphene or AgNW webs based electrodes. Correlated electron microscopy and spectroscopy techniques will be used to optimize device performance and to infer from properties of individual 3D nanoarchitectures properties of large area devices.

Nanomaterials for Energy Harvesting Applications II

Room: Coquina Salon A

Session Chairs: Silke Christiansen, Helmholtz-Zentrum für Materialien und Energie Berlin (HZB); Ralf Riedel, TU Darmstadt

3:20 PM

(ICACC-S7-004-2016) Electrospun Ceramic Nanofibers as High Performance Photoactive and Piezoelectric Materials (Invited)

M. Nalbandian[1]; G. Ico[1]; J. Nam[1]; N. V. Myung*[1]; 1. University of California, Riverside, USA

Electrospinning, a simple synthesis technique that forms ultra-long nanofibers from a polymeric solution via an electrical charge, has been widely used for many potential applications. In this work, various ceramic nanofibers were synthesized via electrospinning technique with controlled morphology and dimension toward optimal photocatalytic and piezoelectric properties. Through systematic tuning of parameters during electrospinning, TiO2, BiVO4, and BaTiO3 nanofibers of controlled diameter, crystallinity, and grain size were developed. Photocatalytic activity of TiO2 and BiVO4 (as well as noble metal co-catalyzed TiO2 and BiVO4) was tested toward phenol as a model pollutant, analyzing the specific physical properties that are linked to optimal micropollutant degradation. Based on photocatalytic studies, the electrospun nanofibers with minimal diameter and optimal crystal phase outperformed commercial photocatalysts (i.e., Aeroxide P25), with the co-catalyzed nanofibers having even greater photoactivity. BaTiO3 nanofibers were also synthesized via electrospinning with controlled physical properties and still undergoing optimization toward high piezoelectric performance. In all, electrospun nanofibers can be systematically tuned to make use of their nano-scale properties for energy and environmental applications.

3:50 PM

(ICACC-S7-005-2016) Interfacial Energetics Controls for Visible-Light Driven Photocatalysts for Efficient Photoelectrochemical Water Oxidation (Invited)

J. Wu*[1]; J. Yang[1]; B. Cheng[1]; H. Cho[1]; 1. National Cheng Kung University, Taiwan

In this work, nN^+ heterojunction photoanodes have been constructed on the basis of the considerations of interfacial energetics to improve the performances of the visible-light driven photocatalysts, such as hematite and bismuth vanadate, in photoelectrochemical (PEC) water splitting cells. Charge distribution and surface potential measurements, which are conducted by Kelvin probe force microscopy in dark and under illumination, indicate the improvement of charge separation in the photoanode by the formation of energy-matched nN^+ heterojunction. A built-in field in the space charge region of the heterojunction facilitates the charge separation in the photoanode. The enhancement of the PEC performance is thus measured in the nN^+ heterojunction photoanode. Moreover, by using hydrogen peroxide as a hole scavenger in the PEC cell, it also demonstrates that charge separation efficiency in the heterojunction photoanode is superior to that in the pristine photoanode. The details of the PEC properties of the nN^+ heterojunction photoanodes will be discussed in the presentation.

4:20 PM

(ICACC-S7-006-2016) Graphene oxides and their hybrids for CO_2 conversion and solar fuels (Invited)

L. Chen*[1]; 1. National Taiwan University, Taiwan

Photocatalytic conversion of CO_2 to hydrocarbons makes possible simultaneous solar energy harvesting and CO_2 reduction, two birds with one stone for the energy and environmental issues. Here, I will present our progress in using graphene oxides (GOs), along with their hybrids, as promising photocatalysts for CO_2 reduction. Modified Hummer's method was applied to synthesize the base GOs. In addition, a novel one-step electrochemical method has been developed to directly exfoliate graphite into reduced graphene oxide (RGO) nanosheets at room temperature. In both methods, the oxidation degree and the bandgap can be tuned. The photocatalytic CO_2 to methanol conversion rate of GOs under visible light is six-fold higher than the TiO_2. To enhance carrier generation and separation, Cu and MoS_2 nanoparticles were deposited on GO as co-catalysts or sensitizers. Not only methanol, but also acetaldehyde was detected. A total solar to fuel yield of 170 times enhancement relative to the commercial P-25 has been demonstrated. In all these hybrids, the photo-catalytic performance is always superior to that of individual constituent component. Detailed preparation and characterization of the catalysts will be presented. The role and interplay of the constituent components will also be discussed.

4:40 PM

(ICACC-S7-007-2016) ZnO/$BiVO_4$ Core-Shell Hierarchical Nanosturctured Array for Photoelectrochemical Water Splitting

J. Yang*[1]; J. Wu[1]; 1. National Cheng Kung University, Taiwan

In this work, ZnO/$BiVO_4$ core-shell hierarchical nanostructured arrays were constructed on fluorine-doped tinoxide (FTO) substrates for use in photoelectrochemical (PEC) water splitting. The ZnO nanorod (NR) array was grown on the FTO substrate by chemical bath deposition (CBD) method and the $BiVO_4$ nanoparticles shell layer were subsequently formed on the surface of NR array using spin coated method. Compared to the thin-film $BiVO_4$ photoanode, a eleven-fold enhancement of the photocurrent density is measured in the PEC water splitting cell with the ZnO NR/ $BiVO_4$ core-shell array photoanode. An optimized photocurrent density of 1.8 mA/cm^2 at 1.23 V versus reversible hydrogen electrode (RHE) under AM 1.5 at 100 mW cm^{-2} is obtained. The one-dimensional ZnO NR arrays provide a large surface area for the deposition of $BiVO_4$ layer with the well-controlled thickness. The photoholes can

therefore efficiency transport to the surface of the photoanode for water oxidation. The charge separation and injection efficiency were investigated using hydrogen peroxide as hole scavenger in PEC and photocurrent transient measurements. The results will be reported in detail in the presentation.

5:00 PM

(ICACC-S7-008-2016) Photocatalytic Hydrogen Generation Catalyzed by Co-catalysts over Sensitized Graphene

G. Lu*[1]; 1. Lanzhou Institute of Chemical Physics, China

Photocatalytic hydrogen generation has been extensively studied as method for solar hydrogen generation. However, the poor light absorption of catalysts in visible region and short lifetime of excited charge are the major factors that limiting reaction efficiency. We have recently demonstrated a general strategy to increase the hydrogen efficiencies of catalysts under visible light irradiation by sensitizing of catalyst with dye and promoting charge transfer using graphene. The graphene serves as highly conductive carries that can considerably increase the rate of charge transfer and their lifetimes and inhibit recombination of electron and hole. These dye-sensitized graphene hybrid catalysts showed signicantly enhanced performance for solar hydrogen generation. The enhanced photoelectrochemical performance of sensitized catalyst was also attributed to the improved charge separation. This talk will highlight our recent results devoted to the developing graphene-based dye sensitized catalysts and co-catalysts for solar hydrogen generation.

5:20 PM

(ICACC-S7-009-2016) $BiVO_4$-TiO_2 Nanostructured Heterojunction Photoanode for Photoelectrochemical Water Oxidation

B. Cheng[1]; J. Yang[1]; H. Cho*[1]; J. Wu[1]; 1. National Cheng Kung University, Taiwan

In this work, porous bismuth vanadate ($BiVO_4$) thin film has been deposited on fluorine-doped tin oxide (FTO) by metal organic decomposition for the application to photoelectrochemical water splitting. Titanium oxide (TiO_2) thin layer which is grown by combing hydrothermal method and chemical bath deposition is developed between FTO and $BiVO_4$ for increasing the photocurrent density in photoelectrochemical water oxidation. The results show that an optimal TiO_2-$BiVO_4$ nanostructured heterojunction photoanode produces a photocurrent density of 0.8 mA/cm^2 at a potential of 1.23V versus RHE under illumination of AM 1.5G (100 $mWcm^{-2}$). By using hydrogen peroxide (H_2O_2) as a hole scavenger, it demonstrates that charge separation efficiency in the TiO_2-$BiVO_4$ photoanode is superior to that in the $BiVO_4$ photoanode. However, charge injection efficiency in the TiO_2-$BiVO_4$ photoanode is lower than that in the $BiVO_4$ photoanode. By depositing cocatalyst Co-Pi on the surface of TiO_2-$BiVO_4$ photoanode, the onset potential shift toward the cathodic direction. A 104 % increase of the photocurrent density at a potential of 1.23V versus RHE is measured in the Co-Pi/TiO_2-$BiVO_4$ photoanode.

S8: 10th International Symposium on Advanced Processing and Manufacturing Technologies for Structural and Multifunctional Materials and Systems (APMT10)

Functional Ceramics Processing I

Room: Coquina Salon B

Session Chairs: Surojit Gupta, University of North Dakota; Pavol Sajgalik, Institute of Inorganic Chemistry, Slovak Academy of Sciences

1:30 PM

(ICACC-S8-001-2016) Foaming of Plaster of Paris to Produce Porous Gypsum (Invited)

E. Roch Isern[1]; G. L. Messing*[1]; 1. The Pennsylvania State University, USA

In this paper we describe the factors affecting the formation of lightweight and highly porous gypsum with a homogeneous bimodal pore size distribution using the direct-foaming of plaster of Paris with a nonionic surface-active agent. During the setting process, gypsum formation is accompanied by an increase in viscosity and was thus used to stabilize pores formed during foaming. To quantify the relationships between time, temperature and viscosity, we measured the viscosity and temperature rise of the plaster of Paris slurry during gypsum formation and correlated the consequent microstructure, including pore size and density, with the foaming process parameters. Interestingly, the non-ionic surfactant appears to retard gypsum crystallization and thus extends the working time at higher water to solid ratios. Gypsum foams of 32% density with a submicron matrix pore size, and relatively uniform macropore size of 104 μm were obtained. Based on theoretical models, the thermal conductivity of gypsum with this microstructure relative to standard gypsum is predicted to decrease by 38% and the sound absorption is predicted to increase by 20%. Preliminary mechanical properties of the foamed gypsum will be presented.

2:00 PM

(ICACC-S8-002-2016) Fabrication and Magnetoelectric Properties of Laser Annealed PZT Thick Film on Amorphous Magnetostrictive Metal Substrate (Invited)

S. L. Kang*[1]; H. Palneedi[1]; D. Maurya[2]; S. Priya[2]; S. Choi[3]; J. Ryu[4]; 1. KAIST, The Republic of Korea; 2. Virginia Tech, USA; 3. Korea Institute of Materials Science, The Republic of Korea; 4. Korea Institute of Materials Science (KIMS), The Republic of Korea

The magnetoelectric (ME) coupling between piezoelectric and magnetostrictive properties is attractive for potential applications in sensors, transducers, energy harvesters, etc. Film-based ME composites, which consist of piezoelectric (typically PZT) and magnetostrictive layers, are especially suitable for application to integrated magnetic/electric devices. Thermal processing, which is necessary for improving the quality of PZT films after the composite fabrication, unavoidably leads to surface oxidation and crystallization of the amorphous magnetostrictive metal substrate as well as chemical interdiffusion between the two phases. These effects deteriorate ME properties. Using a granule spray in vacuum process (GSV), a PZT thick film was deposited on a Metglas substrate in the present study. The PZT film was annealed with a continuous wave 560 nm laser to minimize deteriorative effects of the commonly applied thermal annealing. The laser processed PZT/Metglas composites exhibited a ME voltage coefficient two orders of magnitude larger than that of the conventionally thermal processed composites, demonstrating the beneficial effect of the laser annealing. We also report the effects of various processing parameters, including laser power, scan speed, and PZT film thickness, on microstructural evolution as well as electric, magnetic, and ME properties.

2:30 PM

(ICACC-S8-003-2016) Processing Stable Porous Silicon (SPS) as an Anode for Lithium Ion Battery (Invited)

I. Dutta*[1]; S. O'Malley[1]; F. Behan[1]; B. Kent[1]; J. Chang[1]; R. Youngman[1]; B. Wheaton[1]; D. Baker[1]; B. Abel[1]; 1. Corning Incorporated, USA

Recently, there has been an increasing demand for energy storage devices in both consumer electronics and transportation. This demand is predicted to grow significantly in the coming years >$10B. The most prominent chemistry for these applications is Lithium Ion Battery (LIB). Graphite, which is the incumbent anode material has reached its full capacity utilization in the modern LIB pack. A significant effort is underway worldwide to identify the next low cost material which has significantly higher energy density compared to graphite but with similar electrochemical cycle life. Silicon particles of different sizes, shape and morphology have shown significant promise to be the next material of choice. Silicon has significantly higher capacity (~3700 mAh/g) compared to graphite (~350 mAh/g). However, pulverization of Si during electrochemical cycling, resulting in catastrophic failure, has been the biggest barrier for this material being widely commercialized todate. The different paths range from nano-Si particles to wire microstructure to porous microstructure. Recently Corning Incorporated filed several patents in the field of a porous Si microstructure that provides high electrochemical capacity (>2000mAh/g) as well as superior cycling performance. This presentation will focus on some of the process innovations that have been used to produce this Stable Porous Silicon (SPS) material.

2:50 PM

(ICACC-S8-004-2016) Ceramic membranes for treatment of challenging process streams (Invited)

T. Fahrenwaldt*[1]; T. Wölfel[1]; V. Prehn[1]; 1. Inopor GmbH, Germany

Inopor GmbH is a member of the Rauschert Group, a 115 year old company started in Germany for technical ceramic production. In 2001 Rauschert partnered with IKTS-Fraunhofer Society to develop ceramic filtration technologies. In 2006 Inopor was formed as a joint-venture for the production of ceramic membranes for cross-flow filtration. Inopor offers ceramic membranes for micro- through nanofiltration with a pore cut-off of 450 Da and less. The membranes are used in extremely corrosive and abrasive water-based fluids and solvents. Typical applications are in chemical and pharmaceutical industries, and food and beverage processing. Rauschert's ceramic manfacturing knowledge, including in-house tool design and production, allows Inopor to offer a range of materials and geometries, and customer-specific solutions. Inopor® ceramic membranes have shown promising results in initial testing for treatment of "Produced Water" (PW) in the oil and gas industry. Four barrels of water are used to recover one barrel of oil from oil sands; this water must be recycled in the future. The PW has a complex chemistry and high abrasive content, due to oil and tar residuals, and high concentrations of salts and particles. This presentation is an overview of applications of Inopor® membranes for treatment of process streams and industrial effluents, including challenges and solutions of waste water treatment in technical ceramic production.

3:30 PM

(ICACC-S8-005-2016) Performance of Ceramic, Microchannel Heat Exchangers

C. Lewinsohn*[1]; J. Fellows[1]; 1. Ceramatec, Inc., USA

Ceramic, microchannel heat exchangers can improve the efficiency, lower the cost, and reduce emissions of a large number of energy intensive applications. Microchannel designs enable the use of ceramics in reliable and highly efficient heat exchangers. In addition, ceramic microchannel heat exchangers can be fabricated for use on an industrial scale at economical costs, relative to components made from high temperature alloys.These unique ceramic, microchannel heat exchangers, offer high effectiveness at temperatures far above existing technology, offering step changes in system efficiencies and concomitant reductions in emissions. Microchannel designs couple multiscale physical behavior of enhanced transport at the microscale with macroscale heat and mass flows. Advanced ceramic materials allow operation at temperatures currently unobtainable by conventional materials. Ceramatec has developed an innovative approach to fabricate microchannel components using advanced ceramic materials to produce systems capable of high efficiency under conditions beyond the regime of existing technology. Ceramatec's modular design allows industrial scale systems to be built from identical, engineered microchannel components assembled in arrays of modules for numerous applications.The effect of microchannel designs on internal flow and heat transfer will be presented.

3:50 PM

(ICACC-S8-006-2016) Preparation of New Barium Titanate-based Nano-complex Ceramics with High-density Heteroepitaxial Interfaces by Solvothermal Solidification Method and Their Dielectric Property (Invited)

S. Wada*[1]; 1. University of Yamanashi, Japan

Recently, a new technique was proposed to prepare nano-structured ceramics with heteroepitaxial interfaces between barium titanate ($BaTiO_3$, BT) and potassium niobate ($KNbO_3$, KN) prepared at low temperatures below 300 C, and their dielectric and piezoelectric properties were enhanced. On the other hand, bismuth ferrite ($BiFeO_3$, BF) had smaller unit cell volume by 1 % than that of BT. Therefore, we expected that the BT unit cell can be compressed and their dielectric properties for the BT-BF nano-structured ceramics were quiet smaller than those for the BT-KN nano-structured ceramics. To confirm the above idea, we prepared BT-KN and BT-BF nano-structured ceramics were prepared by solvothermal method in this study, and their dielectric properties were compared on the view of unit cell volume change of BT. After the reaction, the compacts were washed by ethanol, and dried at 200 C. These nano-complex ceramics prepared in this study were porous with a porosity of around 25 ~ 35 %. The dielectric measurements showed that for the BT-KN nano- structured ceramics with KN/BT ratio of 1, the dielectric constant was 300 at 20 C and 1 MHz, while for the BT-BF nano-complex ceramics with BF/BT ratio of 1, the dielectric constant was 70.

4:10 PM

(ICACC-S8-007-2016) Integration of multiferroic $Bi_{3.25}La_{0.75}Ti_{2.5}Nb_{0.25}Fe_{0.125}Co_{0.125}O_{12}$ thin films by using ZnO buffer layer

D. Coathup*[1]; M. Liao[2]; Z. Li[3]; H. Yan[3]; B. Shi[1]; H. Ye[1]; 1. Aston University, United Kingdom; 2. National Institute for Materials Science (NIMS), Japan; 3. Queen Mary University of London, United Kingdom

The authors report on the growth of multiferroic $Bi_{3.25}La_{0.75}(Ti_{2.5}Nb_{0.25}Fe_{0.125}Co_{0.125})O_{12}$ (BLT) thin films by sputter deposition on the silicon substrates with regard to the buffer layer and post annealing effects. The BLT thin films directly deposited on the silicon substrates are amorphous or pyrochlore phase. The insert of the ZnO buffer layer between the BLT thin films and the silicon substrate facilitates the formation of a ferroelectric phase. At a low buffer layer thickness of 20 nm, pyrochlore and ferroelectric phases coexist in the BLT thin films. Pure ferroelectric BLT thin films are successfully obtained on the silicon substrate by using a thicker ZnO film (170 nm) buffer layer. The BLT thin films on the buffer layers crystallize at an annealing temperature as low as 550 °C and become preferentially c-axis oriented at the annealing temperature above 650 °C. The multiferroic BLT thin films exhibit excellent electrically insulating performance and the dielectric constant is as high as 90. The ZnO layer not only facilitates the formation of multiferroic phase of BLT thin films, but also acts as a semiconducting channel for memory devices at high temperatures.

4:30 PM

(ICACC-S8-008-2016) Immobilization mechanism of inorganic toxic ions at solid/liquid interface of hydroxides (Invited)

C. Tokoro*[1]; 1. Waseda university, Japan

Solid/liquid interface of several hydroxides, such as ferrihydrite and aluminum hydroxide, plays an important role for immobilization of toxic elements in environmental water. Distribution of inorganic toxic elements between hydroxides and solution at the interface could be quantitatively estimated when the immobilization mechanism was categorized into two main types; one is surface complexation and another is surface precipitation. Many experimental results obtained from sorption isotherm, zeta potential measurement, XRD (X-ray diffraction) analysis and XAFS (X-ray adsorption fine structure) analysis showed an evidence for formation of surface precipitation at the hydroxides interface in a specific condition despite solubility product is not saturated in solution. For example, surface precipitation of ferric arsenate, aluminum arsenate, and magnesium and boron compounds was observed at the interface of ferrihydrite, aluminum hydroxide and magnesium hydroxide, respectively. XAFS investigation suggested that surface complexation of arsenate ion to ferrihydrite was precursor and gradually changed to surface precipitation of ferric arsenate. Therefore, the surface precipitation should occur only at the interface between hydroxide and solution, when the solubility product of the precipitation is saturated partially at the interface, despite it being unsaturated in bulk solution.

4:50 PM

(ICACC-S8-009-2016) Application of DEM simulation and multiple classification analysis to estimate particle size distribution in ball milling

S. Fukui*[1]; Y. Tsunazawa[1]; C. Tokoro[1]; 1. Waseda university, Japan

The discrete element method (DEM) has been applied to ball milling for simulating the behavior of grinding media, however, direct estimation of particle distribution after milling is difficult in DEM simulation. The objective in this study is to develop a method to estimate the particle size distribution in ball milling using calculated results obtained by DEM simulation. To estimate the particle size distribution, we investigated a correlation between experiment and simulation values in particle distribution after ball milling. In experiment, about 2 mm of lime particle was ground and the particle size distribution was obtained by sieving. And then, by fitting to Gaudin-Schuhmann distribution equation, the average particle size and the distribution modulus, which indicates distribution width, were calculated. In simulation, the collision energy of grinding media was calculated. Then, we conducted multiple classification analysis for experiment and simulation values. As a result, the total of normal collision energy obtained by simulation correlated both of average particle size and distribution modulus obtained by experiment in ball milling. These results suggested that it was possible to estimate the particle size distribution in ball milling using these correlativity with DEM simulation.

5:10 PM

(ICACC-S8-010-2016) Impedance analysis of polycrystalline 3C-SiC on silicon substrate

Z. Liu*[1]; H. Zhuang[2]; W. Li[1]; C. Gu[1]; H. Ye[3]; 1. Institute of Physics, CAS, China; 2. Institute of Materials Engineering, University of Siegen, Germany; 3. Aston University, United Kingdom

Silicon carbide (SiC) is one of the greatest candidates for power devices among the wide band semiconductor materials, due to its excellent properties such as high chemical stability, high electron mobility, good biocompatibility, high breakdown voltage etc. Polycrystalline cubic SiC (3C-SiC) has the largest electron mobility which enlarges its application potential on field emission transistors, but the polycrystal nature may have effect on the capacitance properties. Impedance spectroscopy (IS) is a suitable way to characterize the interface property between two kinds of materials or crystal grains. However, this hasn't been used to study the microscope structure of 3C-SiC film. In this paper, we found out that titanium can form ohmic contact on 3C-SiC film, which was demonstrated by circular transmission line method (CTLM). The 3C-SiC film was deposited on slightly doped p-type Si wafer by microwave plasma chemical vapour deposition (MPCVD). IS measurement was applied on the SiC-Si structure with different DC bias. The Raman measurement shows that there are amorphous carbon phase in the film, which was confirmed by the fitted R and C data through equivalent circuit model.

S10: Virtual Materials (Computational) Design and Ceramic Genome

Novel Computational Methods and Multi-scale Modeling I

Room: Ponce DeLeon

Session Chair: Gerard Vignoles, University of Bordeaux 1

1:30 PM

(ICACC-S10-001-2016) Simulation of Complex Materials Structures with Charge Optimized Many-Body (COMB) Potentials (Invited)

S. R. Phillpot*[1]; 1. University of Florida, USA

Many device structures combine the functionality of materials with very different bonding types: metallic, ionic and covalent. Traditional empirical potentials have been designed to consider one type of bonding only. The Charge Optimized Many-Body (COMB) approach allows for the seamless simulation of structures composed of dissimilar materials. This is because COMB includes a charge equilibration method that allows each atom to autonomously and dynamically determine its charge, and a sophisticated description of bond order, by which the strength of an individual pair bond is modulated by the presence and strength of other local bonds. Simulations using COMB potentials are orders of magnitude faster than electronic-structure calculations, can consider much larger systems and can easily simulate dynamically behavior. The power of this approach is illustrated from problem of interest for various condensed phase systems including U/UO_2, Zr/ZrO_2 and Cu/SiO_2

2:00 PM

(ICACC-S10-002-2016) Chemical bond investigations of MAX-phases and MXenes by *ab initio* calculations and soft X-ray spectroscopy (Invited)

M. Magnuson*[1]; 1. IFM, Sweden

The electronic structures of the 2D ceramic materials MAX-phases and MXenes were investigated by ab initio electronic structure calculations in comparison to polarized soft X-ray absorption and X-ray emission spectroscopy using synchrotron radiation. These nanolaminated carbide and nitride compounds represent a class of layered materials with a combination of properties from both metals and ceramics. Bulk-sensitive soft X-ray absorption and emission techniques in fluorescence mode are shown to be particularly useful for detecting detailed symmetry in the electronic structure and yield anisotropy information about internal monolayers and interfaces. Calculated spectra using density-functional theory (DFT) including core-to-valence dipole matrix elements are found to yield consistent spectral functions to the experimental data. By varying the constituting elements and structures, a change of the electron population is achieved causing a change of covalent bonding between the laminated layers, which enables control of the macroscopic properties of the MAX-phase materials. Angle- and polarization-resolved measurements reveal differences in the occupation of the orbitals across and along the laminate basal plane. For MXenes, the role

of functional -OH, -O and -F temination groups and their local symmetries as well as phonons at the interfaces are discussed.

2:30 PM

(ICACC-S10-003-2016) Incentivized Participation for Standard Data Format and Exchange Mechanisms for Condensed Matter Electronic Structure Simulations (Invited)

P. Rulis*[1]; 1. University of Missouri - Kansas City, USA

Millions of hours of computer time are spent every year to simulate the quantum mechanical properties of an amazing array of materials. The computed results represent a vast amount of valuable information that could be tremendously beneficial to others. After the results are published it should, in principle, be a simple matter for another researcher to access the literature and repeat, compare, modify, and extend a given calculation using the same or similar methods. A number of tools and organizations have developed in recent years to promote such data sharing. This infrastructure is critical to the pursuit of a "genetic" approach to materials science. Crucial to the success of such methods is the participation of electronic structure program users and developers. This talk will present a brief summary of the current state of affairs followed by the results and progress of recent efforts to address the difficulty of standardizing the format and mode of sharing computed data. An incentivized approach forward will also be discussed.

Novel Computational Methods and Multi-scale Modeling II

Room: Ponce DeLeon

Session Chairs: Simon Phillpot, University of Florida; Paul Rulis, University of Missouri - Kansas City

3:20 PM

(ICACC-S10-004-2016) A multiscale study of elasticity in highly textured pyrocarbons (Invited)

J. Leyssale[2]; A. Gamboa[1]; B. Farbos[1]; S. Jouannigot[1]; G. Couegnat[1]; A. P. Gillard[1]; G. L. Vignoles*[1]; 1. University Bordeaux, France; 2. Massachusetts Institute of Technology, USA

Highly textured laminar pyrocarbons are employed in carbon/carbon and other thermostructural composites for aerospace and energy applications. The design of these materials requires a good knowledge of their mechanical properties, but (i) experimental data are rather scarce, and (ii) elastic moduli values are scattered, for at least two reasons. First, different methods have been used, and second, these properties depend strongly on the precise structure and texture of these materials. All reported values are much lower than the tensile modulus of graphite. Modeling is therefore a precious help to understand these facts. First, molecular dynamics is used to compute effective stiffness tensors of a series of pyrocarbon models recently obtained by the IGAR (Image-Guided Atomistic Reconstruction) technique, as well as on graphite. The results are put in relation with the structural and textural parameters of these materials. Compression buckling is also investigated. Then, these results are used to predict the indentation moduli. Comparison to the experimental values obtained on the materials which served as bases for the IGAR models gives a good agreement and a consistent trend when varying the structural and textural parameters. Finally, texture effects at the μm scale will be investigated by PLOM image analysis and used as a basis to explain the low values of the tensile Young moduli.

3:50 PM

(ICACC-S10-005-2016) Modeling of the damage of the MMCs with Lamellar Microstructure

R. Piat*[1]; M. Kashtalyan[2]; 1. Darmstadt University of Applied Science, Germany; 2. CEMINCACS, School of Engineering, University of Aberdeen, United Kingdom

Metal-ceramic composites offer many advantages over monolithic metals and their alloys such as high specific stiffness and strength, better creep, fatigue and wear resistance, and good thermal properties. One of the recent advances in this area has been made possible thanks to innovative ceramics preforms, fabricated by freezing a water-alumina suspension and subsequent freeze-drying and sintering. As the result these metal/ceramic composites possess a hierarchical lamellar microstructure, with randomly orientated individual regions (domains), in which all ceramic and metallic lamellae are parallel to each other. Metal-ceramic composites with hierarchical lamellar microstructure exhibit pronounced elastic and plastic anisotropy at the domain level. Stress fields in a single-domain sample of metal-ceramic composite containing multiple cracks in the ceramic layer are investigated. The cracked microstructure for different steps of the damage is modeled by analytical and computational approaches. Stress field is determined used a modified 2-D shear lag approach and a finite element method. The result obtained by finite elements analysis is consistent with experimental results. According to the obtained result, the average axial stress between the two cracks is decreasing with decreasing the distance between the cracks.

4:10 PM

(ICACC-S10-006-2016) Modeling the rapid solidification and mechanical response of thermal sprayed chromium oxide coating

T. Pinomaa*[1]; T. Andersson[1]; S. Gurevich[2]; A. Laukkanen[1]; N. Provatas[2]; 1. VTT Technical Research Centre of Finland, Finland; 2. McGill University, Canada

Thermal spray coatings are deposited by melting and accelerating a powder of micron-sized particles, which hit a substrate and accumulate into a submillimeter-thick lamellar material film. Computational models can be used to systematically relate coating properties with processing conditions, such as powder particle cooling rate. The coating microstructure forms via rapid solidification, which is modeled with a multi-order parameter phase field model. As a basic example, we model the solidification in a chromium oxide (Cr2O3) coating deposition. A set of simulated rapidly solidified chromium oxide microstructures are sampled to produce a complete synthetic coating. The mechanical properties of the synthetic coating is assessed with finite element analysis. The cohesion in the inter-lamellar boundaries is treated separately. Subsequently, a scanning electron microscopy (SEM) image of a real coating is segmented into distinct phases via image processing. We then compare the synthetic and SEM coatings: first their microstructural features, and secondly their mechanical properties.

4:30 PM

(ICACC-S10-007-2016) Modeling of high-temperature heat transfer in foams and fibrous preforms from 3D images

G. L. Vignoles*[2]; A. Ortona[1]; J. Vicente[3]; F. Panerai[4]; 1. SUPSI, Switzerland; 2. University Bordeaux, France; 3. University Marseille, France; 4. Analytical Mechanics Associates, Inc., USA

Heat transfer in highly porous refractory materials, like bonded carbon fiber felts used for thermal protection systems, or ceramic open-cell foams considered for high energy conversion, involves simultaneously, among other phenomena, conduction through the solid and radiation in the void space. The coupling of these two phenomena has seldom been addressed in a simultaneous fashion in modeling studies. We will present the results of the application of a recent original code that computes effective conductivities from the strong coupling of conduction and radiation in 3D images, be them

ideal or obtained by X-ray CMT. Whatever the considered material, the distinction of three different regimes (pure conduction; mixed; radiation-dominated) can be done; transition criteria will be given to distinguish between them. A generalization of the classical Rosseland model will be proposed. On foams, we will discuss the impact of structural & geometrical parameters on the effective properties. Comparison between the behavior of random foams (as scanned by CMT) and of periodic foams will be carried out. On fibrous media, comparison with actual experimental data will be discussed. For all media, an eigenvector study will be carried out, showing how the effective tensor is rearranged depending on the heat transfer regime. G. V. and J. V. acknowledge support from CNRS through a PEPS/INSIS grant "MaTRaCC".

4:50 PM

(ICACC-S10-008-2016) Micro-Computed Tomography Image Based Thermo-Elastic Properties Studies of Freeze-Cast MMCs

R. Piat*[1]; Y. Sinchuk[2]; A. De Marcos[3]; B. NAIT-ALI[3]; 1. Darmstadt University of Applied Science, Germany; 2. University of Poitiers, France; 3. Laboratoire Science des Procédés Céramiques et Traitements de Surface, France

The current investigations deal with the comparison of the elastic moduli and thermal conductivity of a freeze cast preforms and metal-ceramic composites with lamellar microstructure determined experimentally and calculated using FE method. Different single- and poly-domain specimens have been investigated with a self-programmed tool based on micrographs concerning the orientation of the lamellae of the freeze cast preform. Tensile specimens have been manufactured in order to realize the position of single domains within the ceramic preform and the gauge length, respectively. The effective thermal conductivity was measured using the laser flash method on porous preform samples obtained by freeze casting and cut in two directions: parallel and perpendicular to the ice front formation. The realistic models based on the X-ray computed tomography images of the microstructure are used for creation of the 3D FE models. Obtained models are based on the finite element mesh created from binary volumetric images obtained by segmentation CT scans of the material. Numerical testing using these models and corresponding 2D models are provided and obtained thermo-mechanical properties of the composite are compared with experimental results for the samples with identical microstructure. The results of the numerical modeling are in good agreement with experimental results.

5:10 PM

(ICACC-S10-009-2016) Quantifying structure prediction via virtual diffraction

S. P. Coleman*[2]; E. Hernandez[2]; M. A. Tschopp[1]; J. S. Dunn[1]; 1. U.S. Army Research Laboratory, USA; 2. US Army Research Laboratory, USA

In this work, virtual x-ray and electron diffraction are used to quantify the ability of select empirical interatomic potentials to correctly predict the complex structure of boron based ceramics. Recently developed virtual diffraction capabilities within large-scale molecular dynamics simulations are enabling greater connections to experimental and first principles simulation data. In this work, these connections are used to quantify the deviation between predicted energy minimized structures that stem from limitations within the empirical potentials. The deviation identified from virtual diffraction methods can help aid the selection and development of more ideal interatomic potentials.

S12: Materials for Extreme Environments: Ultrahigh Temperature Ceramics (UHTCs) and Nano-laminated Ternary Carbides and Nitrides (MAX Phases)

Structure-property Relationships of MAX Phases

Room: Tomoka B

Session Chair: Yury Gogotsi, Drexel University

1:30 PM

(ICACC-S12-001-2016) Recent advances in MAX phases solid solutions (Invited)

T. Cabioch*[1]; P. Chartier[1]; V. Mauchamp[1]; S. Dubois[1]; 1. University of Poitiers, France

The MAX Phases are layered hexagonal carbides and nitrides with the general formula: $M_{n+1}AX_n$, (MAX) where n = 1 to 3, M is an early transition metal, A is an A-group (mostly IIIA and IVA, or groups 13 and 14) element and X is either carbon and/or nitrogen. Isostructural solid-solutions can be obtained on the M, A or X sites, thus forming either quaternary carbides or nitrides such as $(M'_xM"_{1-x})_{n+1}AX_n$ and $M_{n+1}(A'_xA"_{1-x})X_n$, or carbonitrides in the case of X-site solid-solution. The synthesis of such MAX phases solid solutions is a wide open field since several hundreds of stable solid solutions system should exist. In this contribution, we will first have structural considerations for these solid solutions and then focus on the possibility to tune or improve some physical properties of MAX phases by using solid solutions effects. The possibility to synthesize new MAX phases such as $(Cr,V)_{n+1}AlC_n$ with (n=1,2,3) or $(Mo,Ti)_{n+1}AlC_n$ (with n=2,3) will also be discussed as well as ordering phenomena on the M sites which can occur in such phases. Finally, the interest for introducing novel elements (Mn, Cu,…) in the structure of the MAX phases will be discussed especially for magnetic properties.

2:00 PM

(ICACC-S12-002-2016) Discovery of carbon-vacancy ordering in Nb_4AlC_{3-x} under the guidance of first-principles calculations

H. Zhang*[1]; T. Hu[1]; X. Wang[1]; Z. Li[1]; M. Hu[1]; E. Wu[1]; Y. Zhou[1]; 1. Institute of Metal Research, China

Carbon-vacancy ordering is an interesting phenomenon in carbides. In this presentation, we talk about the discovery of carbon-vacancy ordering in Nb_4AlC_{3-x} under the guidance of first-principles calculations. The presence of an ordered phase with structural carbon vacancies in Nb_4AlC_{3-x} ($x \approx 0.3$) ternary carbide is predicted by first-principles calculations, and experimentally identified for the first time by transmission electron microscopy and micro-Raman spectroscopy. Consistent with the first-principles prediction, the ordered phase, o-Nb_4AlC_3 ($Nb_{12}Al_3C_8$), crystalizes in $P6_3/mcm$ with a = 5.423 Å, c = 24.146 Å. Coexistence of ordered (o-Nb_4AlC_3) and disordered (Nb_4AlC_{3-x}) phase brings about abundant domains with irregular shape in the bulk sample. The transformation from o-Nb_4AlC_3 to Nb_4AlC_{3-x} can be induced by both heating and electron irradiation. Our findings may offer substantial insights into the roles of carbon vacancies in the structure stability and order-disorder phase transformation in machinable ternary carbides.

2:20 PM

(ICACC-S12-003-2016) A high throughput combinatorial approach to the exploration of the effect of M site alloying on the solid solution behaviour of Ti2AlC MAX phase

A. Talapatra*[1]; T. Duong[1]; W. Son[1]; H. Gao[1]; R. Arroyave[1]; M. Radovic[1]; 1. Texas A&M University, USA

In this work, we report the phase diagrams of the (TixM(1-x))2AlC, where M = V, Cr, Mn, Fe, Co, Ni, Cu, Zn systems calculated by combining first-principles calculations and cluster expansion Monte Carlo simulations. The variation in the MAX phase solid – solution's

behavior due to substitution on the M site by elements along the 4th row in the periodic table is characterized. On the left of the 4th row (M = V, Cr) ideal solution behavior is seen, while strong ordering tendencies are observed on moving to the right end of that row. Stable ternary solid solution compounds are isolated and analyzed for all the systems.

2:40 PM

(ICACC-S12-004-2016) Experimental Study of Physical and Mechanical Properties of $Ti_3(Al,Si)C_2$ solid solutions

H. Gao*[1]; W. Son[2]; T. Duong[2]; A. Talapatra[2]; R. Arroyave[2]; M. Radovic[2]; 1. Texas A&M, USA; 2. Texas A&M University, USA

A series of $Ti_3(Al_{1-x}Si_x)C_2$ solid solutions (0<x<1) are reaction sintered from Ti, Si, Al and TiC powders through Spark Plasma Sintering. With substitution of Si element, the a-lattice parameter remains constant at 0.307 nm, however, the c-lattice parameter decreased linearly from 1.858 nm to 1.763 nm. The specific heat capacity of $Ti_3Al_06Si_{0.4}C_2$ is compared to that of end members, while CTE of $Ti_3Al_06Si_{0.4}C_2$ decreased due to the stronger bonds between Si and Al atoms. Resonant Ultrasound Spectroscopy (RUS) measurement indicates that the Young's modulus and shear modulus are increasing at room temperature with increasing amount of Si substitution. Vickers hardness results demonstrate that there is significant hardening effect on $Ti_3(Al_{1-x}Si_x)C_2$ solid solution. With Si content increasing, H_v increased from 4.1±0.14 GPa of Ti_3AlC_2 and 4.2±0.37 GPa of Ti_3SiC_2, up to 5.6±0.2 GPa of $Ti_3(Al_{0.4}Si_{0.6})C_2$. The mechanical properties of Ti_3AlC_2, $Ti3Al_06Si_{0.4}C_2$ and Ti_3SiC_2 are also characterized at room and high temperatures, respectively. At room temperature, there was no obvious strengthening effect, only up by 7.6% at $Ti_3Al_06Si_{0.4}C_2$. At 1100 °C, the strength of Ti_3SiC_2> $Ti_3Al_06Si_{0.4}C_2$>Ti_3AlC_2. It indicates that with Si substitution, the mechanical properties of $Ti_3Al_06Si_{0.4}C_2$ at elevated temperatures was improved from Ti_3AlC_2 end member.

Materials Design, New Composition and Composites I

Room: Tomoka B

Session Chair: Thierry Cabioch, University of Poitiers

3:20 PM

(ICACC-S12-005-2016) MXenes, two-dimensional carbides and nitrides made from MAX phases (Invited)

Y. Gogotsi*[1]; 1. Drexel University, USA

In 2011, we discovered a totally new class of two-dimensional (2D) materials – transition metal carbides and nitrides – we labeled MXenes. They are simply made by selective etching of the 'A' element from MAX phases and suffix 'ene' is used to show their similarity to graphene. To date, by etching MAX powder in HF, we have successfully produced more than 15 different MXenes, such as Ti_2C, Ti_3C_2, V_2C, Nb_2C, Ta_4C_3, etc. MXene family is expanding very rapidly and may become the largest family of 2D materials. Their elastic constants along the basal plane are expected to be similar to or even higher than that of the binary carbides. Moreover, they offer an unusual combination of metallic conductivity and hydrophilicity and show very attractive electrochemical properties for potential use in energy storage. MXenes are also promising for membrane applications and as reinforcement to make strong multifunctional composites, among many more applications. In this presentation, a brief overview of synthesis, characterization and thermal stability of different MXenes, and their performance in different applications will be discussed.

3:50 PM

(ICACC-S12-006-2016) Electronic structure of two dimensional titanium carbide MXene materials: insights into the surface functionalization groups

D. Magne*[1]; V. Mauchamp[1]; S. Celerier[2]; P. Chartier[1]; T. Cabioch[1]; 1. Institut PPRIME, France; 2. IC2MP, France

$Ti_3C_2T_x$, where T≡OH or F are surface functionalization groups, belongs to the large family of MXene which are two-dimensional (2D) transition metal carbide or carbonitride synthetized from MAX phases. In this 2D material family, $Ti_3C_2T_x$ is the most studied because of its properties for energy storage applications among others. In this system, the surface groups play a key role: they affect the energy storage capacities or modify their optical properties. Given their crucial role, these functionalization groups have been intensively investigated but mainly from a theoretical point of view. In this context, we present a combined experimental and theoretical investigation of the electronic structure of $Ti_3C_2T_x$ based on valence electron energy-loss spectroscopy. Besides evidencing important similarities between the $Ti_3C_2T_x$ and TiC valence electron gases behaviors, a clear interband transition related to the most stable site of the T functionalization groups is identified in the VEEL spectrum. This spectral signature, allowing the investigation of the T groups at the nanometer scale,is shown to have a prominent effect on the optical properties of the MXene. In particular, it leads to a 40% variation of the optical conductivity in the middle of the visible energy range, which is of major interest for optical or sensing applications.

4:10 PM

(ICACC-S12-007-2016) Large-Scale Delamination of Multi-layered MXenes Derived from MAX Phases (Invited)

M. Naguib*[1]; R. Unocic[1]; B. L. Armstrong[1]; J. Nanda[1]; 1. Oak Ridge National Laboratory, USA

MXenes are new family of two dimensional transition metal carbides and carbonitrides derived from MAX phases. During MXenes synthesis, the aluminum, in the MAX phase is replaced by a mixture of functional groups (OH, O, and F; represented hereafter by T_x). The latter weakens the bonding between $M_{n+1}X_n$ layers which then allows sonication to separate the layers from each other. However, the low yields of delaminated flakes are too small to be used in many applications where fully delaminated layers are required. Thus, most of the explored applications for MXenes have focused on stacked MXenes multi-layered powders, i.e. not fully delaminated ones. Herein we present a general approach to delaminate multi-layered MXenes using an organic base such as tetrabutylammonium hydroxide to induce swelling that in turn weakens the bonds between the MX layers. Simple agitation or mild sonication of the swollen MXene in water resulted in the large-scale delamination of the MXene layers. This approach was found to be effective for different MXenes, and different organic bases can potentially yield large quantities of delaminated MXenes. An overview for recent progress in the MXene research will be discussed as well.

4:40 PM

(ICACC-S12-008-2016) Experimental evidence of a new $[Ti_{(1-y)}Cu_y]_3[Al_xCu_{(1-x)}]C_2$ MAX phase solid solution

S. Dubois*[1]; M. Nechiche[2]; V. Gauthier[1]; A. Joulain[1]; V. Mauchamp[1]; T. Cabioch[1]; X. Milhet[1]; S. Azem[2]; P. Chartier[1]; 1. PPRIME Institute, France; 2. University of Tizzi Ouzou, Algeria

In this work, Ti_3AlC_2 MAX phase powders were first prepared at 1450°C for 2 hours from 1.9TiC:1.05Al:1.0Ti initial reactant powder mixture. High-energy milling of Ti_3AlC_2 and Cu powders was then performed during 20 minutes with a ball to powder mass ratio of 5 in order to form large aggregates containing alternative lamellas of Ti_3AlC_2 and Cu. Then, a new $[Ti_{(1-y)}Cu_y]_3[Al_xCu_{(1-x)}]C_2$-Cu Metal Matrix Composite has been produced by sintering the mixture of co-milled Ti_3AlC_2 and Cu powders. In a next step, a selective chemical attack has been performed to extract the metallic Cu. The solid

phase and the chemical solution have been analysed. *Inductively Coupled Plasma* optical emission spectrometry analyses of the chemical solution allows extracting the chemical composition of the solid solution (i.e.: $[Ti_{0.93}Cu_{0.07}]_3[Al_{0.52}Cu_{0.48}]C_2$ and the dissociation rate of the MAX phase (0.7%). From XRD analysis, it is demonstrated that metallic Cu is no longer present in the solid phase whereas SEM-EDXS and WDS characterization confirms the solid solution composition. Transmission electronic microscopy and Electron Energy Loss Spectroscopy confirms the presence of Cu atoms in the solid solution.

5:00 PM

(ICACC-S12-009-2016) YSZ/Nb_2AlC MAX phase composites for crack healing applications

M. Stumpf*[1]; T. Fey[1]; P. Greil[1]; 1. Friedrich-Alexander-University Erlangen-Nuremberg, Germany

Thermal barrier coating systems owe their high temperature stability to a ceramic top coat, which is composed of yttria-stabilized zirconia (YSZ). This coating is prone to failure due to the brittle nature of the ceramic. Herein, a novel processing method to bestow a crack-healing possibility to YSZ ceramics by incorporating a MAX Phase filler is presented. The MAX Phases Nb_2AlC (211) and Nb_4AlC_3 (413) were synthesized by a pressureless in-situ reaction method from a mixture of NbC, Nb and Al powders. The influence of raw material composition on MAX phase formation was evaluated by XRD. The synthesized 211 phase was used to fabricate composites composed of a YSZ matrix and a Nb_2AlC filler by planetary milling and subsequent uniaxial pressing and sintering. Characterization of the resulting composites was carried out by XRD, SEM and μ-CT. Using the pressureless synthesis route the 211 and 413 phases were successfully prepared. The importance of aluminum during synthesis was shown, proving the stabilization of the 413 phase at hyperstoichiometric Al-contents. YSZ/MAX composites could be homogeneously prepared by sintering. Additional thermodynamic calculations using HSC Chemistry 8.1 show the composite behavior in different atmospheres and temperatures. The obtained results indicate that Nb-Al-C based MAX phases can be used as filler in YSZ ceramics, allowing for further studies regarding their crack-healing capability.

S13: Advanced Materials for Sustainable Nuclear Fission and Fusion Energy

Accident Tolerant Fuels I and Spent Nuclear Fuels

Room: St. John

Session Chairs: Michael Jenkins, Bothell Engineering and Science Technologies; Josef Matyas, PNNL

1:30 PM

(ICACC-S13-001-2016) Development of Accident Tolerant Fuel for LWR Application: Current Progress and Technical Challenges (Invited)

S. Johnson*[1]; 1. Westinghouse Electric Company, USA

Largely in response to the severe accident at the Japanese Fukushima Daiichi nuclear power station in 2011, work has been progressing on developing Light Water Reactor (LWR) in-core materials with resistance to core uncovery events. These *Accident Tolerant Fuels* (ATF) specifically include fuel assembly cladding and fuel pellet materials exhibiting significant improvement in resistance to high temperature steam and significant performance improvement relative to the currently used UO_2/Zr alloy fuel system. Generally, for both LWR cladding and fuel, new significantly different materials would provide the greatest steam resistance and performance benefits, but also presents the greatest development challenge. This talk will present the current ATF cladding and fuel concepts under development, with primary focus on materials under development by Westinghouse. These concepts include SiC_f/SiC ceramic matrix composite cladding, coated cladding, Fe-base cladding, U_3Si_2 and UN high density fuel, and others. The current development state of these materials for LWR fuel application will be discussed, including progress to date and status of in-core experiments. Additionally, specific technical challenges that need to be solved for future commercial LWR fuel application of these materials will be detailed.

2:00 PM

(ICACC-S13-002-2016) Development and Property Evaluation of SiC Composite Tubes for Nuclear Fuel Cladding (Invited)

W. Kim*[1]; D. Kim[1]; H. Lee[1]; J. Park[1]; 1. Korea Atomic Energy Research Institute, The Republic of Korea

SiC ceramics and composites have attractive properties regarding nuclear applications, including the excellent high temperature properties, irradiation tolerance, inherent low activation and other superior physical/chemical properties. Therefore, they have been considered for use as reactor core materials in various types of advanced nuclear reactors. In recent years, there have also been efforts on applying the SiC_f/SiC composites to nuclear fuel claddings of various types of reactor systems such as LWR, AHTR, GFR, and SFR. In this study, we fabricated SiC composite tubes with different structures and investigated mechanical properties of the composite tubes. Tubular samples with dimensions of 10 mm in length and outer diameter with a wall thickness of about 0.7 mm were used for the evaluation of mechanical properties before and after thermal shock tests. Thermal shock experiments were performed using a furnace with a vertical quartz tube at 1200°C. After thermal shock tests, changes in hoop strength and microstructural damages such as microcracking and debonding between each layer were characterized.

2:30 PM

(ICACC-S13-003-2016) Micro-mechanical Properties of SiC Composites

N. Rohbeck*[1]; P. Xiao[1]; 1. University of Manchester, United Kingdom

Within the Accident Tolerant Fuel design concept Silicon Carbide (SiC) composite tubes are proposed as a novel nuclear fuel cladding material for commercial light water reactors. Nowadays high-quality, nuclear-grade SiC nanofibers are available, which can be used to build suitable fiber architectures that are then infiltrated using chemical vapor infiltration (CVI) to form a SiC_{CVI}/SiC_{fiber} composite. The thus obtained material consists of a finely grained, stoichiometric CVI SiC matrix phase with the embedded SiC nanofibers providing improved toughness. This study aims to investigate the overall mechanical behavior of these composites using development specimens provided by General Atomics (USA). Therefore nanoindentation is employed to evaluate the mechanical characteristics of the matrix phase and fibers individually. However, the elastic modulus between these two phases differs immensely, which affects the elastic behavior of the composite overall. Furthermore, the CVI technique leads to some porosity, which also influences the elastic modulus of the final material. Hence mechanical testing in form of a micro-bending test is conducted to obtain more representative data for the overall component. In addition, detailed microstructural characterization has been carried out using Raman Spectroscopy and Scanning Electron microscopy (SEM).

2:50 PM

(ICACC-S13-004-2016) Damage Accumulation in Nuclear Grade SiC/SiC Tubular Composites during Mechanical Testing

G. Jacobsen*[1]; J. Sheeder[1]; X. Huang[2]; L. Alva[2]; K. Shapovalov[2]; C. Deck[1]; 1. General Atomics, USA; 2. University of South Carolina, USA

Silicon Carbide (SiC) matrix, SiC fiber reinforced ceramic matric composites (SiC/SiC) are an excellent core material candidate for advanced reactors and accident tolerant fuel due to it retention

of strength at high temperature and stability under irradiation. Understanding how damage accumulates in these advanced engineered composites is required for licensing and lifetime prediction models and while typical stress strain plots are a useful overview of material behavior, they provide limited information on microscale level damage. Acoustic emission tests were used to track individual micro-cracking events. Pattern recognition in combination with waveform analysis was used to help distinguish matrix cracking from fiber breaking, fiber sliding, and other frictional events. Digital image correlation was used to map full field strain during testing and in some cases high frame rates were used to capture information just prior to specimen failure. Strain maps show that the composite experience large, highly localized strain that exceeds the strains typically reported in stress-strain plots. The microscopic damage progression dissipates energy and results in prominent pseudo-ductile failure behavior. NDE analysis using X-ray computed tomography was used to analyze defect distribution and its relevance to the observed damage accumulation.

3:30 PM

(ICACC-S13-005-2016) Developments in Ceramic and Glass Composite Material (GCM) Wasteforms for Difficult Radioactive Wastes (Invited)

W. E. Lee*[1]; D. Pletser[1]; N. E. Ahmad[1]; C. Hutchison[1]; Y. Hsieh[1]; R. K. Chinnam[1]; 1. Imperial College London, United Kingdom

A legacy of the world's nuclear programmes is a cornucopia of waste types. To underpin safety cases so allowing long-term but temporary waste storage or permanent disposal a variety of durable wasteforms have been developed to host these wastes. Initially, these were largely vitreous for High Level Waste and cementitious for Intermediate Level Waste but as the relatively straightforward wastes have been immobilised more creative solutions are needed for the difficult legacy wastes such as those in the UK's Legacy Ponds and Silos (LP&S) at Sellafield, those in the USA's Hanford site and those being created in the clean-up at Fukushima in Japan. This talk will illustrate the range of wasteforms available for immobilising difficult wastes from these global programmes with specific focus on ceramics and GCMs for the UKs LP&S wastes and those being generated at Fukushima.

4:00 PM

(ICACC-S13-006-2016) Corrosion of Copper-Coated Steel Containers for Used Nuclear Fuel Storage (Invited)

S. Ramamurthy*[1]; T. Standish[1]; D. Zagidulin[1]; J. Chen[1]; R. Jacklin[1]; D. Shoesmith[1]; P. Keech[2]; 1. University of Western Ontario, Canada; 2. Nuclear Waste Management Organization, Canada

Copper-coated steel used fuel containers (UFCs) are currently being considered by the Nuclear Waste Management Organization (NWMO) for permanent disposal of used nuclear fuel in a Canadian deep geological repository (DGR). The proposed coating structure consists of an electrodeposited copper coating for the container and cold sprayed copper coating for sealing the final closure weld. Understanding the long-term corrosion performance of UFCs is critical because regulations require containment be achieved for many thousands of years after emplacement. With this in mind, an extensive research program is underway to evaluate the corrosion performance of these coatings. This presentation will summarise the corrosion processes that have been hypothesized for UFCs in a DGR. A detailed discussion of two research topics will be included: (a) comparison of the long-term corrosion behaviour of the copper coatings to that of the high-purity copper for which extensive information currently exists under waste disposal conditions, and (b) galvanic corrosion at fault locations in the copper coating. Although it is unlikely such faults will exist, they would provide the most likely failure pathway if present. The results from the long-term electrochemical and galvanic corrosion experiments, and the data from the follow-up analytical measurements, including micro CT X-ray tomography technique, will be presented.

4:30 PM

(ICACC-S13-007-2016) *In-situ* structural investigations on monazite-type $La_{0.2}Gd_{0.8}PO_4$-ceramics under heavy ion irradiation

S. Neumeier*[1]; P. K. Kulriya[2]; Y. Arinicheva[1]; G. Deissmann[1]; D. Bosbach[1]; 1. Forschungszentrum Jülich GmbH, Germany; 2. Inter-University Accelerator Centre, India

In the last decades, various ceramic materials have been proposed as potential waste forms for the immobilization of special nuclear waste streams, such as separated plutonium from civilian or military sources, or separated minor actinides. Among them, monazites (monoclinic $LnPO_4$, *Ln* = La - Gd) appear as promising candidates due to their specific physico-chemical properties including high structural flexibility, high chemical durability, and high radiation resistance. Pellets of single phase $La_{0.2}Gd_{0.8}PO_4$ solid solution have been obtained by co-precipitation and subsequent uniaxial hot-pressing at 1250°C for 6 h. The phase transformations in $La_{0.2}Gd_{0.8}PO_4$ with monazite structure as consequence of irradiation with 100 MeV Au ions at different ion fluences varying from $1x10^{12}$ ions/cm^2 to $1x10^{14}$ ions/cm^2 are investigated using *in-situ* grazing-incidence X-ray diffraction (XRD). In the *in-situ* XRD experiment, $La_{0.2}Gd_{0.8}PO_4$ samples are irradiated with swift heavy ions and a sequential *in-situ* diffraction pattern is recorded. After that, the ion fluence is successively increased until amorphisation of the sample is discernable in the diffraction patterns. The experimental results related to irradiation-induced structural processes during amorphisation and recrystallisation of $La_{0.2}Gd_{0.8}PO_4$ will be discussed in detail and compared to complementary computational studies.

4:50 PM

(ICACC-S13-008-2016) Chasing iodine in low-activity waste off-gas condensate

J. Matyas*[1]; R. M. Asmussen[1]; N. Qafoku[1]; 1. PNNL, USA

The Low-Activity Waste Vitrification Facility at the Hanford Waste Treatment and Immobilization Plant will generate an aqueous off-gas condensate containing radionuclides such as ^{129}I and ^{99}Tc. Instead of recycling this stream back to the vitrification facility, a treatment with sorbent is being considered that would shorten the duration of the vitrification campaign and decrease the quantity of waste glass produced. A sorbent under investigation for the removal and sequestration of iodine from condensate is silver-functionalized silica aerogel. This material exhibits excellent sorption properties for iodine in nuclear fuel reprocessing off-gas streams, with iodine capacities up to 480 mg/g and decontamination factors in excess of 10,000. Batch experiments up to one week long were carried out in deionized water and in a dilute salt solution with neutral pH (sodium and ammonium salts of nitrate, chloride and fluoride) containing 10 ppm of iodide or iodate. After loading with iodine, the sorbent was consolidated using hot isostatic pressing or spark plasma sintering at moderate temperatures and pressures. The presentation will highlight findings of this study and discuss the sorbent performance and waste form development.

5:10 PM

(ICACC-S13-009-2016) Suggestive Improvements to the Spent Nuclear Fuel Dry Storage cask system

D. Miller*[1]; R. Kanakala[1]; 1. University of Idaho, USA

Spent Nuclear Fuel (SNF) is collected in water pools and in dry storage casks due to not having any permanent repositories. These dry storage casks expose the SNF to more vulnerability than a repository would. The dry storage casks are not meant to be permanent and were only designed to last less than 100 years whereas the repository standard is >10,000 years. There is an increased risk of a release of radioactive material due to an accident from dry storage casks as they may only reach a third to half of their projected life, due to many degradation mechanisms. One such degradation mechanism is proximity to coastal areas where the salt content in the air is high. This causes accelerated corrosion of metal components while freeze/

thaw cycles are cracking and spalling the concrete portions. This paper discusses the types of materials these dry storage cask systems are made of and how they are vulnerable to corrosion/wear and how they can be better constructed so that the SNF is safer until a repository can be opened. These improvements include using a higher grade of concrete, using stainless steels or other metals that are resistant to corrosion, or housing the casks inside a structure. The additional costs of these measures will be justified if they prevent a spread of contamination to the environment.

S14: Crystalline Materials for Electrical, Optical and Medical Applications

New Direction I

Room: Tomoka C
Session Chair: Kenji Toda, Niigat University

1:30 PM

(ICACC-S14-001-2016) A new insight on the concept of stoichiometry for oxides (Invited)

S. Uda*[1]; 1. Tohoku University, Japan

The essential concept regarding the 'stoichiometry' proposed by Dalton has been considered to introduce an extended stoichiometry. We redefined 'stoichiometry' in such a way that a material in which the activities of all the constituent elements can be unity is stoichiometric since the unity of activity yields zero mixing term in chemical potentials. Such an extended stoichiometry widens the presence of stoichiometric compositions from a single point to a range described by a line. Constituent elements include impurities and even vacancies, which has not been allowed in the conventional stoichiometry. In order for the activity of an element to be unity, we need to assign the chemical potential itself to the standard-state chemical potential to exclude the mixing term. This is possible only when one degree of freedom is available for each of constituent elements. The degree of freedom is examined in each crystal site by the subtraction of number of constraints from that of constituent elements. Considering all of these the validity of the essential concept of stoichiometry has been thermodynamically proved. Then we experimentally showed the presence of the new stoichiometry by developing MgO-doped $LiNbO_3$ that is simultaneously congruent and stoichiometric. In the crystal the unity of activity of elements is valid not only in the solid but also in the liquid.

2:00 PM

(ICACC-S14-002-2016) Single crystal growth of NbN and NbTiN for superconductive single photon detectors (Invited)

F. Mercier*[1]; N. Tsavdaris[1]; D. Hazra[2]; M. Hofheinz[2]; E. Blanquet[1]; 1. CNRS-SIMAP, France; 2. CEA, France

Quantum optics is undergoing tremendous progress, both conceptually and experimentally. One important remaining challenge is single photon detection with near-unity efficiency, high time resolution, low dark counts and photon number resolution. To fulfill such requirements, high quality niobium nitride (NbN) and niobium titanium nitride ($Nb_xTi_{1-x}N$) must be synthesised. Till now, the thin films necessary for superconductive devices are mostly synthesized by physical vapor deposition methods. The aim of this study is to introduce chemical vapor deposition technique (CVD), as an alternative technique to process single crystal superconducting niobium nitride-based thin films. In this work, NbN and $Nb_xTi_{1-x}N$ thin films have been grown by halide CVD from NbClx(g), TiClx(g) and NH3(g) precursors, diluted in H2(g). Substrates are (0001) sapphire, (0001) GaN and (0001) AlN. The influence of experimental parameters on the composition of the thin film and its structural properties will be given. In particular, the stability of the cubic structure, the only structure which has the superconductive properties, will be discussed regarding the growth parameters. Influence of structural properties on superconductive behavior will also be given. Finally, the potentiality of the CVD technique to synthesis high quality niobium nitride-based thin films and multilayers structures will be presented.

2:30 PM

(ICACC-S14-003-2016) Oxide single crystals grown by the flame-fusion method (Invited)

S. Kawaminami*[1]; S. Asaka[1]; K. Mochizuki[1]; 1. Shinkosha Co., Ltd., Japan

Shinkosha is manufacturing sapphire, rutile and strontium titanate (STO) using the flame-fusion method (FFM). Their optical properties will be talked, in particular their colors, absorption and fluorescence. The FFM has some advantages such as rapid growth rate, simple equipment, without use of crucible, and easy to add dopants. Therefore the FFM is a still beneficial method in recent days. Sapphire crystals grown by FFM are mainly used for watch windows. Usually, small amount of Ti are doped to grow cylindrical shape and to reduce small bubbles. When UV light irradiated, Ti-doped sapphire emit blue fluorescence, and then its color changes to brown. It is considered brown color is caused by color center (trapped hole at Al vacancy). Rutile is applied as birefringence material for optical components, and STO is a representative crystal for perovskite structure so that used as substrates for functional thin film growth. As-grown rutile and STO crystals have dark-blue color and electrical conductivity because they are grown in H_2-O_2 combustion flame. After heat treatment in air, these color change to faint yellow and they have electrical insulation. By heat treatment in H_2, rutile has dark-blue color and conductivity, but STO keeps its transparency and resistivity. It is thought this difference causes by hydrogen behavior, more specifically in case of STO hydrides are occupying O sites.

Optical Material I

Room: Tomoka C
Session Chair: Michel Ferriol, Université de Lorraine

3:20 PM

(ICACC-S14-004-2016) Polarization-dependent absorption behavior in the monoclinic LYB and LGB compounds doped with Ytterbium ions (Invited)

W. Gebremichael[1]; Y. Petit[2]; A. Fargues[2]; P. Veber[2]; M. Velazquez[2]; V. Jubera[2]; L. Canioni[1]; I. Manek-Hönninger*[1]; 1. University of Bordeaux, France; 2. CNRS, France

Ytterbium-doped crystals have proven to be attractive laser media and are used in industrial laser systems. This is mainly due to the relatively small Stokes shift of these materials, which limits the heating effect during the laser process. Moreover, the absorption spectrum of the Ytterbium ion matches perfectly the emission wavelength of high power InGaAs laser diodes for pumping those laser crystals. Owing to the relatively large gain bandwidth depending on the host matrices Yb-doped crystals are suitable for ultrafast lasers and amplifiers down to the femtosecond regime. Curiously, many of the commonly used materials, as e.g. double-tungstates, belong to the monoclinic system, such low symmetry being known to show non trivial optical specificities. In this contribution we show the absorption properties of two different Yb-doped monoclinic borate compounds under polarized light. The studied crystals are $Li_6(Gd)_{0.75}Yb_{0.25}(BO_3)_3$ and $Li_6Y_{0.75}Yb_{0.25}(BO_3)_3$, respectively, and were grown by the Czochralski method. We focused on the study of their absorption at the zero line transition as a function of the polarization direction of the incident light for two different crystal cuts of each compound. We will discuss the different frames that should be considered in these materials due to their monoclinic character, as well as the optimal crystal orientation for absorption.

3:50 PM

(ICACC-S14-005-2016) Crystal growth of non-linear optical crystal in SICCAS (Invited)

A. Wu*[1]; L. Su[1]; J. Xu[1]; Y. Zheng[1]; X. Chen[2]; 1. Shanghai Institute of Ceramics, Chinese Academy of Sciences\", China; 2. Shanghai Jiaotong University, China

Both large-aperture NLO (non-linear optical) crystal high-average power frequency conversion and UV/VUV (ultraviolet / vacuum ultraviolet) NLO crystal are important directions for the investigation and growth on NLO crystal growth. Large-aperture YCOB non-linear plate was demonstrated to the frequency conversion candidate material for high-average power laser at Lawrence Livermore National Laboratory. Among these ferroelectric fluoride crystal, $BaMgF_4$ with a decreasing transparency towards the cut off wavelength at about 130 nm, is an attractive candidate for deep UV laser. Shanghai Institute of Ceramics, Chinese Academy of Sciences (SICCAS) is an important institute on crystal growth in China. In the past years, SICCAS has grown large-aperture YCOB crystal with modified Bridgman method and $BaMgF_4$ single crystals with the temperature gradient technique. In this work, we will introduce the situation of SICCAS on the crystal growth and frequency conversion in both YCOB and $BaMgF_4$ single crystals.

4:20 PM

(ICACC-S14-006-2016) Investigation on the electro-optical crystals and switchers: From crystal growth to laser applications (Invited)

J. Wang*[1]; H. Yu[1]; X. Wang[2]; 1. Shandong University, China; 2. Shandong Academy of Sciences, China

The Electro-optics effect is one of nonlinear optical effects that has significant applications in optical and laser technologies. It consists of two main effects named Pockels and Kerr effects which can be used in the generation of pulsed lasers with huge energy and short pulses. However, constrained by the available electro-optical (EO) crystals and switchers, the EO switched lasers are limited to be those with low repetition rates, tens of milli-joules, especially in near infrared spectra region. In the last ten years, we have been developing novel EO crystals and switchers in which the langasite (LGS) and potassium tantalate niobate (KTN) were chosen for the Pockels cells and Kerr switcher, respectively. In this paper, the LGS and KTN EO crystals and switchers are reported and developed including the crystal growth, characterization and applications in pulsed lasers. Based on the growth of high-quality LGS crystals and its crystalline physics, the novel Pocekles cells were invented and the high repetition-rate, hundreds of milli-joules and expanded to mid-infrared pulsed lasers were realized. The large size KTN crystals were grown and the Kerr switcher with half-wave voltages of 70 V was developed.

4:50 PM

(ICACC-S14-007-2016) Enhanced conversion of polycrystalline to single-crystal $Sr_5(PO_4)_3F$ in an electric field

Y. Liu*[1]; J. Zheng[1]; Y. Wu[1]; 1. Alfred University, USA

Fluorapatite-type $Sr_5(PO_4)_3F$ is a good candidate for a high-power laser application. However, due to the size limitation and high cost associated with single-crystal growth, it is necessary to find alternatives to fabricate the single crystal. The objective of this work is experimentally and theoretically to demonstrate that solid-state conversion of polycrystalline to single-crystal $Sr_5(PO_4)_3F$ can be achievable by a field-assisted sintering. Single-crystal seeds embedded in $Sr_5(PO_4)_3F$ nanopowders were consolidated through spark plasma sintering and pressureless field-assisted sintering techniques. The effects of high and low electric fields on $Sr_5(PO_4)_3F$ solid-state conversion were studied. In order to avoid the decomposition of the materials and enhance the sintering rate, fluoride additive was added to enhance the efficacy of conversion during a solid-state conversion. The electrostatic force at the interface between polycrystalline and single crystal is crucial in determining grain boundary migration. The kinetic correlations between grain boundary migration and space charge under the external electric field were also investigated. A theoretical analysis and experimental results demonstrated that conversion of fluorapatite crystals from ceramics is possible and could be expedited by an applied electric field.

5:10 PM

(ICACC-S14-008-2016) Crystal growth between 1250°C and 1100°C of cubic rare-earth sesquioxides by the flux method

M. Velazquez*[1]; P. Veber[1]; G. Buse[1]; G. Gadret[2]; O. Plantevin[3]; P. Goldner[4]; D. Rytz[5]; M. Peltz[5]; E. Veron[6]; R. Belhoucif[7]; P. Douissard[8]; T. Martin[8]; 1. CNRS, France; 2. LICB, UMR 6303 CNRS-Université de Bourgogne, France; 3. CSNSM, UMR 8609 CNRS-Université d'Orsay, France; 4. PSL Research University, Chimie ParisTech – CNRS, Institut de Recherche de Chimie, France; 5. Fee GmbH, Germany; 6. CEMHTI-CNRS UPR 3079, France; 7. Faculté de Physique, Laboratoire d'Électronique Quantique, USTHB, Algeria; 8. ESRF - The European Synchrotron, France

Developing large optical grade cubic rare-earth sesquioxides (RE_2O_3, RE=Sc,Y,Gd,Tb,Lu) single crystals stands as one of the most challenging endeavours of today's crystal growth. In recent years, we have unveiled a new flux method for growing such crystals, essentially for optical applications (lasers, scintillators, Faraday rotators). The obvious challenge to their growth in bulk single crystalline shape imposed by their high melting point (~2400°C) is rendered more difficult by series of structural phase transitions occurring upon cooling from the melting point. The case of Tb_2O_3 turns out to be complicated by its mixed valence character which results in an easy oxidation at intermediate and high temperatures. The crystal growth of cubic Gd_2O_3:Yb^{3+} laser crystal, $Lu_{1.56}Gd_{0.41}Eu_{0.03}O_3$ scintillation crystal and Tb_2O_3 crystal has never been achieved nor reported. We present the first crystal growth of these crystals by a hydrogen free and controlled atmosphere flux method which uses a heavy metal free solvent working between 1250°C and 1100°C, that is, at less than half their melting temperature. Cubic millimeter-sized Tb_2O_3 crystals extracted from as-grown boules exhibit a Verdet constant which is at least three times higher than that of a commercial $Tb_3Ga_5O_{12}$ (TGG) crystal. Laser operation with Yb^{3+}-doped Y_2O_3 and Gd_2O_3 crystals was also proved.

5th Global Young Investigator Forum

Nanocomposites and Nanostructured Materials and Energy Generation, Saving and Storage

Room: Coquina Salon F

Session Chairs: Valerie Wiesner, NASA Glenn Research Center; Eva Hemmer, INRS; Riccardo Marin, INRS; Manabu Fukushima, National Institute of Advanced Industrial Science and Technology (AIST)

1:30 PM

(ICACC-GYIF-001-2016) On the Design of Novel Structural Materials for Multifunctional Applications (Invited)

S. Gupta*[1]; 1. University of North Dakota, USA

In this presentation, I will present research findings on three different areas of materials research: (a) MAX phases (novel natural laminates) and their composites, (b) novel sustainable structural materials, and (c) green manufacturing. During Part A, recent results on the mechanical behavior of MAX and their composites will be presented. Briefly, $M_{n+1}AX_n$ (MAX) phases (over 60+ phases) are thermodynamically stable nanolaminates displaying unusual, and sometimes unique, properties. These phases possess a $M_{n+1}AX_n$ chemistry, where n is 1, 2, or 3, M is an early transition metal element, A is an A-group element, and X is C or N. The MAX phases are highly damage tolerant, thermal shock resistant, readily machinable, and with Vickers hardness values of 2–8 GPa, are anomalously

soft for transition metal carbides and nitrides. MAX phases display nonlinear, hysteretic, elastic behavior due to kink band formation in the basal planes. Recently, it was demonstrated that MAX Phase-based composites can be used as shafts against SA (Super Alloys) foils for different foil bearing applications at 50,000 rpm from RT till 550°C during thermal cycling. Thus, there is a huge potential that these materials can be used for different tribological and engineering systems, for example, air-foil bearings, gas turbine seals, cylinder wall/piston ring lubrication for low-heat rejection diesel engines, various furnace components, among many others. During Part B, recent studies about the development of novel sustainable materials will be presented. This part will focus on the development of green cements. During Part C, novel practices for enhancing green manufacturing will be discussed.

2:00 PM

(ICACC-GYIF-002-2016) Fabrication of Si-CNT/graphene nanocomposites for high-performance lithium-ion batteries

L. Xiao*[1]; Y. Sehlleier[1]; C. Schulz[2]; H. Wiggers[2]; 1. University of Duisburg-Essen, Germany; 2. Center for Nanointegration Duisburg-Essen (CENIDE), Germany

Silicon has emerged as one of the most promising anode materials for next-generation lithium-ion batteries (LIBs) owning to its natural abundance, relatively low working potential and its high theoretical storage capacity of 3579 mAh/g. In this study, Si nanoparticles (NPs) were synthesized in a well-designed hot-wall reactor from monosilane as silicon precursor. This process enables producing high purity Si NPs (average crystallite size of 20 nm) with a large production rate of 0.5 – 1.0 kg/h. Crystal size, morphology and crystallinity of the Si NPs can be tuned by adjusting the synthesis parameters. However, pristine silicon suffers from degradation during electrochemical testing. To improve the stability and performance of the as-synthesized Si NPs for battery applications, the preparation of carbon-based nanocomposites such as Si-CNT and Si-CNT/reduced graphene oxide (Si-CNT/graphene) has been investigated. As a highly promising product, Si-CNT/graphene nanocomposites with approx. 50 wt.% loading of Si NPs were prepared. They provide capacities of 1660, 1560 and 750 mAh/g at C-rates of 0.2, 1.0 and 10 C, respectively. Moreover, improved nanocomposite anode materials demonstrate excellent cycle stability with capacity retentions of up to 90% after 500 cycles.

2:20 PM

(ICACC-GYIF-003-2016) Sodium Titanates as Promising Anodes for Sodium-ion Battery Application

A. Rudola*[1]; P. Balaya[1]; 1. National University of Singapore, Singapore

The challenge with renewable sources of energy such as solar or wind is to adequately deal with their intermittent nature as cheaply as possible. For this purpose, a battery technology not reliant on lithium would be key as lithium is relatively scarce in the earth's crust which could influence its future cost and hence, the future price of lithium-ion batteries (LIBs). Sodium-ion batteries (NIBs), reliant on globally abundant sodium resources, would be ideal for this purpose if their performance could be comparable to that of LIBs. Over the past five years, there has been tremendous focus on NIBs. Due to this, some NIB cathodes have been shown to rival LIB cathodes in terms of performance. In this presentation, we will share our results on the sodium storage performance of sodium titanates as very promising anodes meant for grid storage NIBs. The first phase, $Na_2Ti_6O_{13}$, could be very appealing for regulating the frequency of the grid and dealing with the minute-by-minute fluctuations of renewable power plants owing to its extremely stable cycling exceeding 5,000 cycles. The second phase, $Na_2Ti_3O_7$, could not only be applied for the above purpose, but could also be used for load-leveling applications due to its higher capacity and very low voltage activity. We will discuss the sodium storage mechanism and performance of these phases and also demonstrate full cell performance with these anodes.

2:40 PM

(ICACC-GYIF-004-2016) Efficiency enhancement in Giant Core/Alloyed-Shell Quantum Dots Luminescent Solar Concentrator

H. Zhao[1]; D. Benetti*[1]; L. Jin[1]; Y. Zhou[1]; F. Rosei[1]; A. Vomiero[2]; 1. INRS, Canada; 2. Institute of Metal Research, Italy

Luminescent solar concentrators (LSCs) can minimize the cost of solar cells by reducing the photoactive area of the solar cell and boosting the photoconversion efficiency (PCE). The optical properties of CdSe/CdS core/shell quantum dots (QDs) have been optimized for large area high efficiency LSC, yet their performance is hindered due to limited light absorption above 500 nm, with poor spectral matching with sun light. Here, we demonstrate the application of giant $CdSe/Cd_xPb_{1-x}S$ core/shell QDs as light harvesters in high performance LSCs with over 1.15% of PCE and almost 40% of Luminescent Quantum Efficiency (LQE). We synthesized the new "giant" $CdSe/Cd_xPb_{1-x}S$ QDs via a successive ionic layer absorption and reaction (SILAR) approach, with high quantum yield (QY, 40%), narrow size distribution (<10%) and stable PL in a wide temperature range (100 K ~300 K). These thick alloyed-shell QDs were, then, embedded in a polymer matrix, resulting in a highly transparent composite with the absorption spectrum covering the range 300 nm to 600 nm. The prototype LSC based on alloyed shell exhibited a ~15% enhancement in efficiency with respect to the pure CdS shell, thanks to the contribution of the Pb dopant. Our results demonstrate an easy approach to enhance light absorption in giant QDs by metal doping, indicating a promising route to broaden the absorption spectrum in LSCs.

3:20 PM

(ICACC-GYIF-005-2016) Dielectric properties of $BaTiO_3$ nanocube 3D architectures (Invited)

K. Mimura*[1]; K. Kato[1]; 1. National Institute of Advanced Industrial Science and Technology (AIST), Japan

The high performance and high integration dielectric devices with minimum size are strongly demanded in recent years. To fabricate such devices, dielectric properties of the constituent materials should be enhanced with decreasing their size in near future. Barium titanate (BT) is well-known as typical dielectric materials. However, the dielectric properties of BT nanoparticles decreased with decreasing their size. Nanocrystals and their unique properties due to their shapes and interfaces have attracted attention over the years. We focused on the bottom-up process of single-crystalline BT nanocubes (BT NCs) as the new nano-sized materials for dielectric devices. BT NCs were synthesized by hydrothermal method with Ti aqueous compound and organic surfactants. BT NCs had about 15 nm in an edge length with sharp edges and uniform size distribution. 3D architecture of BT NCs was fabricated by self-assembly process via dip-coating technique. High-ordering structure was yielded and face-to-face conjugation of BT NCs was confirmed after sintering at 1123 K. Dielectric constant of BT NC assembly showed above 3000 which was very high value compared with that of solution-derived BT-based thin films. Moreover, the patterning of the assemblies was conducted by using patterned substrate with polymer molds. This bottom-up process using nanocubes as building blocks is expected to apply for the next generation devices in future.

3:50 PM

(ICACC-GYIF-006-2016) Control of phase distribution and microstructure in high temperature piezoelectrics for modification of properties

B. Kowalski*[1]; A. Sehirlioglu[1]; 1. Case Western Reserve University, USA

In recent years there has been a push for the development of high temperature piezoelectrics, usually in a morphotropic phase boundary (MPB) region to provide enhanced dielectric and electromechanical properties, for terrestrial and aerospace applications. Manipulation of the properties is often achieved through substitution on the A-site and/or B-site, controlling grain size, or

introduction of secondary phases. Sintering can be achieved at a range of temperatures for a given material system, however competition with coarsening can lead to a variety of properties related to microstructure, compositional heterogeneities, and core-shell structure in specimens that are similarly high density. The work that will be presented focuses on varying processing temperature to control properties for MPB phases containing $BiScO_3$, $PbTiO_3$, and $Bi(Zn_{0.5}Zr_{0.5})O_3$. For compositions near an MPB, there is usually a mixed rhombohedral and tetragonal phase and the ratio of these phases is related to the resultant properties. However, the mixed phase can be controlled by varying the processing temperature. Preliminary data shows that lowering the sintering temperature from 1100°C to 1000°C increases the rhombohedral phase while also increasing d_{33} from 473 pm/V to 570 pm/V and the planar coupling factor (k_p) from 0.39 to 0.42.

4:10 PM

(ICACC-GYIF-007-2016) Filled $Nd_zFe_xCo_{4-x}Sb_{12-y}Ge_y$ skutterudites: processing and thermoelectric properties

J. Mackey*[1]; A. Sehirlioglu[1]; F. Dynys[2]; 1. Case Western Reserve University, USA; 2. NASA Glenn Research Center, USA

Skutterudites have proven to be a useful thermoelectric system as a result of their enhanced figure of merit (ZT>1), cheap material cost, favorable mechanical properties, and good thermal stability. The majority of skutterudite interest in recent years has been focused on binary skutterudites like $CoSb_3$. Binary skutterudites are often double and triple filled, with a range of elements from the lanthanide series, in order to reduce the lattice component of thermal conductivity. Ternary and quaternary skutterudites, such as $Co_4Ge_6Se_6$ or $Ni_4Sb_8Sn_4$, provide additional paths to tune the electronic structure. The thermal conductivity can further be improved in these complex skutterudites by the introduction of fillers. The $Nd_zFe_xCo_{4-x}Sb_{12-y}Ge_y$ system has been investigated as a p-type thermoelectric material, and is stable up to 600°C. The influence of Fe and Ge content, along with filler Nd, was investigated on thermoelectric transport properties. In addition to the chemical influence on properties, some processing details of the system will also be addressed.

4:30 PM

(ICACC-GYIF-008-2016) Teramometry - Temperature Sensing Using THz Radiation

R. Naccache*[1]; A. Mazhorova[1]; M. Clerici[2]; L. Razzari[1]; F. Vetrone[1]; R. Morandotti[1]; 1. INRS, Canada; 2. Heriot-Watt University, United Kingdom

The rapid ascent of nanoscience has garnered significant attention in recent years. Much of the interest generated has dealt with the use of nanoparticles in imaging and therapeutics. Of particular interest are the metal nanoparticles, which show a surface plasmon resonance following excitation with an appropriate irradiation source. An interesting by-product of the plasmon resonance effect is a localized temperature increase. Detection and imaging are possible *via* the use of Terahertz waves, which possess absorption and refractive indices that are sensitive to temperature changes. Here we report on the use of NIR plasmonic heating of gold nanoparticles and the underlying effects on Terahertz radiation. A thermometric relationship is studied in liquid and solid model systems.

4:50 PM

(ICACC-GYIF-009-2016) Synthesis of hollow silica nanoparticles using poly acrylic acid- amine compound template

Y. Nakashima*[1]; M. Fuji[1]; T. Shirai[1]; 1. Nagoya Institute of Technology, Japan

Hollow silica nanoparticles are comprised of silica shell and inner cavity. It has a lot of advantages; low density, high surface area, low thermal conductivity, etc. Therefore, this has received increasing attention and has been applied in diverse fields. Synthesis of hollow silica nanoparticles method that using poly acrylic acid (PAA)-ammonia solution mixture was as size template was proposed. The mixture is dissolved in water, but it is stable in alcohol, therefore the mixture can be a template for hollow particle in alcohol and can be easily removed it by addition of water. But this method need long reaction time (>12h), because template is collapsed by stirring during making silica shell. Herein, the mixture droplet can be strong by cross-linking of PAA using amine compounds which interact with carboxylic acid. In order to investigate effect of amines on hollow particle formation, three types of amine compound were used. In this work, it is aimed shortening of the reaction time by changing ammonia catalyst. The PAA-amine compounds were formed with around 100 nm droplets and hollow silica particles were synthesized in all condition. In addition, it was composed after adding tetraethyl orthosilicate (TEOS) which is source of silica shell even one hour later. Because the template was stronger than PAA-ammonia by cross-linker which is amine compound and silica shell can be easily formed.

5:10 PM

(ICACC-GYIF-010-2016) Shaping of ceramic microspheres using vibrational droplet coagulation

J. Pype[1]; B. Michielsen*[1]; S. Mullens[1]; V. Meynen[2]; 1. VITO, Belgium; 2. University of Antwerp, Belgium

The recent growth of interest in uniform microspheres for different applications has led us to produce spherical ceramic beads of different sizes and architectures. During the past years many methods have been developed to shape microspheres using different techniques, such as: spray drying, extrusion dripping, vibrational droplet coagulation and rotating disk atomization. In order to obtain uniform microspheres the vibrational droplet coagulation was selected as most controlled and versatile. The technique enables the shaping of microspheres with different architectures varying from dense to hollow as well as core-shell. The current research stipulates the impact and important role of combining both variations in powder loaded suspension composition (loading, type and amount of alginate, powder particle size, crystal phase, ...) and process parameters of the vibrational droplet technique (nozzle size and architecture, pressure, amplitude, frequency, ...). Beyond expectations, a broad window of control was found based on the combination of both process and suspension characteristics. By controlling the resulting suspension composition, sinter profile and temperature, the porosity and mechanical strength can vary depending on the requirements of the application.

FS2: Advanced Ceramic Materials and Processing for Photonics and Energy

Solar Energy I

Room: Coquina Salon G

Session Chairs: Riad Nechache, Ecole de Technologie Superieure; Daniel Chua, National University of Singapore

1:30 PM

(ICACC-FS2-001-2016) Interfacing organic, inorganic and carbon-based nanomaterials for energy applications (Invited)

G. Fanchini*[1]; 1. University of Western Ontario, Canada

Large-area, solution-processed, graphene laminates are of interest for a number of applications in renewable energy. Interest stems from their ease of preparation, by vacuum filtration of suspensions of graphene oxide or exfoliated graphene flakes. Over the last few years, our group has worked on two essential optimization processes of graphene laminates for solar energy and, specifically: i) investigation of their work function for efficient photocarrier collection ii) improvement of their thermal conductivity for efficient heat evacuation from plastic photovoltaics and mitigation of their degradation, and iii) interfacing them with a variety of organic and inorganic nanomaterials In order to investigate the work function of graphene

laminates, we used Kelvin Probe Force Microscopy, in the dark and under Far-Field and Near-Field Scanning Optical Microscope illumination. We observed a significant photoinduced increase in the open circuit voltage in thin film solar cells assembled on graphene laminates, which corresponds to similar changes in the electronic work function of the graphene electrode. The observed phenomena are in agreement with a dynamic graphene-insulator-metal model taking into account the specific photophysical properties of graphene as a zero-band gap semiconductor.

2:00 PM

(ICACC-FS2-002-2016) Heterostructured nanomaterials for solar energy applications (Invited)

H. Zhao*[1]; 1. INRS, Quebec Univeristy, Canada

Near infrared (NIR) QDs have attracted much attention due to their unique size-tunable optical properties. In this talk, we focus on the synthesis of NIR colloidal PbS@CdS core@shell QDs, the investigation the photoelectron transfer rate from QDs to wide bandgap semiconducting mesoporous films and further fabrication of photoelectrochemical (PEC) devices. We have synthesized high-quality PbS or PbS@CdS QDs via cation exchange. The as-synthesized QDs were loaded into the mesoporous metal oxide thin film by a link-assisted methods. The different electron affinity of the oxides (SiO_2, TiO_2 and SnO_2), the core size and the shell thickness allow to fine tune the electron injection rate by determining the width and height of the energy barrier for tunneling from the core to the oxide. Theoretical modeling using the semi-classical approximation provides an estimate for the escape time of an electron from the QD 1S state, in good agreement with experiments. The results demonstrate the possibility of obtaining fast charge injection in NIR QDs stabilized by an external shell. We further developed a new hybrid photoanode architecture for PEC H_2 generation. The optimized photoanode results in a remarkable saturated photocurrent density of 11.2 mA/cm^2, which is the highest reported value in a PEC system using NIR QDs as sensitizers.

2:30 PM

(ICACC-FS2-003-2016) Near Infrared Colloidal Quantum Dots for Efficient and Durable Photoelectrochemical Hydrogen Production

L. Jin*[2]; B. AlOtaibi[5]; D. Benetti[3]; S. Li[2]; H. Zhao[1]; Z. Mi[5]; A. Vomiero[4]; F. Rosei[1]; 1. INRS, Canada; 2. Institut National de la Recherche Scientifique, Canada; 3. Institut national de la recherche scientifiqueIn, Canada; 4. Institute of Metal Research, Italy; 5. McGill University, Canada

The increasing demand in renewable and sustainable energy has fueled considerable efforts toward photoelectrochemical (PEC) H_2 generation. TiO_2 and ZnO demonstrated to be promising photocatalysts, yet require UV-light activation due to their wide band gap (3.2 eV). To enhance their light absorption, quantum dots (QDs) have been developed as light absorbers to sensitize the metal oxides. Despite the remarkable results obtained by QDs optically active in the visible range, almost 95% of solar energy was not converted. Near infrared (NIR) QDs were recently introduced into PEC system, while unsolved issues related to high charge recombination and poor photostability resulted in quite low H_2 production. Here, we developed a PEC hybrid photoanode architecture which is composed of a TiO_2 mesoporous frame, functionalized by colloidal NIR core@shell QDs via electrophoretic deposition (EPD), and followed by a CdS capping layer, acting as passivating layer and optically active component for light adsorption. We report the highest saturated photocurrent density value (11.2 mA/cm^2) in a stand-alone PEC system using NIR QDs as sensitizer and a dye-sensitized solar cell as external bias. The PEC system showed a stable saturated current density under high intensity illumination (800 mW/cm^2), demonstrating its high potential to be combined with a solar concentrator for H_2 production.

3:10 PM

(ICACC-FS2-004-2016) Electrodes for photoelectrochemical cells: structure-driven functional performances (Invited)

I. Concina*[1]; 1. University of Brescia & CNR-INO SENSOR Lab, Italy

The rapid depletion of natural Earth's capital calls for scientists to get involved in the designing of functional materials, meeting the need for rational preparation, green chemistry and enhanced performances.[1] Semiconductor metal oxides (MOX) are flexible platforms suitable for different functional applications, such for instance solar energy conversion and photocatalysis. This lecture focuses on rational design of MOX nanostructures as critical tool to satisfy the need for enhanced functionality in photovoltaic devices. Focus will be given to: 1. hybrid photoanodes composed of TiO_2 nanoparticles and 1D/2D carbon materials;[2,3] 2. ZnO nanostructures for optimization of light management and charge transport in Grätzel's cells;[4] 3. self-assembled Cu_2S nanostructures as efficient photocathodes in semiconductor sensitized solar cells;[5] 4. multi-layer ZnO@SnO_2 architecture to modulate chemical capacitance and recombination resistance. Emphasis will be paid to the exploitation of simple, cheap and low environmental impact techniques for advanced functional material preparation.

3:40 PM

(ICACC-FS2-005-2016) Design of electrospun hybrids for energy applications

F. Navarro Pardo*[1]; D. Benetti[1]; L. Jin[1]; H. Zhao[1]; A. Vomiero[2]; F. Rosei[1]; 1. Institut National de la Recherche Scientifique, Canada; 2. Luleå University of Technology, Sweden

Nanostructured materials have shown a great potential for improving the performance of devices used in a number of applications. Among them, electrospun nanofibers represent attractive one-dimensional materials due to their unique features such as high specific surface areas and high porosities. Electrospinning of polyamide 6 has allowed us the fabrication of nanofiber/net structured films in which the nanofibers act as a support of nano-nets comprising interlinked ultrathin nanofibers. We have used these nanostructured films as a sacrificial template for TiO_2 nanoparticle deposition which in turn served as a scattering layer in photoanodes of dye sensitized solar cells (DSSCs). Additionally, we have obtained electrospun hybrids by sputtering of metals onto polyamide nanofibers. Cathodes fabricated with different coatings of a Pt/Pd alloy and density of nanofibers have been tested in DSSCs, these has allowed us to obtain an improved efficiency of the cells when compared to conventional sputter coated cathodes. Furthermore, we have also tested the performance of these nanostructured cathodes for photoelectrochemical water splitting; our copper nanofiber based cathodes have shown promising results, which indicate they can be a substitute for the typically used Pt cathodes. Therefore, here we present that the electrospun hybrids we fabricated have great versatility for their use in energy conversion devices.

4:00 PM

(ICACC-FS2-006-2016) Microstructure Analysis of the Epitaxial Growth of Electrodeposited Cu_2O on Gold Nanoislands

E. L. Kennedy*[1]; J. B. Coulter[1]; D. P. Birnie[1]; 1. Rutgers University, USA

Cuprous oxide is a well-known wide-bandgap material with a E_{gap} commonly reported around 2.0 eV. With this bandgap it is a great candidate for the top cell of a stack tandem solar cell architecture paired with silicon. However the actual reported efficiencies of single junction devices are usually much lower than would be expected, probably rooted in possible defects/nonstoichiometry or microstructural flaws. We report on electrodeposited thin films and their growth modes under different conditions. Microstructural improvements have been made using gold nanoisland seeding layers before electrodeposition, these are mainly focused on growing columnar shaped grains. Cu_2O that has been electrodeposited has a flowering/dendritic microstructure. When the electrodeposition is

seeded appropriately the dendrite arms from the flower no longer grow resulting in nicely faceted grains and a columnar shape. This well-crystallized columnar structure is meant to increase the hole collection by avoiding recombination at grain boundary defects as a means of increasing the efficiency. SEM and TEM were used to verify the growth of the grains and the relationship between the gold nanoislands and the Cu_2O.

4:20 PM

(ICACC-FS2-007-2016) Mixed Halide Perovskite Solar Cells Structure Having An $Al_xZn_{(1-x)}O$ Nanorod Electron Transport Layer

L. K. Duong*[1]; J. Ting[1]; 1. National Cheng Kung University, Taiwan

In the present work, we have investigated the use of ZnO nanorods (NRs) and Al doped ZnO (AZO) NRs in perovskite solar cell. ZnO NRs were synthesized using chemical bath deposition. The effect of deposition condition on the NR characteristics was studied. Desired NR layers were used for the deposition of perovskite, $CH_3NH_3PbI_3$, using either a two-step sequential deposition or a one-step deposition technique. The deposition of the perovskite on the NR layer was optimized by examining the morphology, thickness, crystalline structure, optical absorption, and photoluminescence property. Solar cells were fabricated using selected NR and perovskite layers, having either glass or plastic substrates. The resulting cells were evaluated using a sun light simulator, current-voltage measurement, and incident photon-to-electron conversion efficiency. The effects of the characteristics of the NR layers on the cell performance are addressed.

4:40 PM

(ICACC-FS2-008-2016) Intergrown of mixed-phase TiO_2/PVDF membranes

J. Z. Tan*[1]; R. Caruso[1]; X. Wang[2]; 1. University of Melbourne, Australia; 2. Commonwealth Scientific and Industrial Research Organization (CSIRO), Australia

Titania, an important industrial product, has been extensively studied over the last century because it is cheap, non-toxic, abundantly available, and has excellent transmittance. The presence of mixed crystal phases (anatase:rutile ratio of 80:20) in the commercially available Evonik P25 titania nanoparticulate powder gives superior photocatalytic performance under UV irradiation.[1] However, recovery of the nanoparticulate powdered catalyst is always troublesome and an extra cost for industrial application. Therefore, the intergrowth of mixed-phase TiO_2 on a flexible membrane of polyvinylidene fluoride (PVDF), could mitigate the catalyst recovery issue. Electronspun membranes of PVDF incorporating tetrabutyl titanate were fabricated. By manipulating the parameters of the solvothermal solution and the concentration of tetrabutyl titanate, the TiO_2 precursor, the growth of TiO_2 on the electrospun PVDF membranes ranged from pure single rutile or anatase phase to bicrystalline (any two polymorphs of rutile, anatase, brookite) and tricrystalline mixed-phases. *In situ* synchrotron powder x-ray diffraction results showed the transformation of anatase to rutile phase when the solvothermal treatment duration was prolonged. The fabricated TiO_2-PVDF composite membranes were used for photocatalytic dye degradation and CO_2 photoreduction reactions and the performance was compared to P25.

5:00 PM

(ICACC-FS2-009-2016) Enhanced photovoltaic properties in dye sensitized solar cells by surface modification of SnO_2 photoanodes

K. Basu*[1]; D. Benetti[3]; H. Zhao[2]; F. Vetrone[2]; A. Vomiero[4]; F. Rosei[2]; 1. "University du Quebec, Institut National de la Recherche Scientifique, Canada; 2. INRS, Canada; 3. Institut national de la recherche scientifiqueIn, Canada; 4. Luleå University of Technology, Sweden

Herein, we report the fabrication and testing of DSSCs based on SnO_2 nanoparticles of average size ~20 nm. Fluorine-doped Tin oxide (FTO) conducting glass substrates were treated with TiO_x or $TiCl_4$ precursor solutions to create a blocking layer before tape casting the SnO_2 mesoporous anode. In addition, SnO_2 photoelectrodes were treated with the same precursor solutions to deposit a TiO_2 passivating layer covering the SnO_2 nanoparticles. We found that the modification enhances the short circuit current, open-circuit voltage, and fill factor, leading to nearly 2-fold increase in PCE, from 1.48% without any treatment, to 2.85% achieved with $TiCl_4$ treatment. The superior PV performance of the DSSCs assembled with modified photoanode is attributed to enhanced electron lifetime and suppression of electron recombination to the electrolyte, as confirmed by electrochemical impedance spectroscopy. These results indicate that modification of the FTO and SnO_2 anode by titania can play a major role in maximizing the PCE.

Tuesday, January 26, 2016

40th Jubilee Symposium: Engineered Ceramics: Current Status and Future Prospects

Engineered Ceramics II

Room: Coquina Salon C
Session Chairs: Jonathan Salem, NASA Glenn Research Center; Sylvia Johnson, NASA-Ames Research Center

8:30 AM

(ICACC-JUB-008-2016) Ceramic Composites for High Temperature Aerospace Structures (Invited)

D. B. Marshall*[1]; B. N. Cox[1]; O. Sudre[1]; 1. Teledyne Scientific, USA

The use of textile-based 3-D fiber architectures in ceramic composites provides new opportunities for the design of aerospace structures optimized for light weight and high temperature performance. Textile forming methods can also enable other functionality, including active cooling, mitigation of thermal stresses, and shape-morphing structures. The major challenges and strategies for realizing the potential of these textile-based CMC structures will be discussed.

9:00 AM

(ICACC-JUB-009-2016) Life Limiting Behavior of SiC-Based Composites (Invited)

R. J. Kerans*[1]; 1. Air Force Research Lab Materials & Mfg Dir (emeritus), USA

It is expected that components used in normal service in combustion atmospheres will degrade by way of minor local matrix cracking permitting crack growth through fatigue assisted internal environmental degradation. The progression of damage is affected by intermediate temperature effects, fatigue mechanisms, interaction of fatigue and oxidation, and wear characteristics of the fibers and fiber coatings. Consideration of this progression suggests approaches to design and life management for improved life.

9:30 AM

(ICACC-JUB-010-2016) 20 Years of Carbon/Ceramic Brakes: Development, Status and Perspectives (Invited)

W. Krenkel*[1]; 1. University of Bayreuth, Germany

Early attempts in the ninetees of last century of C/C-SiC composites for frictional applications (e.g. clutches and brakes) have proven their suitability by demonstrating high coefficients of friction and low wear rates. Seven years later the enhancements of C/C-SiC induces their implementation as series products for high performance braking systems in automotive and industrial applications (e.g. brake discs, pads for elevator emergency brakes). High coefficients of friction which are constant over a wide range of sliding velocities can be achieved in frictional systems with an appropriate counterpart material and the adjusted design. The development of an automotive brake system consisting of C/C-SiC brake discs and organic based pads led to a lifetime brake. The low wear rate over the whole lifetime of the vehicle makes a brake disc change obsolete. The further success of these innovative materials is strongly dependent on the reduction of production costs and the development of lightweight ceramic brakes with life cycle costs (LCC) comparable to the current cast iron brakes. The presentation describes the development and evolution of carbon/ceramic brake discs and pads, summarizes the state-of-the-art, and gives a perspective to future demands and challenges in process technology and material development.

10:20 AM

(ICACC-JUB-011-2016) Reaction-Forming of Ceramic Composites using Metallic Aluminum (Invited)

N. Claussen[1]; R. Janssen[1]; N. Travitzky*[2]; 1. Hamburg University of Technology, Germany; 2. University of Erlangen-Nuernberg, Germany

Reaction synthesis offers affordable routes to fabricate homogeneous, fine-grained materials with advanced properties suitable for applications at room and elevated temperature. The present paper concentrates on syntheses using metallic aluminum to form alumina containing composites. Powder metallurgical as well as casting / infiltration techniques are used with Al reacting in the solid as well as liquid state. The reaction techniques outlined were analyzed and developed at the Technical University at Hamburg in collaboration with partners outside. The variability potential in view of raw materials, processing parameters, microstructural tailorability and shaping capability is discussed.

10:50 AM

(ICACC-JUB-012-2016) Ceramic Matrix Composites and CMH-17 (Invited)

L. J. Schioler*[1]; 1. National Institute of Aerspace, USA

Currently, a group of volunteers from industry, government, and academia are working on updating what was MIL-HNBK-17, the Department of Defense guide to materials, properties, and testing of composites. In 2006, the US Army transitioned the task of updating the handbook to the Federal Aviation Administration. Volume 5 of the handbook is Ceramic Matrix Composites, which has not been updated since 2002. All the other volumes have been updated and are now called CMH-17 – the Composite Materials Handbook-17. Since much progress has been made on CMCs in the past 13 years and they are increasingly being introduced into commercial aerospace applications, an update is critical. In this talk, we review the changes, progress, and status of Volume 5.

11:20 AM

(ICACC-JUB-013-2016) Carbons as reinforcements for High Temperature Composites (Invited)

L. M. Manocha*[1]; 1. Sophisticated Instrumentation Center for Advanced Research and Testing (SICART), India

Carbon, because of its electronic structure and inherent physical properties arising out of its processing methods, has been a material of interest as such or as reinforcements in High performance composites with Carbon or Ceramics as matrix system. It could be in the form of macro materials such as cokes to micro materials like carbon fibers and to naomaterials from carbon black to graphene. Each form of carbon material has characteristic properties in terms of mechanical, thermal etc. which decide its application with a suitable matrix system and end application. This is a material which has seen continuous innovations and every five to ten years a new form is developed with improved properties aiming at making full potential use of intrinsic mechanical, thermal and electrical properties of graphite structure. Further, these materials need to be given specific surface modifications to maximum utilization of reinforcement properties in final composites. Many times, these surface interactions between reinforcements and matrix affect the structure and properties of the matrix as well. A journey to these developments from cokes to graphene as reinforcements in composites will be presented.

S1: Mechanical Behavior and Performance of Ceramics & Composites

Reliability & Life Predictions

Room: Coquina Salon D

Session Chairs: Tatsuya Hinoki, Kyoto University; Emmanuel Maillet, GE Global Research

8:30 AM

(ICACC-S1-012-2016) From Testing to Modelling – Prediction of Mechanical Behavior of Ceramic Matrix Composites (Invited)

D. Koch*[1]; Y. Shi[1]; S. Hofmann[1]; 1. Institute of Structures and Design, Germany

The application of Ceramic Matrix Composites (CMC) strongly depends on the precise prediction of the failure behavior under real loading conditions. Therefore a comprehensive modeling approach is necessary which describes experimental testing results dependent on microstructure and fiber orientation as well as local defects like delamination or voids. The deterministic simulation presented here is based on a design chain consisting of non destructive investigation of microstructure, inverse laminate theory for definition of laminate properties, finite element modeling for calculation of critical stresses and strains, definition of failure criteria, and resulting failure prediction considering effects of defects. Experimental data from alloxide composite Whipox as well as from C/C-SiC processed via liquid silicon infiltration are used in order to proof the design chain. It is shown that in-plane strength and stiffness of Whipox can be predicted precisely considering any fiber orientation. The impact of interlaminar defects on failure prediction is shown on C/C-SiC composites. Here defects are implemented in the finite element model considering microstructural information from computer tomography and ultrasonic inspection. With use of fracture mechanical data damage evolution and valid failure prediction is possible and design and optimized engineering of CMC components is achievable.

9:00 AM

(ICACC-S1-013-2016) Experiment and Simulation of the Formation of Green Bodies from Alumina Powder

A. Piccolroaz*[1]; M. S. Swan[1]; 1. University of Trento, Italy

Creating nearly-constant density and residual-stress fields throughout the entire green body is necessary for producing high-quality, high-performance ceramics consistently. The use of computational tools for virtual prototyping of molds and processes help to accelerate development and decrease costs. The possible benefits are particularly advantageous for the production of large green bodies with complex geometries. The present research introduces a novel constitutive model for ceramic powder compaction

and includes: a new formulation for elastic behavior of the powder phase, a reformulation of the compaction law, and an elastic stiffening. This new computational model is calibrated on uniaxial compaction (disk forming) and triaxial compression experimental data for Martoxid KMS 96 alumina powder. Once the model has been calibrated, the parameterization is used to predict the compaction behavior of the alumina powder in the formation of green bodies.

9:20 AM

(ICACC-S1-014-2016) Characterization of Stress To Predict The Reliability of Brittle Materials (Invited)

T. Buchheit[1]; M. C. Teague[1]; R. L. Johnson[1]; S. P. Meserole[1]; D. R. Tallant[1]; K. Ewsuk*[1]; 1. Sandia National Laboratories, USA

Brittle failure in polycrystalline ceramics and composites presents a challenging reliability concern. Among other things, a quantitative prediction of brittle failure requires an accurate determination of stress. While finite element analysis is routinely used to predict continuum-scale stress that governs certain aspects of brittle failure, reliable tools to characterize and validate predictions of microstructure-scale stress have been lacking. Advances in photoluminescence (PL) spectroscopy have now established the potential to map microstructure-scale stress on the basis of spectroscopy measured peak shifts (i.e., due to strain). Methods to precisely measure peak shifts, process large data sets, and map stress will be presented. Results from characterizing the residual strain/stress in polycrystalline alumina joined to Fe-Ni-Co Kovar through a brazing operation, and in bonded, misoriented sapphire bi-crystals will be discussed. Results of mapping spatially resolved stress from PL spectroscopy measurements to grain orientation (i.e., microstructure) characterized using electron backscatter diffraction (EBSD) will also be discussed. Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's national Nuclear Security Administration under contract DE-AC04-94AL85000.

9:50 AM

(ICACC-S1-015-2016) In-situ Optical Coherence Tomography Inspection of laser–structured polycrystalline ceramics

C. Wolf*[1]; I. Kinski[1]; C. Jürgens[1]; G. Eberhardt[2]; A. Lehmann[1]; G. Unglaube[1]; 1. Fraunhofer Institute for Ceramic Technologies and Systems, Branch Material Diagnostics, Germany; 2. LDT Laser Display Technology GmbH, Germany

Optical Coherence Tomography (OCT) is an optical, thus non-contact and non-destructive measurement technology, capable of generating high-speed 3D data with a high-resolution of up to 1 µm. Therefore, OCT can be used to investigate defects in polycrystalline ceramic materials. A class of materials that can be investigated using OCT are ceramics, which are used for wavelength conversion in optical systems. Often these ceramics are laser-structured in order to enhance the efficacy of light decoupling. To ensure its mechanical stability it is decisively important to identify any damages of the materials' structure before putting the conversion element into operation. Another example is the quality of laserstructured electrolyte stabilized cells, which are used in planar SOFC, which has a predominant effect on their robustness and cycleability in later operation. The OCT is capable to identify structural defects like fractures in this ceramic electrolytes. In addition to mere visualization, thickness and porosity measurements as well as error detection, e.g. pin holes and inclusions are supplied by OCT. Furthermore, the detection of fissures, within the structured regions can be achieved. As a worst case scenario undetected fissures can result in the unintended destruction of the entire specimen, making OCT an inevitable technology for quality control and non-destructive testing.

10:30 AM

(ICACC-S1-016-2016) Thermal cycling effect on mechanical properties of balsa core sandwich composites immersed in water saline solution

S. Emami*[1]; E. Toubia[1]; 1. University of Dayton, USA

Composite sandwich structures are now finding their place in several important industries; recently, interest on these sandwiches increased in civil engineering applications especially as a bridge deck, but for using these materials needs to know about the reliability of these materials in environmental conditions for a long period of time and providing a basis for structural design that is comparable with existing standards for other common construction materials.In presence of water saline solution, 200 cycles of freeze-thaw in the range of -20°C to 20°C with each cycle period of 12 hours were applied on 40 samples of composite sandwiches of balsa wood core with glass fiber-vinyl ester skin, the mechanical properties of core shear bending and compression strength of composite before and after each 50 cycles were studied. because of nature of uncertainties in their mechanical and structural properties, reliability model for thermal cycling were introduced, it was shown that freeze-thaw can cause significant reduction of mechanical properties, 30% and 20% for core shear and compression strength respectively,glass transition temperature with immersion in saline water having large effect on interface of skin-core and fiber-matrix bond deterioration and matrix cracking, that means sensitivity of interface in this environmental condition.

10:50 AM

(ICACC-S1-017-2016) There is plenty of room…between layers: Novel concepts to design tough and reliable ceramic systems

R. Bermejo*[1]; 1. Montanuniversitaet Leoben, Austria

In an attempt to reduce the variable strength in ceramics, a "flaw-tolerant" approach has been pursued for building tougher and more reliable materials. Bio-inspired layered architectures have been proposed, combining layers with different microstructures or properties. A research line has been followed using ceramic-ceramic layered composites with tailored internal compressive residual stresses in embedded layers, in order to provide a barrier to crack propagation and, in some cases, even stop cracks. It has been shown that a lower bound for the strength of the material can be defined (*threshold strength*), below which failure does not occur. In the present research, the potential of building composites with embedded "protective" features to obtain highly reliable ceramic components has been explored. Novel concepts have been attempted using a non-conventional disposition of "embedded" compressive layers to obtain spatially tailored strength and toughness, thus providing "*plenty of room*" in the interior of the structure (*e.g.* for specific functional designs). In addition, texturing of the microstructure in the embedded layers has shown preferential paths for conducting propagating cracks (*graceful failure*). As a result, combination of "*flaw tolerance*" and "*graceful failure*" is proposed as a novel strategy to fabricate tougher and more reliable ceramic systems.

11:10 AM

(ICACC-S1-018-2016) Understanding the structural integrity of ceramic-based functional components

M. Gruber[1]; K. Macurova[1]; M. Pletz[1]; P. Supancic[1]; R. Danzer[1]; F. Aldrian[2]; R. Bermejo*[1]; 1. Montanuniversitaet Leoben, Austria; 2. TDK, Austria

Functional components consist of a ceramic substrate with external and/or internal metallization (e.g. electrodes, contact pads). The combination of different materials with different coefficients of thermal expansion induces internal stresses that can lead to cracks and/or reduce the component strength. In this work different architectures combining metal and glass layers on the surface of ZnO substrates were investigated experimentally and numerically in order to identify weak points in ceramic-based functional components.

Mechanical testing using three-point bending was performed on samples taken after different fabrication steps. Results were interpreted according to Weibull theory. A parametric model was developed to (i) calculate residual stresses generated during cooling down from the maximum temperature of the corresponding process, and (ii) simulate the propagation of initial cracks. Numerical predictions revealed different locations of stress concentration during thermo-mechanical loading depending on the sample geometry. Experimental results showed a strong effect of the geometry on the component strength distribution. These results in combination with fractographic analyses and *ex-situ* Focused Ion Beam experiments in pre-loaded samples were used to validate the model and assess the location of failure. This approach can be used to predict critical configurations of functional components.

11:30 AM

(ICACC-S1-019-2016) Facility for Testing SiC Fiber Tows at Elevated Temperature in Silicic Acid-Saturated Steam

S. Robertson[1]; K. Sprinkle[1]; M. Ruggles-Wrenn*[1]; 1. Air Force Institute of Technology, USA

Investigating stressed oxidation and scale crystallization kinetics of advanced SiC fibers at elevated temperature in steam is critical to assessing effects of oxidation on mechanical properties of SiC-SiC composites. Moisture in oxidizing environment changes oxidation rates, reduces scale viscosity and lowers scale crystallization temperatures. To study these phenomena, a facility was developed for creep testing SiC fiber tows at elevated temperatures in air, steam and silicic-acid saturated steam. The facility was validated through creep testing of Hi-Nicalon™-S fibers at 800°C in silicic-acid saturated steam. Details of the test facility design, development and experimental validation are presented.

11:50 AM

(ICACC-S1-020-2016) Characterization of local deformation of silicon carbide matrix composites with artificial surface flaws by various damage monitoring techniques

T. Nozawa*[1]; K. Ozawa[1]; H. Tanigawa[1]; 1. Japan Atomic Energy Agency, Japan

A silicon carbide matrix (SiC/SiC) composite is a promising candidate for nuclear fission and fusion applications as well as future aerospace vehicles. Because composites' failure initiate from inherent internal/surface flaws as potential failure origins, notch sensitivity and damage tolerance issues have widely been evaluated in view of qualification of the material for the practical application. For that purpose, surface and volumetric damage accumulation monitoring techniques were being developed by adopting digital image correlation and acoustic emission, etc. and visual images of 2D/3D damage profiles are available. Based on these technologies, this study aims to further evaluate the detailed failure behavior of SiC/SiC composites. Specifically tensile damage behavior was evaluated for SiC/SiC composites with artificial surface notches or center hole by applying acoustic emission and digital image correlation together to comprehensively understand the damage mechanism of composites as well as to provide fundamental data to determine key parameters for the component design.

S2: Advanced Ceramic Coatings for Structural, Environmental, and Functional Applications

Thermal Barrier Coatings II

Room: Coquina Salon H
Session Chair: Gregoire Witz, Alstom

8:30 AM

(ICACC-S2-010-2016) Multifunctional, Multilayered Thermal Barrier Coatings: Interplay among Design, Materials and Manufacturing

V. Viswanathan*[1]; G. Dwivedi[1]; S. Sampath[1]; 1. Stony Brook University, USA

The approach of depositing multilayered architectures of TBCs to incorporate disparate spatial and through thickness functionalities has been of significant interest.Such concepts have been necessitated by the need to incorporate multiple ceramic compositions within a single coating to meet concurrent damage threats of delamination induced failure, erosion and attack of molten silicate ash.The atmospheric plasma spray process readily enables such layered design and manufacturing strategies. While the fundamental aspects of microstructure, property and performance of such multilayered YSZ as well as YSZ-GDZ coatings have been investigated in recent years, there still remain issues to be considered pertaining to the incorporation of such coatings at a component level. This works seeks to address issues such as the efficacy of multilayer TBCs on different substrates, bond coat types and chemistry as well as erosion and ash mitigation via a three layered YSZ architecture. Results suggest that such multilayer coating concepts could find application even in the areas of TBC repair. We also outline some of the challenges that require concurrent consideration while extending these multilayered TBC architectures to components with complex geometries thereby providing a framework for effectively utilizing such advanced coatings in manufacturing.

8:50 AM

(ICACC-S2-011-2016) Opportunities and challenges of multi-phase ceramic topcoats

C. Macauley*[1]; C. G. Levi[1]; 1. University of California Santa Barbara, USA

Novel ceramic topcoat compositions for thermal barrier coating systems are integral to the development of more energy efficient turbine engines. Among other properties, the topcoat must have adequate intrinsic toughness and the ability to mitigate molten silicate attack. The suite of topcoat compositions currently used in turbine engines includes those based on the tetragonal crystal structure such as yttria stabilized zirconia (8YSZ) and those based on the rare earth-rich pyrochlore structure such as $Gd_2Zr_2O_7$ (GZO). Unfortunately neither composition exhibits both adequate toughness and the ability to minimize degradation caused by molten silicates. This study explores the potential of multi-phase coatings in the ZrO_2-$YO_{1.5}$-$TaO_{2.5}$ system to satisfy both requirements. First, the phase equilibria must be understood in order to identify promising multi-phase compositions. Next, various toughness tests including indentation and nano-indentation are used to probe the factors that influence the toughness of multi-phase materials such as grain size, volume fraction, crystal structure, and grain orientation. Materials used in the study were synthesized by precursor-derived methods, densified and characterized at relevant length scales. Insights gained regarding the efficacy of adding a second phase to increase toughness will be discussed in relation to their implication for novel TBC development.

9:10 AM

(ICACC-S2-012-2016) First-Principles Calculations Along the ZrO2-YTaO4 Quasi-Binary

S. Heinze*[1]; C. G. Levi[1]; A. Van der Ven[1]; 1. UC Santa Barbara, USA

The ZrO2-YTaO4 quasibinary contains a single tetragonal phase that is stable up to 1500°C and non-transformable to monoclinic zirconia upon cooling, desirable characteristics for the tetragonal phase used in thermal barrier coatings (TBCs). However, the mechanism by which the tetragonal crystal structure is stabilized over the monoclinic crystal structure and the effects of the stabilization mechanism on mechanical properties such as toughness are not well understood. In this study, we use a combined first-principles and experimental approach to investigate how ordering patterns affect the free energy of the tetragonal solid solution and the implications for toughening mechanisms like ferroelastic switching. It was found that short-range ordering is likely to exist in the tetragonal phase and that it hinders the ability of the phase to undergo ferroelastic switching.

9:30 AM

(ICACC-S2-013-2016) Thermal cycling behavior and Cyclic Thermogravimetric Analysis of a new TBC system made by Spark Plasma Sintering

F. Nozahic*[1]; C. Estournes[1]; D. Monceau[1]; 1. CIRIMAT, France

The SAMBA project deals with the creation of a new, unique self-healing thermal barrier coating (TBC) for gas turbines and other thermally loaded structures in order to realize a significant extension of the lifetime of critical high-temperature components. The concept invented by Sloof et al.(2013) is based on novel Al2O3 coated Mo-Si particles embedded in the TBC layer, typically consisting of yttria-stabilized zirconia. In this study, the SPS technique was first used to produce simultaneously 7YSZ/NiCoCrAlY bi-layer coatings on Hastelloy X superalloy substrates. The thickness of the as-sintered 7YSZ coatings (without Mo-Si particles) was 250 μm, the porosity level was about 22%. Homogeneous structures with good adherence were obtained and in-situ formation of Al_2O_3 TGO interlayer was observed after SPS. Good performances of these coatings under thermal cycling at 1100°C in laboratory air reveal a good quality of the TBC systems. In a second step, a complete TBC system with uncoated Mo-Si particles embedded in the top coat was prepared. Cyclic Thermogravimetry Analysis (CTGA) was used to characterize the oxidation behavior of this system and the resistance to failure of both systems, with and without Mo-Si particles, under thermal cycling.

CMAS-related TBC Degradation and Mitigation Stragtegies I

Room: Coquina Salon H

Session Chair: Marie-Helene Vidal-Setif, ONERA

10:10 AM

(ICACC-S2-014-2016) Phase Relationships and Composition Trends in Reactions Between Rare Earth Containing TBCs and Silicate Melts (Invited)

D. L. Poerschke*[1]; C. G. Levi[1]; 1. University of California Santa Barbara, USA

The degradation of TBCs by molten silicate (CMAS) deposits has received considerable attention. Of particular importance is understanding the nature of the (i) infiltration process, (ii) thermochemical interaction between melt and coating, and (iii) resulting thermocyclic stresses in the coatings. These efforts, involving experience from both ex-service hardware and laboratory experiments, have revealed a wide range of reaction products arising through either intrinsic crystallization of the melt in a thermal gradient (i.e. anorthite, pyroxene, spinel) or through reaction with dissolved coating constituents (i.e. apatite, cuspidine, garnet, zircon). The ability of these reactions to mitigate coating degradation is determined by the reaction product identities that influence the crystallization morphology and kinetics. There is limited systematic understanding, however, about the effect of variations in the coating or deposit composition on the reaction product constitution. The present work addresses this need by combining information about the phase equilibria for the underlying systems with thermodynamic modeling and targeted experiments to elucidate the compositional trends and reaction sequences. The results offer insight into the factors controlling the crystallization reactions and provide guidance for the design of improved coating systems.

10:40 AM

(ICACC-S2-015-2016) Cyclic durability testing of thermal barrier coatings with CMAS application: effect of CMAS deposition mechanism

A. Harris*[1]; E. Jordan[1]; 1. University of Connecticut, USA

The deleterious interaction between thermal barrier coatings (TBCs) and ingested debris, composed primarily of oxides of Calcium, Magnesium, Aluminum, and Silicon (CMAS) is becoming one of the major life-limiting factors in the design of gas turbine engines. Laboratory-scale experiments must be developed in order to properly quantify this effect and explore mitigation strategies. To ensure the engine relevance of the test, experiments should be combined with modeling efforts and engine experience. Using a custom-built thermal gradient rig, TBC samples were subjected to thermal cycling with CMAS application. CMAS was applied using several methods: during cycling, CMAS was incrementally deposited onto the TBC using either a liquid chemical precursor solution or mixed oxide powders; or CMAS was pre-deposited before cycling as a continuous layer using the Solution Precursor Plasma Spray Process. The effect of these different deposition methods were compared using material characterization techniques including X-ray diffraction, scanning electron microscopy, and energy-dispersive X-ray spectroscopy.

11:00 AM

(ICACC-S2-016-2016) Thermo-Chemical Interactions of Environmental and Thermal Barrier Coating Materials with CMAS

A. Krause*[1]; H. Garces[1]; L. R. Turcer[1]; N. P. Padture[1]; 1. Brown University, USA

Metallic hot-section components in gas turbine engines are insulated and protected by thermal barrier coatings (TBCs). TBCs are porous and are typically made out of ZrO_2 ceramics because of its low thermal conductivity and high fracture toughness. However, ceramic-matrix-composites (CMCs) are being researched to replace the metallic hot-section components to allow for higher operating temperatures. Environmental barrier coatings (EBCs) are necessary for protecting CMCs that oxidize rapidly in the presence of water vapor. EBCs need to be dense and are typically made out of silicates for a better thermal-expansion match with the CMC to prevent spallation. Both TBCs and EBCs are susceptible to degradation by CaO-MgO-Al_2O_3-SiO_2 (CMAS), which enters the engines in the form of sand, ash, debris, etc. and deposits on the coatings. CMAS is molten at high temperatures and can penetrate open pathways and grain boundaries, and cause dissolution, resulting in premature failure. New coating ceramics are necessary to resist CMAS attack. A screening process has been developed to help predict CMAS mitigation capabilities of various ceramics. Thermochemical interaction studies are conducted on selected ceramics to evaluate their CMAS mitigation capability. Model studies, with extensive characterization, are also conducted to evaluate the mitigation mechanism and kinetic properties in the CMAS-glass.

11:20 AM

(ICACC-S2-017-2016) Potential High Fracture Toughness, CMAS Resistant, TBC Compositions in Ln-Al-Zr-O Ternary Systems

M. D. Hill*[1]; J. A. Shunkwiler[1]; M. Schmitt[2]; D. E. Wolfe[2]; 1. Trans-Tech, Inc., USA; 2. The Pennsylvania State University, USA

Many lanthanide rich zirconate and hafnate based thermal barrier coatings have excellent CMAS resistance and thermal conductivity lower than that of the industry standard yttria stabilized zirconia material. However, relative to yttria stabilized zirconia, materials such as cubic lanthanide rich pyrochlores have reduced fracture toughness due to their inability to exhibit ferroelastic toughening. Novel chemistries in the Ln-Al-Zr-O system will be presented which have the potential to show improved fracture toughness while having a greater resistance to CMAS penetration than YSZ. The focus is on creating a dispersed second phase with a high aspect ratio which allows for crack bridging to take place. Preliminary EB-PVD trials over a range of compositions show a multitude of phases and the erosion resistance properties are compared to that of standard YSZ.

11:40 AM

(ICACC-S2-018-2016) Melt-infiltration of 7 YSZ TBC on the Example of two Artificial Volcanic Ash Variants

P. Mechnich*[1]; 1. German Aerospace Center (DLR), Germany

The ingestion and subsequent deposition of volcanic ash (VA) is considered a major threat to performance and lifetime of aero-engines. Infiltration of ceramic thermal barrier coatings (TBCs) of combustor walls, turbine blades and vanes by molten VA deposits is associated with loss of strain tolerance, making them susceptible to "cold shock" fracture and subsequent spallation. An estimation of possible TBC damages by VA requires knowledge on dose, thermal history, and melt infiltration kinetics. Due to the high chemical and mineralogical variability of natural volcanic ashes, the selection of a test standard suitable for TBC infiltration experiments is still a major issue. Artificial volcanic ashes (AVA) providing tailored chemical composition and particle morphology are considered promising for standardized laboratory testing. The infiltration behavior of standard 7-YSZ TBC by two AVA test dusts similar to recent eruptions in Iceland, (Ejafjalla, 2010 and Grimsvotn, 2011), is discussed in the light of physical melt properties such as viscosity. It turns out that only small variations of the chemical composition may have major influence on melt infiltration onset and progress.

S3: 13th International Symposium on Solid Oxide Fuel Cells (SOFC): Materials, Science and Technology

Electrolysis / Interconnects

Room: Crystal

Session Chairs: Toshio Suzuki, National Institute of Advanced Industrial Science and Technology (AIST); Jeffry Stevenson, Pacific Northwest National Lab

8:30 AM

(ICACC-S3-009-2016) Challenges in Broadening Applications for Solid Oxide Electrolysis Cells (Invited)

S. Elangovan*[1]; J. Hartvigsen[1]; D. Larsen[1]; J. Elwell[1]; 1. Ceramatec, Inc., USA

Hydrogen production using solid oxide electrolyzers was demonstrated more than thirty years ago. Recent advances in solid oxide fuel cells for intermediate temperature operation have resulted in renewed interest in electrolysis. Ceramatec's work in this intermediate temperature range focused on steam electrolysis to produce hydrogen as well as co-electrolysis of steam and carbon dioxide to enable storage of renewable energy while providing an opportunity to recycle carbon dioxide. While in theory the same set of materials developed for solid oxide fuel cells can be used in the electrolysis mode, certain degradation mechanisms such as delamination and cation migration in the oxygen electrode are specific to electrolysis mode. Ceramatec has also recently extended the application of electrolyzers to upgrade bio-based products, as well as electrolysis of dry carbon dioxide to produce oxygen for potential deployment for manned mission to Mars. Additional degradation mechanisms and operational challenges need to be addressed in such unconventional applications. For example, dry carbon dioxide electrolysis on Mars introduces both a materials and operational challenges for the fuel electrode. Similarly, deoxygenation of complex organic molecules of bio-oil introduces additional catalytic and coking challenges for the fuel electrode materials.

9:00 AM

(ICACC-S3-010-2016) Development of Solid Oxide Electrolysis Cell for Hydrogen Production and Power Storage Systems (Invited)

M. Yoshino*[1]; 1. Toshiba Corporation, Japan

By expansion of the introduction of the renewable energy utilization, the storage of surplus electric power and the absorption of the fluctuation are necessary. "Power To Gas" using the electrolysis can be one of the solution to those problems, and hydrogen is a candidate medium for the energy storage. The High temperature steam electrolysis with solid oxide electrolysis cell (SOEC) is prospective for higher efficiency than conventional low temperature electrolysis methods. Toshiba is developing hydrogen production system using SOEC and electrical power storage system with SOEC/SOFC. The electrolysis properties and durability has been evaluated with single cells, and configuration of the cell stack with various shapes has been examined to increase the hydrogen production capacity. A part of this study is carried out in a project commissioned by METI and NEDO.

9:30 AM

(ICACC-S3-011-2016) Study of detailed degradation behavior of solid oxide electrolyzer cells (SOEC) (Invited)

G. Schiller*[1]; M. Hoerlein[1]; F. Tietz[2]; 1. DLR - German Aerospace Center (DLR), Germany; 2. Forschungszentrum Juelich, Germany

High temperature electrolysis has a high potential for the efficient production of hydrogen or syngas. For a further development of this promising technology, development work on materials and cells as well as extensive operational experience is still needed. A main objective is the improvement of the degradation behavior by elucidating the relevant degradation mechanisms. Cathode-supported cells were fabricated by ceramic processing and sintering for electrochemical characterization in electrolysis operating mode. For a systematic investigation of the influence of the operating parameters temperature, fuel gas humidification and current density on SOEC long-term degradation a series of measurements over 1000 hours in the temperature range 750-850 °C with different fuel gas humidity (40-80 mol%) and different current densities between 0 and 1.5 A/cm^2 has been performed. The progress of degradation was monitored in-operando approximately every 150 h by impedance spectroscopy. Results of electrochemical cell characterization are shown and observed degradation phenomena and their underlying mechanisms based on different electrochemical processes are explained. Post-mortem investigations have been conducted to localize and identify the rate limiting processes and to clarify the correlation between degradation processes and operational parameters.

10:00 AM

(ICACC-S3-012-2016) Pressurised operation of Solid Oxide Electrolyzers

J. B. Hansen*[1]; S. Højgaard Jensen[2]; 1. Haldor Topsøe A/S, Denmark; 2. DTU, Denmark

Pressurised operation of electrolyzers for hydrogen production provides several benefits on a system level and has been practiced both with alkaline as well as PEM based plants. Experimental and system studies on Solid Oxide Cell based plants are, however, very limited so far. This paper will present recent experimental findings on stack operation up to 25 bar as well as techno-economic analysis of hydrogen plants using the obtained experimental results. Although the OCV for pressurized operation increases for thermodynamic reasons the area specific resistance decreases for kinetic reason so that approximately the same current density can be obtained at the thermoneutral operating voltage. Significant capital and operating cost savings can be achieved by pressurized operation.

10:40 AM

(ICACC-S3-013-2016) Effects of yttrium addition on properties of advanced metallic alloys for SOFC interconnect application

A. Yeh[1]; K. Su*[1]; 1. Nation Tsing Hua University (Taiwan), Taiwan

The effects of 100 ppm yttrium addition in three advanced alloys, Ni-based, Ni-Fe-based, and Fe-based alloys on the oxidation behaviours, electrical resistance and Cr evaporation at 800°C have been investigated for potential application as the solid oxide fuel cell interconnect. Minor amount addition of yttrium can affect the oxide scale formation, electrical property and the Cr evaporation rate. For oxide scale formation, the yttrium addition makes alumina more continuous for Ni-based alloy, suppresses the formation of internal oxidation and base metal oxidation for Ni-Fe-based alloy, enhances the continuity of chromia for Fe-based alloy, and makes the oxide scales thinner for all the three alloys. The ASR is lowered as a result of the thinner oxide scales and the different configurations of oxide scale. The Cr evaporation is affected by the changed oxide scales. In this work, the effects of the very minor addition of yttrium will be discussed.

11:00 AM

(ICACC-S3-014-2016) Properties of TiC-Ni-Mo Using Nanosize TiC Powders

J. Kong*[1]; R. Koc[1]; 1. Southern Illinois University Carbondale, USA

The sintering behavior to form TiC-Ni-Mo cermet using a nanosize TiC powders was investigated in flowing Argon gas at 1500oC. Nano-sized titanium carbide powders with high purity, high surface area, and low cost were synthesized from carbon coated Ti containing precursors utilizing a patented process [R. Koc and G. Glatzmaier, U.S. Patent No: 5,417,952]. The sintering studies showed that an increase in theoretical density (TD) with increase in molybdenum content. TiC based cermets were characterized using X-ray diffraction (XRD), Vickers hardness, scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). Electrical conductivity and oxidation resistance results for potential applications as the interconnect for Low/Intermediate Temperature Solid Oxide Fuel Cells will be presented and interpreted.

11:20 AM

(ICACC-S3-015-2016) Morphological and electrical characterization of Mn-Co spinel protective coatings for solid oxide cells interconnects

S. Molin[2]; A. Boccaccini[3]; M. Bindi[4]; P. Leone[1]; A. Sabato[1]; M. Salvo[1]; F. Smeacetto*[1]; 1. Politecnico di Torino, Italy; 2. DTU, Denmark; 3. University of Erlangen-Nuremberg, Germany; 4. Edison S.p.A., Italy

Cr-containing stainless steels are widely used as interconnects for solid oxide cells. Cr-containing species can poison the air electrode and subsequently cause degradation in the stack. One of the best materials, found to date to block chromium evaporation on the oxygen side of the interconnect, is the $(Mn,Co)_3O_4$ spinel. Although this coating has been extensively studied and has been demonstrated highly effective in reducing corrosion rates, still no clear correlation exists between the coating thickness, preparation methods and the protective properties. Electrophoretic deposition, thermal co-evaporation and RF magnetron sputtering methods were used for the preparation of the Mn-Co based coatings, for both thin and relatively thick coatings (from 1 μm to 13 μm). Crofer22APU steel was used as substrate and Mn-Co coated samples by the three different techniques were electrically tested for 5000 hours at 800°C under a 500 mA cm^{-2} current load to determine their ASR. After tests, the samples were morphologically analyzed by SEM and TEM (with selected area electron diffraction, SAED) to determine chromium diffusion, oxide scale thickness and possible reaction at the interfaces. The relationships between coating thickness, homogeneity, and effectiveness of the protective nature of the coatings are reviewed and discussed.

11:40 AM

(ICACC-S3-016-2016) Dual layer coatings for the oxygen side of interconnects for Solid Oxide Electrolysis Stacks

S. Molin*[1]; V. Venkatachalam[1]; K. Andersen[1]; M. Chen[1]; P. Hendriksen[1]; 1. Technical University of Denmark, Denmark

High temperature corrosion of stainless steel interconnects in Solid Oxide Fuel Cell and Electrolysis Cell stacks is one of the major degradation cause during their long term operation. Protective coatings for interconnects are thus required to hinder high temperature corrosion and possible evaporation of reactive chromium species from steel interconnects. In this work a concept of a dual layer coating will be presented. Firstly a thin layer (< 100 nm) of reactive element is coated directly on the interconnect and then a thick (< 20 μm) coating is applied. Thin coating (based e.g. on Ce, Y, La, Gd) serves primarily to lower the corrosion rate whereas thick coating (based on $MnCo_2O_4$ spinel) block chromium evaporation. By application of the dual layer coating a synergistic effect is expected that will allow to produce interconnects with long lifetimes and low chromium evaporation. The projects ForskEL 2013-1-12013 "Solid oxide electrolysis for grid balancing" and ForskEL 2015-1-12276 "Towards solid oxide electrolysis plants in 2020" funded by Energinet.dk are gratefully acknowledged.

12:00 PM

(ICACC-S3-017-2016) A Development of Plasma Sprayed Protective LSM Coating in INER

C. Chang*[1]; C. Hwang[1]; C. Tsai[1]; S. Yang[1]; W. Shong[1]; T. D. Huang[1]; M. Wu[1]; 1. Institute of Nuclear Energy Research, Taiwan

A relatively dense $La_{0.8}Sr_{0.2}MnO_{3-\delta}$ (LSM) layer was successfully produced by atmospheric plasma spraying (APS) technique on SOFC metallic interconnector surface as protective coating in Institute of Nuclear Energy Research (INER). The long term stability of small scale APS-LSM coating (1×1 cm^2) on Cr-contained interconnector reveals a very low increasing rate of area specific resistance (ASR) with only about 1.244, 0.746 and 1.230 μWcm²/hr for Crofer 22H, Crofer 22APU and SS441 substrates, respectively. The long-term ASR experiment had been performed in ambient air at 800°C for about 10,000 hrs. In order to examine the performance of APS-LSM coating in real applications, LSM coatings with large area of 10×10 cm^2 were produced on the cathodic surfaces of Corfer 22H interconnector and stack frame, and these interconnector and stack frame were then adopted to form a SOFC single cell stack with a plasma-sprayed metal-supported solid oxide fuel cell (MS-SOFC). The stability experiment of this single MS-SOFC stack with LSM protective layer was performed at 700°C and 400 mA/cm^2. The measured degradation rate was only about 0.77 %/1000hr during the testing time of 1,750 hrs. This degradation behavior implies that both of the LSM coating and metal-supported solid oxide fuel cell made by INER reveal an inspiring performance.

S4: Armor Ceramics

Developments in Synthesis and Processing II

Room: Coquina Salon E
Session Chair: Victoria Blair, US Army Research Laboratory

8:00 AM

(ICACC-S4-011-2016) Integrated Investigation on the Amorphization Behavior of B4C

M. Asadikiya[1]; Y. Zhong*[1]; 1. Florida International University, USA

Boron carbide (B4C), a low-density and extremely hard material (HV10 36 GPa, density 2.52 kg/m^3), is an ideal candidate for light-weight armor. However, the amorphization has prevented it from wide application. It is well accepted but experimentally not verified that SiC additive could improve the amorphization stability of B4C. In this work, we use the integrated approach to investigate the amorphization behavior of B4C. Thermodynamic calculations are being carried out to predict and optimize the sintering condition of boron carbide. Different sintering aids including SiC have been used in the B4C SPS sintering process. Amorphization stability of the sintered B4C samples has been studied by SEM, XRD, and in-situ Raman spectroscopy at high pressure using diamond anvil cell technique.

8:20 AM

(ICACC-S4-012-2016) Reduction of Silicon Carbide in Silicon Doped Boron Carbide for Sinterability and Increased Toughness

A. M. Etzold*[1]; R. A. Haber[1]; 1. Rutgers University, USA

Silicon doped boron carbide has been produced in an effort to enhance the ballistic properties of boron carbide, specifically its toughness. Silicon doping is done via the addition of silicon and amorphous boron to existing boron carbide powders within a temperature range of 1800-2000°C. However, by the nature of the system and the temperature ranges used, large silicon carbide contamination is present. The use of a rapid carbothermal reduction furnace within a temperature range of 2150-2250°C with the ability to quench the sample would allow for thermodynamically favorable conditions for the production of boron carbide over silicon carbide and the formation of silicon doped boron carbide without contamination, using base constituent compounds rather than preformed boron carbide. The prepared powders are analyzed through x-ray diffraction, carbon analyses, and boron titration in order to determine their phases and stoichiometries, while bonding is analyzed via Raman spectroscopy. The results demonstrate the feasibility of incorporating silicon atoms into the boron carbide lattice without the issues caused by silicon carbide formation.

8:40 AM

(ICACC-S4-013-2016) Tailored Interface Controlled Layered B_4C Ceramic Tiles Produced by Field Assisted Sintering Technology (FAST) for Body Armor Applications

J. Singh*[1]; 1. Pennsylvania State University, USA

Boron carbide (B_4C) is one of the hardest known materials, ranked third behind diamond and cubic boron nitride. B4C is the preferred choice materials for body armor protection applications. However, B_4C material has poor fracture toughness and often exhibited stress induced amorphous phase formation that could be minimized by new architecture of ceramic tiles, i.e., making composite layered structure. Similarly, fracture toughness of the B4C could be increased 100 to 300 % by making composite having various volume fraction refractory metal carbides, borides or both. Simulation has demonstrated that increasing the tensile strength (i.e., fracture toughness) of the monolithic ceramic tile could lead to increase in ballistic limit, decreased damage to ceramic, and increased erosion of the striking projectile. In addition, layering the target with thin layers of a stronger ceramic material between regular B_4C leads to increased damage within the ceramic. In addition it also lead to additional erosion of the projectile, implying that an increase in ballistic limit velocity would occur. This research effort will shed a light towards the benefit of new architecture of light weight ceramic plates for body armor applications.

9:00 AM

(ICACC-S4-014-2016) Effect of Alumina and Silica Additives on the Densification Behavior of Hot-Pressed Boron Suboxide

E. R. Shanholtz*[3]; P. E. O'Shannessy[4]; J. LaSalvia[1]; K. Behler[5]; K. A. Kuwelkar[2]; 1. Army Research Laboratory, USA; 2. Rutgers University, USA; 3. ORISE, USA; 4. Drexel University, USA; 5. TKC Global, USA

Because of its high hardness and low density, boron suboxide has potential for armor applications. However, decomposition and reactivity at high temperatures are challenges to achieving dense homogeneous bodies. Consequently, pressure-assisted densification methods must be used, and densification temperatures kept relatively low. In this study, the effect of alumina and silica additives on the densification behavior of boron suboxide has been investigated. Alumina and silica powders (5 vol.%) were acoustically mixed with boron suboxide powder in ethanol. Dried powder mixtures were hot pressed between 1650ºC – 1850ºC for two hours under 50 MPa applied uniaxial pressure. To minimize reaction with the graphite die and punches, boron nitride spacers and spray were utilized. An LVDT with data acquisition system was utilized to monitor densification. Final densities were determined by the Archimedes method. X-ray diffraction suggests the presence of amorphous boron (5-10 wt.%) in the starting boron suboxide powders. Full densification for the boron suboxide powders without additives was achieved at 1850ºC. Additives lowered the temperature for full densification, with alumina slightly more effective than silica. Additionally, the onset of densification was also lower for powders with additives. Details of the experimental procedures and densification results will be presented.

9:20 AM

(ICACC-S4-015-2016) Evaluating the Effect of Powder Oxygen Content on Silicon Carbide Morphology

V. DeLucca*[1]; R. A. Haber[1]; 1. Rutgers University, USA

Silicon carbide is an important technical ceramic material due to its favorable mechanical, chemical, and thermal properties. The mechanical properties are influenced by the microstructure of the material, which will be shown to be affected by the oxygen content of the starting powder. In this study, silicon carbide powders were treated to introduce varying oxygen content levels and were densified via spark plasma sintering (SPS) with boron carbide and carbon additives. The dense silicon carbide bodies were then characterized to examine the effect of varying amounts of oxygen in the starting powders on the resulting grain morphology. Relationships between powder oxygen content and grain size, aspect ratio, and polytype, as well as mechanical properties including elastic modulus and hardness are shown.

9:40 AM

(ICACC-S4-016-2016) Dissolution of excess alumina into single phase magnesium aluminate spinel

J. A. Miller*[1]; I. E. Reimanis[1]; W. Miao[2]; 1. Colorado School of Mines, USA; 2. Corning Incorporated, USA

Certain ceramics show potential for use in transparent armor applications because of their unique combination of optical and mechanical properties. In particular, magnesium aluminate spinel exhibits Knoop hardness values of 160 GPa and in-line transmission as high as 85% in the visible through mid-infrared portion of the electromagnetic spectrum. However, spinel has a relatively low fracture toughness of 1.5-1.9 MPa*m$^{0.5}$. The range of compositions over which single phase spinel is stable increases with temperature. At 25°C, spinel is nearly a line compound described as $MgOnAl_2O_3$ where n=1.00. However, at 1600°C, single phase spinel is stable over

the approximate range of 0.90 ≤ n ≤ 2.05. In this study, a-alumina powder was mixed with stoichiometric (n=1.00) spinel powder to form alumina-rich spinel such that n=2.00. This 2-phase material was hot pressed at 1600°C and 35 MPa for 5, 10, and 20 hours in order to study the dissolution of excess alumina into single phase spinel and how the resulting microstructure affects fracture toughness. The Vickers hardness after 5, 10, and 20 hours did not change significantly, but the fracture toughness varied from 4.05, 3.33, and 3.03 $MPam^{0.5}$, respectively. The amount of second phase alumina present decreased from 39.1 vol.% after mixing, to 32.7, 31.9, to 23.0 vol.% after 5, 10, and 20 hours of hot pressing, respectively. Optical properties will also be discussed.

10:20 AM

(ICACC-S4-017-2016) Multi-layer ceramic armors from bio inspired, structural templates

G. Smith*[1]; G. Dwivedi[1]; S. Sampath[1]; 1. Stony Brook University, USA

Ceramic armor has seen rapid expansion in the past 20 years as the range of military and civilian applications has grown. Ceramics offer many benefits in terms of density, stiffness, extreme hardness, and thermal loading ability, but lack in fracture toughness and extended energy dissipation. Overcoming these shortfalls has been the focus of research over this period and has seen inroads into not only armor applications, but durable ceramic usage engineering applications. Concurrently, there has been significant interest in using bio-inspired hybrid materials concepts to impart enhanced toughness to ceramic compositions. Materials and processes that mimic nacreous layers of an abalone shell has been a subject to intense interest in recent years as an approach to simultaneously engineer strength and toughness. Recent work at Stony Brook University's Center for Thermal Spray Research has shown that epoxy infiltrated thermal sprayed ceramic templates show promising nacre like behavior with meaningful strength and toughness while retaining low density. Since thermal spray is a layered deposition process, it is also feasible to produce multiple layers using different materials and architectures. In this presentation, examples of such layered materials concepts will be presented within the context of their potential applicability in armor systems.

10:40 AM

(ICACC-S4-018-2016) Novel Processing of Metal-Ceramic Interfaces through Ultrasonic Additive Manufacturing

J. Sietins*[1]; B. McWilliams[1]; 1. Army Research Laboratory, USA

There is a need for improved conductive coatings on ceramic tiles to increase their mobility for adaptive armor applications. Previous coating methods such as brazing and soldering can involve high bonding temperatures, resulting in large thermal residual stresses at the interface. Ultrasonic additive manufacturing (UAM) utilizes a 20 kHz frequency, oscillation amplitude, and an applied load through a rolling sonotrode to weld multi-layered structures. This processing method is predominantly used for welding metallic foils or metal matrix composite tapes. This research effort reports the successful UAM attachment of aluminum foils to silicon carbide and boron carbide ceramic substrates. The weld interface appeared to be well consolidated at selected regions, but ceramic fracture was also observed at other locations along the weld interface. Focused ion beam milling was also used to obtain high resolution images of the interface. Bonding mechanisms and technical challenges are discussed as well as suggestions for improving the weld consistency and bond strength through minimizing the ceramic fracture at the interface.

Developments in Materials and Process Modeling I

Room: Coquina Salon E

Session Chair: Nitin Daphalapurkar, The Johns Hopkins University

11:00 AM

(ICACC-S4-019-2016) Computational Implementation of Anisotropic damage failure in brittle materials

R. Ayyagari Venkata S*[1]; D. Mallick[2]; N. Daphalapurkar[3]; A. Tonge[2]; K. Ramesh[1]; 1. Johns Hopkins University, USA; 2. US Army Research Laboratory, USA; 3. The Johns Hopkins University, USA

The process of failure in brittle materials (advanced ceramics) is extremely complex. Its stochastic nature can be attributed to a multitude of factors that include but are not limited to: microstructure, imposed stress state, porosity and flow behavior. A physics based constitutive framework therefore should be functionally dependent on the above factors and be thermodynamically consistent. It has been observed from high strain rate experiments that ceramic materials exhibit a preferential orientation of damage evolution that is highly dependent on stress state. We therefore present a computational implementation of an anisotropic damage model that incorporates micromechanics, rate dependence and anisotropy in damage evolution and can handle the entire spectrum of stress states. Verification, calibration and validation steps are presented for Boron carbide. Comparison of simulations carried out using the material point method (MPM) in UINTAH framework with high-rate experiments will be used to demonstrate the strengths of the implementation as well as scope for future advancements.

11:20 AM

(ICACC-S4-020-2016) A multi-scale model for dynamic failure of ceramics based on efficiently binned flaw populations

F. Huq[1]; L. Graham-Brady*[1]; 1. JHU/APL, USA

Dynamic failure of ceramics under impact or high strain rate loading is a complex phenomenon involving different micro-scale mechanisms occurring due to the preexisting subscale defect population residing in the material. One of the most important mechanisms that govern dynamic failure under uniaxial compression is microcracking from preexisting flaws. In the current work, the statistical distribution of flaws within each sample volume, or finite element, of the material is defined, from which the initial realization of flaw sizes is used as an input condition in the simulation. To reduce computational cost, the initial flaws are grouped into small number of crack families or bins. In every element, a different set of flaw representative sizes and their respective densities is chosen to incorporate spatial variability in the material. A new numerical technique is developed to reduce the computational effort associated with representing the flaw population, through efficient binning that determines the optimum number of bins necessary for a particular simulation. This scheme has been implemented in the context of a simplified 2D micromechanics damage model, demonstrating up to two orders of magnitude speed up in computational efficiency while retaining only 1% error.

11:40 AM

(ICACC-S4-021-2016) Prediction of Raman Spectra and Shear Resistance of Boron Carbide using Density Functional Perturbation Theory

C. Kunka*[1]; A. Awasthi[1]; G. Subhash[1]; 1. University of Florida, USA

Computational chemistry has been employed to establish the Raman spectra, shear resistances, and deformation trends of several boron-carbide polymorphs: $(B_{11}C_p)CBC$, $(B_{11}C_e)CBC$, $(B_{11}C_{2p})BCB$, $(B_{12})CCC$, etc. For density functional perturbation theory (DFPT), the ABINIT solver, Troullier-Martins norm-conserving pseudopotentials, 30-Hartree cutoff energy, and a 4x4x4 rhombohedral supercell were used. Simulated Raman spectra were used to develop a means of identifying polymorph concentration in commercial samples. Further, the influences of the locations of the boron and

carbon atoms on Raman spectra were analyzed. It was found that Raman spectra are highly sensitive to changes in the equatorial, polar, and chain sites. Also, the resistance to shear-induced amorphization was systematically investigated by applying a deformation gradient to each lattice parameter and then allowing the atoms to adopt a new equilibrium. The resulting energy-deformation curves and Raman spectra revealed the points of instability and deformation characteristics. This method was also extended to predict ways to postpone catastrophic failure. In addition, the feasibility of finding other material responses (elasticity, diffusivity, thermal conductivity, etc.) was explored with molecular dynamics (MD).

S6: Advanced Materials and Technologies for Direct Thermal Energy Conversion and Rechargeable Energy Storage

Solid Electrolyte and Solid State Batteries

Room: Tomoka A

Session Chairs: Olivier Guillon, Forschungszentrum Juelich; Ilias Belharouak, Qatar Foundation

8:30 AM

(ICACC-S6-009-2016) Design of Alkali Superionic Conductor Solid Electrolytes using First Principles Calculations (Invited)

S. Ong*[1]; Z. Deng[1]; Z. Zhu[1]; I. Chu[1]; B. Radhakrishnan[1]; Z. Wang[1]; 1. University of California, San Diego, USA

With continued advances in computing power, first principles methods have become a powerful tool in the materials designer's arsenal. A key advantage of first principles calculations is the ability to carry out multi-property optimization of materials for targeted applications. This talk will provide a perspective on the key properties of interest in alkali superionic conductor electrolytes, such as ionic conductivity, stability (phase, electrochemical and aqueous), mechanical properties, etc., and how first principles methods may be used to discovery and design novel alkali superionic conductors. A particular focus of the talk will be on insights into doping strategies in both lithium and sodium superionic conductor solid electrolytes to enhance ionic conductivity.

9:00 AM

(ICACC-S6-010-2016) All-Solid-State Li-ion Batteries for Transformational Energy Storage (Invited)

E. D. Wachsman*[1]; 1. University of Maryland, USA

We have developed transformational, and intrinsically safe, all-solid-state Li-ion batteries (SSLiBs), by incorporating high conductivity garnet-type solid Li-ion electrolytes into tailored tri-layer microstructures, by low-cost solid oxide fuel cell (SOFC) fabrication techniques to form electrode supported dense thin-film (~10μm) solid-state electrolytes. The microstrucurally tailored porous garnet scaffold support increases electrode/electrolyte interfacial area, overcoming the high impedance typical of planar geometry SSLiBs resulting in an area specific resistance (ASR) of only ~2 Ωcm^{-2} at room temperature. The unique garnet scaffold/electrolyte/scaffold structure further allows for charge/discharge of the Li-metal anode and cathode scaffolds by pore-filling, thus providing high depth of discharge ability without mechanical cycling fatigue seen with typical electrodes. Moreover, these scalable multilayer ceramic fabrication techniques, without need for dry rooms or vacuum equipment, provide for dramatically reduced manufacturing cost. Fabrication of supported dense thin-film garnet electrolytes, their ability to cycle Li-metal at high current densities with no dendrite formation, and results for Li-metal anode/garnet-electrolyte based batteries with a number of different cathode chemistries will be presented.

9:30 AM

(ICACC-S6-011-2016) Lithium loss indicated formation of microcracks in LATP ceramics

K. Waetzig*[1]; A. Rost[1]; U. Langklotz[2]; J. Schilm[1]; 1. Fraunhofer IKTS, Germany; 2. Dresden University of Technology, Institute of Materials Science, Germany

Lithium ion conducting ceramics are investigated as candidates for use as solid electrolytes in Lithium-Sulfur and Lithium-air battery concepts. $LiTi_2(PO_4)_3$ have to provide a high Li-ion conductivity and a hermetical tightness for separating the liquid electrolyte of the cathode and anode side. A partial substitution of Ti^{4+} by Al^{3+} improves the conductivity up to $3.0 \cdot 10^{-3}$ S/cm for the composition $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ (LATP). LATP exhibits a high thermal expansion anisotropy and cracks are a result of grain growth during the sintering. At least, it was described, that the formation of microcracks can be inhibited by reducing the critical grain size (< 1.6 μm). In this study, the LATP ceramics were prepared by melting and milling of a glass frit to a powder with a d_{50}-value of 0.7 μm. Sintering at temperatures (T_s) between 800 and 1050 °C was performed by SPS. The phase composition, density, porosity, ionic conductivity, He leakage rate and grain size of the specimens were measured. The highest density (2.82 g/cm) and ionic conductivity ($\sim 1 \cdot 10^{-4}$ S/cm) was reached at T_s between 900 and 1000 °C. The formation of microcracks was observed at T_s=950°C in $AlPO_4$ secondary phase (caused by Lit loss during the preparation). With higher sintering temperatures coarse grains and cracks dominate the microstructure. Two different mechanisms of crack formation are found and an explanation of observed phenomena is given.

10:10 AM

(ICACC-S6-012-2016) $Li_7La_3Zr_2O_{12}$ Interface Modification for Li-dendrite Prevention

C. Tsai*[1]; H. Gehrke[1]; V. Roddatis[2]; V. C. Nair[3]; S. Uhlenbruck[1]; O. Guillon[1]; 1. Forschungszentrum Juelich, Germany; 2. University of Göttingen, Germany; 3. Leibnitz University, Germany

Li metal is the ideal anode for rechargeable batteries. However, the use of metallic Li in a rechargeable battery has not been successful due to the difficulty of suppressing the growth of Li dendrite. Theoretical calculations suggest that dendrite growth can be suppressed if the shear modulus of the electrolyte is more than twice that of metallic Li, or a Li-ion transfer number t_{Li+} approaching 1. Therefore, the garnet-structured $Li_7La_3Zr_2O_{12}$ (LLZ) solid-state Li-ion conductor is an ideal material for use as electrolyte in batteries because of its unity ionic transfer number, high mechanical strength and chemical stability to metallic Li. Nevertheless, Li dendrite formation was reported by Yamamoto et al for their Al- and Ta-substituted LLZ. In this research, Al- and Ta-substituted (Al free) LLZ samples were fabricated by hot pressing as well as regular sintering. Both samples fabricated by hot press synthesis have relative densities larger than 99% and total conductivities of about 1 mS/cm at 25°C. Impedance spectroscopy during dendrite studies shows a rapid decrease in total resistances within a few minutes indicating dendrite formation. Solid-State NMR indicates the presence of metallic Li inside all pellets. This observation is supported by TEM-EELS results. The reason for the dendrite formation as well as a pathway to prevent their growth by interface modification will be discussed in this presentation.

10:30 AM

(ICACC-S6-013-2016) Ionic liquid confined as solid electrolyte for all-solid-state lithium microbatteries

D. Aidouda*[1]; B. Lestriez[1]; D. Guyomard[1]; J. Le Bideau[1]; 1. CNRS UMR 6502, France

With the growing development of micro-devices which request low energy or power sources, lithium microbatteries have developed to meet this need. These systems are meant to replace conventional energy storage systems that cannot meet the size requirements of

present and future microelectronic devices, such as smart cards, battery-assisted RFID tags, wireless sensor, and multiple healthcare applications. Here we present a solid polymer electrolyte, elaborated by the confinement of an ionic liquid in a tridimensional porous polymeric network, which can be an alternative to LiPON for lithium microbatteries. Ionic liquids are room-temperature molten salts and thereby are liquid and constituted only of anions and cations. They have good ionic conductivity, a large electrochemical stability window and are nonflammable. The synthesis of the electrolyte is based on the dissolution of acrylic monomers and photo-initiator in an ionic liquid doped with lithium salt (here PYR13TFSI with LiTFSI). After few seconds of UV irradiation of the mixture, the solid electrolyte is obtained and it is free-standing and flexible. This soft material has an overall ionic conductivity of 1.8 $mS.cm^{-1}$ at 20°C, a very good electrochemical stability. The galvanostatic cycling tests with this electrolyte show capacities reaching 135 $mA.h.g^{-1}$ at a C/10 rate to 100 $mA.h.g^{-1}$ at a C rate with a $LiFePO_4$ facing lithium metal.

10:50 AM

(ICACC-S6-014-2016) All-solid-state thin film Lithium Ion batteries by PVD processing

H. Gehrke*[1]; C. Dellen[1]; C. Tsai[1]; S. Lobe[1]; S. Uhlenbruck[1]; O. Guillon[1]; 1. Forschungszentrum Juelich, Germany

Solid state electrolytes lead to intrinsic advantages in terms of safety, electrochemical- and thermal stability. However, the conductivity of lithium ion conducting solids performs poorly compared to current liquid electrolyte solutions. There are two approaches to overcome this shortcoming. On one hand the conductivity of the materials is improved by process tweaking and on the other hand the electrolyte film thickness is reduced dramatically. Especially for small electrical devices such thin film battery systems seem promising. At IEK-1, thin film batteries by PVD magnetron sputtering are fabricated. This technology is highly compatible to complex multicomponent materials and up scalable to industrial processing standards. Our current research is focused on systems with $LiCoO_2$ cathodes and $Li_{3+x}PON_X$ electrolyte. The high temperatures required to crystalize some of the desired phases cause diffusion, especially of lithium. ToF-SIMS analysis is applied to monitor the lithium distribution in our sample systems. The understanding of the interface behavior is essential to identify relevant factors for battery performance. The processing and first characterization of our all-solid-state-thin-film battery cells based on LiPON electrolyte is presented.

11:10 AM

(ICACC-S6-015-2016) Synthesis of Sodium Zirconium Gallate + Yttria-Stabilized Zirconia by a Vapor Phase Process

L. Ghadbeigi*[1]; Z. Liu[1]; T. D. Sparks[1]; A. V. Virkar[1]; 1. University of Utah, USA

This work presents investigation of vapor phase synthesize of two phase sodium zirconium gallate - yttria-stabilized zirconia (YSZ) ceramics. Two phase samples containing ~70 vol.% Ga_2O_3 and ~30 vol.% yttria-stabilized zirconia (YSZ) were fabricated by sintering powder compacts in air at 1500°C for 1 h and at 1600°C for 1 h and 3h. Single phase samples of Ga_2O_3 were fabricated by sintering at 1500°C for 1 h. Some of the sintered samples were packed in Na-β"-alumina powder of composition ~8.85 wt.% Na_2O, 0.75 wt.% Li_2O and balance alumina and heat treated at 1250°C for up to 20 h. Samples of single phase sintered Ga_2O_3 were also subjected to the same vapor phase treatment by packing in Na-β"-gallate powder. The two phase Ga_2O_3 + YSZ samples converted into a sodium zirconium gallate of composition $Ga_{4.72}Na_{0.7}Zr_{0.29}O_8$ and balance yttria-stabilized zirconia. Reaction of single phase Ga_2O_3 was limited to a thin surface layer. Rapid conversion of Ga_2O_3 + YSZ samples into $Ga_{4.72}Na_{0.7}Zr_{0.29}O_8$ + YSZ occurred by coupled diffusion of O^{2-} ions through YSZ and of Na^+ ions through $Ga_{4.72}Na_{0.7}Zr_{0.29}O_8$ (or $Na_{0.7}Ga_{4.72}Zr_{0.29}O_8$) similar to the conversion of b-Al_2O_3 + YSZ into Na-β"-alumina + YSZ. The phase $Na_{0.7}Ga_{4.72}Zr_{0.29}O_8$ is isostructural with $Na_{0.7}Ga_{4.72}Ti_{0.29}O_8$ which is known to be a one dimensional sodium ion conductor.

S7: 10th International Symposium on Nanostructured Materials: Functional Nanomaterials and Thin Films for Sustainable Energy Harvesting, Environmental and Health Applications

Nanomaterials for Energy Harvesting Applications III

Room: Coquina Salon A

Session Chairs: Pu-Xian Gao, University of Connecticut; Dongling Ma, INRS, Uni. Quebec

8:30 AM

(ICACC-S7-011-2016) Tuning of Titania Nanotubes for Visible-light Responsible Photochemical Function (Invited)

T. Sekino*[1]; K. Fujii[1]; H. Nishida[1]; T. Goto[1]; 1. Osaka University, Japan

Titania nanotube (TiO_2 nanotube, TNT) having nanotubular with a diameter of around 10 nm is a wide-bandgap semiconductor and has excellent photocatalytic property. However, it is usually responsible to UV light due to its bandgap energy of around 3.3 ~ 3.4 eV. In this research, we have modified the TNT to realize high performance environmental and/or energy nanomaterials. One of our strategies lies in doping elements to TNT either alone or at the same time (co-doping). Metal-doped TNTs were synthesized by simple solution processing based on chemical treatment in alkaline solution. Cr, Sm or Ru doped TNTs exhibited optical adsorption peaks in the visible light region, and the bandgap energy decreased depending on the doped elements. Organic dye removal test in aqueous solution revealed that the small amount of metal doping enhanced the visible light photocatalytic performance. On the other hand, we have succeeded to develop visible light responsible TNT by simple chemical treatment using hydrogen peroxide solution at room temeprature. This realized modification of TNT surface chemistry, and resulted in decrease in bandgap energy of TNTs. The modifed TNT exhibited excellent photocatalytic degradation performance for organic dye under the visible light. Detailed materials processing, nanostructures, surface chemistry and photochemical properties will be discussed.

9:00 AM

(ICACC-S7-012-2016) Routes to Nanoparticles Optimized for Energy Technology (Invited)

M. Winterer*[1]; 1. University Duisburg-Essen, Germany

We want to find answers to the question, how device performance can already be influenced at the time of nanoparticle synthesis. This is a big challenge since product design and materials synthesis are far apart. In product design the analysis of a new idea or market need provides product specifications. Nanoparticle synthesis starts from a reactant material and produces powders of certain particle characteristics. I will illustrate this with four examples: aluminum nitride as precursor for phosphors in solid state lighting, gallium oxide as water splitting photocatalyst, aluminum doped zinc oxide as thermoelectric material and titanium dioxide as model material for Chemical Vapor Synthesis.

9:30 AM

(ICACC-S7-013-2016) Composite wide bandgap semiconducting oxides for high-efficiency excitonic solar cells (Invited)

A. Vomiero*[1]; 1. Lulea University of Technology, Sweden

The typical photoanode in dye- and quantum dot- sensitized solar cells is composed of a wide band gap semiconductor, which acts as

electron transporter for the photoelectrochemical system. Anatase TiO2 nanoparticles are one of the most used oxides and are able to deliver the highest photoconversion efficiency in this kind of solar cells, but intense research in the last years was also addressed to ZnO and other composite systems. Modulation of the composition and shape of nanostructured photoanodes is key element to tailor the physical chemical processes regulating charge dynamics and, ultimately, to boost the efficiency of the end user device, by favoring charge transport and collection, while reducing charge recombination. We investigated light harvesting, exciton separation and charge injection and transport in several systems: (i) TiO2 nanoparticles / ZnO nanowires; (ii) Multiwall carbon nanotubes (MWCNTs) / TiO2 nanoparticles; (iii) TiO2 nanotubes; (iv) Hierarchically self-assembled ZnO sub-microstructures. Both dye molecules and semiconducting quantum dots were applied as light harvesters. Possible tailoring of structure and morphology of the photoanodes and of the quantum dots, and their implication in improving the functional properties of these kinds of excitonic solar cells will be discussed in detail.

9:50 AM

(ICACC-S7-014-2016) Nano-sized ceramic materials synthesized from ionic liquids as functional nanomaterials for sustainable energy-harvesting (Invited)

A. V. Mudring*[1]; 1. Iowa State University, USA

There is a high and tremendously growing demand for primary fuels. For that reason the replacement of non-sustainable fossil fuels with sustainable, safe and clean fuels such as hydrogen has become desirable. Hydrogen can be produced through splitting water by sunlight with proper photocatalysts. CeO_2, for example, as a wide band-gap semiconducting material is regarded as a promising material for photocatalysis, especially when brought to the nanoscale. However, it has been realized that the catalytic performance strongly depends on particle morphology and size which is determined by the method of preparation. Thus, improving and exploring techniques to prepare size and shape controlled ceria which relies on a simple approach to reduce the cost of production, using environmentally benign reagents and mild preparation conditions, is desirable. Here the exploration of ionic liquids for synthesis appears to be beneficial, especially when combined with microwave or sono-chemistry. We will discuss novel manufacturing methods using ionic liquids that allow to obtain not only CeO_2 nanoparticles, but other oxide materials such as perovskites, and discuss their performance as efficient photocatalysts.

Nanomaterials for Energy Harvesting Applications IV

Room: Coquina Salon A

Session Chairs: Anja Mudring, Iowa State University; Alberto Vomiero, Institute of Metal Research

10:30 AM

(ICACC-S7-015-2016) Micro and Nano Ionic Thin Film Electrode Structures: What the Future Holds (Invited)

H. L. Tuller*[1]; 1. Massachusetts Institute of Technology, USA

Ever more complex oxides are being investigated and applied as electrodes in energy conversion devices including solid oxide fuel cells, lithium batteries, and solar photovoltaic and photoelectrochemical cells. Surprising little is often known about their energy band, defect and surface structure, or the impact of strain and space charge effects on performance. In the neighboring fields of micro- and nano-electronics, thin films, superlattices and nanocomposites, with engineered strain, space charge and surface structure, are studied and engineered to gain a deeper understanding of charge generation and transport and thereby achieve enhanced performance. A similar approach applied to solid-state electrochemical materials is likely to show similar advances. In this presentation, I summarize recent progress made in the ability to interrogate functional oxide thin films, superlattices and nanocomposites, often under in-situ conditions, and on the nanoscale, to extract detailed information about key aspects of their *structure* (energy band, defect, surface, interface) and relate this to their electrochemical performance. I will then suggest future directions to be taken to advance our ability to fabricate, characterize and design innovative solid state electrochemical materials and devices.

11:00 AM

(ICACC-S7-016-2016) Scalable Nanomaterials Integration toward Ultrahigh Efficiency, Robustness, and Multi-functionality: An example of Nano-array based Catalytic Converters (Invited)

P. Gao*[1]; 1. University of Connecticut, USA

Three-dimensional (3-D) integration of nanostructures or nanostructure arrays into applicable platforms or devices represents the need for meeting ever-increasing demands of human beings for cost-effectiveness, structure sophistication, multi-function enabling, while simplified and efficient practical operations. Such an integration process generally involves a diverse array of nanostructured entities that include various dissimilar nanoscale building blocks such as nanoparticles, nanowires, and nanofilms made of metals, ceramics, or polymers in the nanoscale form. In this talk, I will highlight our latest research progress on the 2-D and 3-D metal oxide based nanostructure integrations toward applicable ultrahigh efficiency, robustness, and improved functionality, with an intention to draw a unique roadmap toward practically and better bridging the gap between nanoscience and nanotechnology in energy and environmental applications. Specifically, examples through design in scalable nanomanufacturing and nano-array based catalytic converters will be used as the connecting dots to display the nanomaterials roadmap linking from scalable 2-D toward 3-D integration.

11:20 AM

(ICACC-S7-017-2016) Harvesting Near-infrared Photons in Solar Cells and Photocatalysis (Invited)

D. Ma*[1]; 1. INRS, Uni. Quebec, Canada

Harvesting near infrared (NIR) photons represents an attractive approach to improve the power conversion efficiency of photovoltaics, since most solar cells are only able to efficiently capture photons in the UV and visible ranges. The same dilemma exists in photocatalysis. In this regard, quantum dots (QDs) are promising for solar cell and photocatalysis applications because of their size-tunable bandgaps, even in the NIR range. Moreover, they show advantages of low cost solution processibility, and high potential for multiple exciton generation and for the facile fabrication of multi-junction solar cells. On the other hand, plasmonic nanostructures have also been recently explored for enhancing the efficiency of solar cells and photocatalysis. Herein, I will present some of our most recent development in the NIR QDs (PbS and PbS/CdS core/shell QDs) and plasmonic nanostructures that have strong resonances in the NIR regime, and their applications in solar cells and photocatalysis.

11:40 AM

(ICACC-S7-018-2016) Control of Anisotropic Growth of Ceria Rods Fabricated by Gas-liquid Co-precipitation

Y. Kubota*[1]; K. Katsumata[2]; N. Matsushita[1]; 1. Tokyo Institute of Technology, Japan; 2. Tokyo University of Science, Japan

Ceria (CeO_2) and Samarium-doped ceria (SDC) are used as electrolytes for solid oxide fuel cells and catalysts. Since the properties depend on their shapes, controlling their shape is important to improve the performances. In this research, the anisotropic growth of CeO_2 and SDC rods were conducted by gas-liquid co-precipitation. This method was carried out by vaporizing the *p*H controller in the sealed vessel. The starting chemicals of $Ce(NO_3)_3.6H_2O$ and

$Sm(NO_3)_3.6H_2O$, as well as the *p*H controller of NH_3 and NH_4HCO_3 were dissolved in deionized water in different beakers. These beakers were maintained at 60°C for 3 days in the sealed vessel. The CeO_2 and SDC rods with high aspect ratio, 1-6 μm in length and 30-80 nm in width, were obtained using NH_3. The growth direction was [011] parallel to the longitudinal axis of the rods. The CeO_2 rods synthesized at R.T. for 3 and 10 days had 0.1-0.3 and 1-4 μm in length, respectively. From these results, it is assumed that length is controllable by synthesis temperature and time. On the other hand, the carbonate rods 10-120 μm in length were obtained for the NH_4HCO_3 used sample. The oxide rods with quite a high aspect ratio 1-27 μm in length were obtained by calcining these carbonates. Gas-liquid co-precipitation is an energy-efficient synthesis method for preparing the functional ceramic rods using only ambient atmosphere and temperature.

12:00 PM

(ICACC-S7-019-2016) High critical currents by flux pinning by 1D nanostructures in thin film superconductor tapes

V. Selvamanickam*[1]; 1. University of Houston, USA

High temperature superconductor (HTS) tapes made by growth of epitaxial thin films on nanoscale single-crystalline-like oxide films on metal substrates have been developed for energy and power applications. These tapes are produced in lengths of a kilometer with current carrying capacity of about 300 times that of a similar-sized copper wire and are being used in cables, generators, energy storage devices and high-field magnets. Since most applications that employ HTS involve high magnetic fields, it is essential that high critical currents are achieved in such fields. Flux pinning by $BaZrO_3$ nanocolumns grown by a self-assembly process simultaneously during epitaxial HTS thin film growth by metal organic chemical vapor deposition (MOCVD) is the approach we have successfully used for this purpose. $(Gd,Y)Ba_2Cu_3O_x$ thin film superconductor tapes with BZO nanocolumns of 5 nm in diameter and 10^{11} -10^{12} cm^{-2} in density have demonstrated a five-fold improvement in critical currents in magnetic fields of a few Tesla. We have also developed a chemical vapor deposition (CVD) process to prefabricate SnO_2 nanowires on single-crystalline-like oxide films on metal substrate which are then embedded in a subsequently grown HTS film. The latest progress in growth of thin film HTS tapes with 1D nanostructures and their influence on critical current will be discussed in this presentation.

S8: 10th International Symposium on Advanced Processing and Manufacturing Technologies for Structural and Multifunctional Materials and Systems (APMT10)

Functional Ceramics Processing II

Room: Coquina Salon B

Session Chairs: Tetsuo Uchikoshi, National Institute for Materials Science; Yiquan Wu, Alfred University

8:30 AM

(ICACC-S8-011-2016) Bioinspired functional materials templated from nature materials (Invited)

D. Zhang*[1]; 1. Shanghai Jiao Tong University, China

Biological materials naturally display an astonishing variety of sophisticated nanostructures that are difficult to obtain even with the most technologically advanced synthetic methodologies. Inspired from nature materials with nano and hierarchical structures, many functional materials are developed based on the templating synthesis method. This review will introduce the way to fabricate novel functional materials based on nature bio-structures with a great diversity of morphologies recently. We focused on replicating the morphological characteristics and the functionality of a biological species. We change their original components into our desired materials with nano and original morphologies faithfully kept. Properties of the obtained materials are studied in details. Based on these results, we discuss the possibility of using these materials in energy harvesting, Plasmonics, splitting water et al. In addition, the fabrication method could be applied to other nature substrate template and inorganic systems that could eventually lead to the production of optical, magnetic or components as building blocks for nanoelectronic, magnetic, or photonic integrated systems. These bioinspired functional materials with improved performance characteristics are becoming increasing important, which will have great values on the development on structural function materials in the near future.

9:00 AM

(ICACC-S8-012-2016) Transparent material drilling and cutting using innovative fiber lasers (Invited)

S. Jiang*[1]; 1. AdValue Photonics Inc, USA

Transparent glass and crystalline materials have been widely used for display and information technologies. The thickness of these materials is reduced to less than 100 micron in order to meet the new design requirements and cost reduction. To process these ultra-thin materials is becoming more and more challenging by using traditional grinding and polishing techniques. In this paper we will present the cutting and drilling of transparent materials using our innovative fiber lasers. The interaction between the lasers and the materials, surface quality, and speed will be described.

9:30 AM

(ICACC-S8-013-2016) Synthesis and characterization of phosphate cathode materials prepared by a polymeric steric entrapment precursor route

D. Ribero*[1]; W. M. Kriven[1]; 1. University of Illinois at Urbana-Champaign, USA

A nano/microscale and pure crystalline phosphate-based structures such as $LiFePO_4$, $NaFePO_4$, $LiTi_2(PO_4)_3$ and $NaTi_2(PO_4)_3$ were synthesized using an organic-inorganic steric entrapment solution, from precursor chemicals of $LiNO_3$, $NaNO_3$, $Fe(NO_3)_3 9H_2O$, titanium (IV) isopropoxide "Tiso" ($Ti[OCH(CH_3)_2]_4$ and $(NH_4)_2HPO_4$ stoichiometrically dissolved in either distilled water or isopropyl alcohol (for the case of Tiso). Long-chain polymers such as polyvinyl alcohol (–[CH_2–CHOH]-*n* or PVA) or ethylene glycol (EG) monomer ($HOCH_2CH_2OH$) were used as the organic carrier for the precursors, which served for the physical entrapment of the metal ions in the network. Synthesis variables such as the dissolving medium, pH, drying conditions, calcination atmosphere and temperature were evaluated in order to produce a single crystalline phase for each composition. In this study we found a way to make pure compounds by controlling the oxidation states of the intermetallic cation (e.g. Fe^{+2} versus Fe^{+3}) which may have wider applications in the synthesis of other compounds having variable oxidation states, leading to potential applications in advanced ceramics, such as Li-ion and Na-ion batteries. The resulting powders of $LiFePO_4$, $LiTi_2(PO_4)_3$, $NaTi_2(PO_4)_3$ and $NaFePO_4$ were characterized by X-ray diffractometry, electron microscopy (SEM/ TEM), surface area and particle size analysis.

10:10 AM

(ICACC-S8-014-2016) Optical Ceramics Processed Through Environmentally Friendly Casting Techniques

Y. Li[1]; Y. Wu*[1]; 1. Alfred University, USA

In the present study, YAG and Al_2O_3 optical ceramics with different complex shapes and thicknesses were prepared via aqueous gel casting and tape casting, followed by vacuum sintering. An environmentally benign copolymer of isobutylene and maleic anhydride was used as both dispersant and gelling agent for the spontaneous gel casting process and as dispersant and binder for the tape casting

process. YAG and Al_2O_3 slurries were mixed by ball milling, followed by degassing under vacuum to remove trapped bubbles. Gel casting and tape casting were then employed to obtain homogeneous green bodies. The casted bodies were subsequently consolidated via vacuum sintering to obtain transparent optical ceramics. The rheological behavior of the suspensions was investigated to study the influence of solids loading and ISOBAM content on the properties of the green bodies. The phase composition and microstructural features of the green bodies and as-sintered optical ceramics were investigated with XRD and SEM, respectively. Optical characterization of the as-sintered optical ceramics was also performed to understand and correlate processing conditions with the resulting optical properties.

10:30 AM

(ICACC-S8-015-2016) Direct fabrication of micro- and nano-diamond structures for advanced sensing applications

J. Pinto*[1]; C. Tang[2]; H. Ye[3]; G. Yang[2]; J. Xuefang[2]; 1. University of Aveiro, Portugal; 2. Changshu Institute of Technology, China; 3. Aston University, United Kingdom

Various diamond films can be successfully prepared on silicon by using a 5 kW microwave plasma chemical vapour deposition reactor by tuning the growth parameters. Many properties of the films such as the morphology, microstructure, orientation or texture, quality, grain size, roughness and impurity incorporation can be adjusted by tuning microwave power, adjusting amount of N2 and O2 or varying thickness of silicon substrates. Due to the physical properties, diamond coatings can provide new applications to fiber sensors, namely fiber Bragg grating sensors. Their mechanical strength and sensitivity can be greatly improved. Novel monitoring solutions for challenging environments can be explored. Direct fabrication of highly ordered diamond films of various nano- and micro-structures, such as vertically aligned diamond micropillars and {100} faceted nanocrystalline diamond self-assembles will be presented. Nanodiamond deposition onto optical fibers and its potential application for advanced sensing will be analyzed and discussed.

10:50 AM

(ICACC-S8-016-2016) Study of high photocatalytic performance β-carbon nitrides using in situ powder x-ray diffraction

J. Z. Tan*[1]; R. Caruso[1]; X. Wang[2]; 1. University of Melbourne, Australia; 2. Commonwealth Scientific and Industrial Research Organization (CSIRO), Australia

Carbon nitride, C_3N_4, materials have been extensively researched after Liu and Cohen predicted that C_3N_4 was a superhard materials. So far, the photocatalytic application of C_3N_4 as a metal-free photocatalyst has focused only on the graphitic phase that was first performed by Wang et. al.

11:10 AM

(ICACC-S8-017-2016) Latest developments in Optical Dilatometry

A. Makitka*[1]; C. Linseis[1]; 1. Linsies, USA

Optical Dilatometry is a special form of dilatometry that is often not noticed or considered as a niche product by scientists from ceramic, polymer or steel industries. But it can provide a lot of advantages compared to standard pushrod dilatometers. The possibility of contact free measurement and the option of 2D and 3D recordings are only two examples out of this long list. For some applications like samples that undergo some phase transitions during the measurement or are outgassing during sintering, it might be also very interesting to get a live image or video during the measurement, which is possible on the newest optical dilatometers, too. Also the determination of contact angles and detection of other surface effects during melting is another interesting point that gets more and more in the focus of many research groups and institutions. To live up to all these expectations, Linseis as a leading manufacturer in fields of thermal analysis recently focused its developments in this field to increase resolution, temperature range and purity of gas atmospheres for optical dilatometers. The resulting instruments, their specifications and possible applications, as well as the actual market situation will be introduced and discussed in this talk

11:30 AM

(ICACC-S8-018-2016) Improved impedance relations based on Curie-Weiss law fractal modification in doped BaTiO3-ceramics

V. Mitic*[1]; V. Paunovic[2]; L. Kocic[2]; 1. Serbian Academy of Sciences, Serbia; 2. Faculty of Electronic Engineering, Serbia

Doped barium-titanate ceramics attracts much interest for its application as resistor with a positive temperature coefficient of resistivity (PTCR), multilayer ceramic capacitor (MLCC), thermal sensor etc. In this article the influence of Er2O3,Yb2O3 and Ho2O3 on microstructure development and dielectric properties of BaTiO3-ceramics has been presented. BaTiO3-ceramics, doped with 0.01 up to 0.5 wt % of Er2O3,Yb2O3 and Ho2O3 were prepared by conventional solid state procedure and sintered up to 1400oC for two hours. Microstructure investigations of doped BaTiO3 is performed using the scanning electron microscopy (SEM) and energy dispersive spectrometer (EDS). Dielectric measurements are carried out as a function of temperature up to 180°C at different frequencies. The low doped samples display the high value of dielectric permittivity at room temperature. A nearly flat permittivity-response is obtained in specimens with higher additive content. Using the Curie-Weiss law and modified Curie-Weiss law, the Curie constant C, Curie temperature Tc and a critical exponent of nonlinearity g are calculated. With novel issue, the fractal correction coefficient a that encounters BaTiO3-ceramics fractal morphology coming separately from grains and pores plus dynamics complexity caused by the flux of different micro particles (electronic gas, ions).

11:50 AM

(ICACC-S8-019-2016) Micro computed tomography characterization of isotropic filler distribution in magnetorheological elastomeric composite

S. Samal*[1]; 1. Technical University of Liberec, Czech Republic

Micro computed tomography characterization of iron filler incorporated elastomeric composite material is investigated. The filler distribution in the elastomeric matrix is calculated using non-destructive techniques of computed tomography using X-ray as the source of the investigation. Three dimensional presentation of filler distribution, amount of porosity in volumetric zone of the material is evaluated using this technique. The overall presentation of filler distribution and self-assembled particles were analysed in the MRE composite. The magnetic couple interaction of filler particles from edge towards centre and to the top surface of the samples were estimated and their role in influence of the mechanical properties were

discussed. The role of pair effect that exit due to magnetic pole of interaction and distribution also contribute from gravitational pull of attraction were discussed briefly in this study.

S10: Virtual Materials (Computational) Design and Ceramic Genome

Modeling of Innovative Ceramics for Functional Applications I

Room: Ponce DeLeon
Session Chair: Per Eklund, Linkoping University

8:30 AM

(ICACC-S10-010-2016) Thermodynamics and thermal behavior of lithium batteries and their materials (Invited)

H. J. Seifert*[1]; 1. Karlsruhe Institute of Technology, Germany

Lithium batteries are presently the most interesting electrochemical devices for energy storage applications in electrical vehicles, renewable energies (solar, wind) and portable consumer electronics. Their high energy and power density combined with excellent electrochemical cycling behavior is the base for numerous commercial applications. However, significantly improved thermal and safety properties at high energy capacity levels are major concerns. Thermodynamics and phase diagrams of advanced ceramics used for lithium battery design are directly linked to electrochemical performances, heat generation and safety behavior. However, such thermodynamic data are largely missing even for the most important cramic cathode materials. The situation is similar for anode materials. Therefore, we aim at investigating thermodynamic properties and phase diagrams and link them to electrochemical and thermal cell behavior. CALPHAD-type thermodynamic models and descriptions of ternary and multicomponent systems are used to calculate reversible open circuit voltages of electrochemical cells. The thermodynamic datasets and additional thermophysical data can then be used for an advanced application-oriented electrochemical-thermal modeling. The ultimate aim is the simulation of thermal behavior, heat generation and physico-chemical conditions for thermal runaway of lithium batteries.

9:00 AM

(ICACC-S10-011-2016) First-principles calculations of Li-ion migration behaviors at solid-solid interfaces in lithium-ion battery materials (Invited)

A. Kuwabara*[1]; H. Yu[4]; C. Fisher[1]; H. Moriwake[1]; H. Zhou[3]; Y. Ikuhara[2];
1. Japan Fine Ceramics Center, Japan; 2. University of Tokyo, Japan;
3. National Institute of Advanced Industrial Science and Technology (AIST), Japan; 4. Beijing University of Technology, China

All-solid-state LIBs is one of the candidates as next generation LIBs because the all-solid-state LIBs can realize higher energy density and safety without liquid electrolytes. In these devices, solid-solid interface boundaries, specifically those between electrodes and electrolytes and grain boundaries within each component, are thought to strongly affect battery performance. Despite their clear scientific and technical importance, however, influences of the interface boundaries on Li-ion migration in battery materials are not understood enough yet. In this report, we present investigation combining scanning transmission electron microscope (STEM) observations with atomic resolution and theoretical calculations based on density functional theory (DFT) regarding interfaces in materials of LIBs. Atomistic structures of a Σ2-type grain boundary of $LiCoO_2$, 90° domain boundaries of a solid electrolyte $La_{0.62}Li_{0.16}TiO_3$, and domain boundaries of a cathode $Li_{1.2}Mn_{0.567}Ni_{0.167}Co_{0.067}O_2$ are revealed by atomic-resolution STEM observation. Li-ion migration behaviors at those interfaces are calculated by DFT calculations. It is revealed that Li ion transports passing through boundaries are suppressed lower compared to that in bulk region.

9:30 AM

(ICACC-S10-012-2016) Catalyst Design for improving kinetic rate of oxygen evolution reactions in Li-O_2 Battery (Invited)

J. Liu*[1]; 1. Shanghai Institute of Ceramics, Chinese Academy of Sciences, China

Developing highly active catalyst for charging reaction in Li-O_2 battery and unraveling the relation of catalytic structure and activity are of great importance for the development of an effective catalyst with improved low round-trip efficiency and power density. Based on first-principles methods, different computational models describing Li_2O_2/catalysts interface were used to calculate catalytic mechanism of doped graphene and transition metal oxides for oxygen evolution reactions (OER) in Li-O_2 battery. Our extensive calculations indicate that electron-withdrawing ability of catalysts plays an important role in reducing charging overpotential and activation barrier of rate-determinant step in OER. In this talk, I will elaborately discuss influence of facet structure of transition metal oxides and properties of doped elements on catalytic activity. Some calculated results have been confirmed by very recent experimental groups. According to the calculated structure-activity relation, some novel possible catalysts are designed and expected to be applied in Li-O_2 battery.

Modeling of Innovative Ceramics for Functional Applications II

Room: Ponce DeLeon
Session Chair: Hans Seifert, Karlsruhe Institute of Technology

10:20 AM

(ICACC-S10-013-2016) Modelling thermal transport properties in complex thermoelectric materials from first principles (Invited)

G. A. Hug*[1]; L. Andrea[1]; L. Chaput[2]; 1. ONERA-CNRS, France; 2. University of Lorraine, France

We present first-principles calculations of the thermal transport properties of pure and doped half-Heusler compounds various composition. The method consists in solving the Boltzmann transport equation for phonon densities in which the lifetimes of phonon modes are fully included. The lifetimes are calculated from a Fermi golden rule formalism where the harmonic and anharmonic interatomic force constants are extracted from density functional theory using a finite size displacements method. A model to account for substitution defects using perturbation theory and configurational analysis is developped to compute thermal conductivity in materials with point defects. At high concentration of dopants the force constants are interpolated from specific composition. The study the thermal properties of half-Heusler compounds provides good insights for understanding the behaviour of the thermal conductivity in these materials. It can be used to guide experimental work for improving the thermoelectric figure of merite of half-Heusler phases.

10:50 AM

(ICACC-S10-014-2016) Development of novel thermoelectric thin film nitrides by an integrated theoretical-experimental approach (Invited)

P. Eklund*[1]; 1. Linkoping University, Sweden

Thermoelectric devices may contribute to energy harvesting in society by directly converting heat into electricity. However, the conversion efficiency of thermoelectric devices of today is limited. The critical material-dependent parameter is the figure of merit ($ZT = S^2T/\rho\kappa$, where ρ is the electrical resistivity, S is the Seebeck coefficient and κ is the total thermal conductivity). In this invited talk, we present recent results from our experimental and theoretical investigations of ScN-based thin film systems. ScN thin films exhibit an anomalously high power factor (S^2/ρ) for transition metal nitrides of

2.5-3.3×10^{-3} W/mK^2 at 800 K. From first-principles calculations, we explain this by nitrogen vacancies generating an asymmetric sharp feature in the density of states which allows low electrical resistivity with relatively large *S*. However, ScN has high thermal conductivity, thus its *ZT* is low (~0.2). To reduce κ, potential strategies are nanostructuring, alloying or nanoinclusion formation. To understand which alloying elements could be of interest at elevated temperatures where diffusion can be activated, we have investigated the trends in mixing thermodynamics of ScN-based solid solutions, correlated with experimental studies. The results are used to discuss suitable candidate materials for strategies to reduce the high thermal conductivity in ScN-based systems.

11:20 AM

(ICACC-S10-015-2016) Understanding the Materials Genomes for Good Thermoelectrics (Invited)

J. Yang*[1]; W. Zhang[1]; 1. Shanghai University, China

Thermoelectric materials are a class of promising energy materials which are important for the energy crisis nowadays. Good thermoelectric materials require high electrical transport properties, measured by power factor (=$S^2\sigma$, where *S* is thermopower, and σ is electrical conductivity), and low thermal conductivity κ (composed of electronic part κ_e and lattice part κ_L). Unfortunately, these parameters are not independent; there are several strong interconnections, which lag the advance of the thermoelectric efficiency. Over the years, several concepts have been proposed to break the interconnections. Among these concepts, large band degeneracy for high power factors, and chemical bond hierarchy for balancing low κ_Ls and reasonable carrier mobilities are widely verified and applicable to various thermoelectric materials. In this talk, the aforementioned dilemmas in thermoelectrics and their solutions will be detailed. Our recent works along the two lines demonstrate how to find the "good genomes" in real thermoelectric material systems.

11:40 AM

(ICACC-S10-016-2016) Chemically Modified Carbon-based Nanomaterials in Energy Application: A First-Principles Computational Study (Invited)

T. Liao*[1]; 1. University of Wollongong, Australia

Inexpensive, metal-free materials of high performance in energy application as diverse as solutions, fuel-cell operation, supercapacitors, and catalyst, is highly desirable to replace currently widely used metal or metal oxides. Modification of carbon-based nanomaterials by the introduction of appropriate elements or functional groups or nanosized particles may enable the manipulation of electronic, structural and chemical properties that allows targeting of superior performance. In this presentation, a strong facilitating effect of heteroatom doping on graphene nanoribbons has been illustrated by DFT calculations, which includes stimulating dissociative adsorption of hydrogen, charge carrier adsorption and transfer in an aqueous environment, and change to the hydrogen evolution reaction with the presence of semiconducting nanoparticles. The calculated results not only confirm the possibility of manipulating the performance of carbon-based electrochemical devices in energy application through chemical functionalization but, more importantly, provides the physical rationale for further design strategies.

S12: Materials for Extreme Environments: Ultrahigh Temperature Ceramics (UHTCs) and Nano-laminated Ternary Carbides and Nitrides (MAX Phases)

Methods for Improving Damge Tolerance, Oxidation and Thermal Shock Resistance

Room: Tomoka B

Session Chair: Frederic Monteverde, CNR-ISTEC

8:30 AM

(ICACC-S12-010-2016) Creating ultra-high temperature ceramic matrix composites (Invited)

J. Binner*[1]; 1. University of Birmingham, United Kingdom

There is an increasing demand for advanced materials with a temperature capability of well over 2000°C, in highly corrosive environments and whilst subject to intense heat fluxes and mechanical stress associated with vibration, for aerospace and other applications. The interaction of environmental conditions together with the requirement that dimensional stability is maintained makes the selection of suitable materials extremely challenging. This paper discusses the design, development, manufacture and testing of a new class of Ultra High Temperature Ceramic Matrix Composites (UHTCMCs) based on C fibre preforms enriched with ultra-high temperature ceramics (UHTC) suitable for application in severe aerospace environments.

9:00 AM

(ICACC-S12-011-2016) Improved ablation resistance up to 3000°C of hybrid TaC-TiC-SiC matrix C/C composites for severely aggressive environments

P. Makurunje*[2]; L. Sigalas[2]; F. Monteverde[1]; 1. CNR-ISTEC, Italy; 2. University of the Witwatersrand, South Africa

A novel hybrid-matrix C/C-SiC-TiC-TaC composite was successfully fabricated by performing reactive melt infiltration (RMI) through pressureless spark plasma sintering (PL-SPS) to permeate a molten non eutectic Si-Ti-Ta based alloy into a porous C/C composite prepared by polymer impregnation and pyrolysis (PIP). The C/C composite preform was of density 1.54 g/cm^3 and open porosity 21%, obtained after 3 cycles of PIP with resole phenolic resin and having an amorphous matrix. A target temperature of 1700°C during PL-SPS was deemed effective for the formation of the C/C-SiC-TiC-TaC composite. The resistance to oxidation of the hybrid TaC-TiC-SiC matrix C/C composite was studied exposing discs at 1600°C for increasing times, 1, 2, 4 and 8 min, using a bottom-loading air furnace. In parallel, the resistance to oxidation/ablation was further investigated by using an oxyacetylene flame at about 3000°C, about 8 s of exposure to the oxyacetylene flame at 4 MW/m^2 heat flux. The tested samples, in both cases, were analysed by XRD and SEM-EDS on the external surfaces as well through the polished cross-sections. Mass changes were also measured. The C/C-SiC-TiC-TaC composite showed excellent thermal conduction properties, thus proving to be a promising candidate for the control surfaces of hypersonic vehicles.

9:20 AM

(ICACC-S12-012-2016) Influence of ZrB_2/SiC Grain Size on the Oxidation Resistance of ZrB_2-SiC Ultra-High-Temperature Ceramic Composites

L. Zhang*[1]; N. P. Padture[1]; 1. Brown University, USA

Ultra-high-temperature ceramics (UHTCs) have potential use as thermal protection systems for hypersonic flights, where oxidation resistance is an important property to consider. To improve oxidation resistance, SiC, which forms a protective silica-rich glass layer during high-temperature exposure to air, has been well-studied

and widely used as an additive in ZrB_2-based UHTCs. However, the influence of grain size of SiC on oxidation resistance of UHTCs is still not clear. In this work, the effect of grain sizes of both ZrB_2 matrix and the SiC additive on the oxidation resistance of UHTC composites is presented. ZrB_2-SiC UTHC composites with tailored microstructures were fabricated using spark-plasma sintering. Box furnace was used to oxidize UHTCs specimens for different times and temperatures in air. The oxidized materials were characterized extensively using scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray diffraction (XRD). Weight change, scale thickness and scale composition were determined to understand the oxidation mechanisms and kinetics, and they were analyzed with help of a modeling effort. Finally, insights gained into the effects of grain size of both ZrB_2 and SiC on oxidation resistance of ZrB_2-SiC UHTC composites will be presented.

9:40 AM

(ICACC-S12-013-2016) Fabrication and Properties of C_f/UHTC Composites by a Reactive Melt Infiltration Processing

K. Wada*[2]; Y. Takazawa[2]; Y. Yano[2]; T. Aoki[1]; T. Ogasawara[1]; S. Iwamori[2]; 1. Japan Aerospace Exploration Agency, Japan; 2. Tokai University, Japan

Ultra-high-temperature materials (UHTMs) capable of a prolonged operation in oxidizing environments at temperatures above 2000°C are required for future space systems such as hypersonic aircrafts and reusable launch vehicles. This paper investigated the possibility of a reactive melt infiltration (RMI) process for fabricating carbon-fiber-reinforced ultra-high-temperature ceramic matrix composites (C_f/UHTCs). In order to introduce Hafnium carbide (HfC) as the matrix, molten Hafnium disilicide ($HfSi_2$) was infiltrated into the porosities of a C/C composite at elevated temperatures under vacuum. The C_f/UHTC fabricated by $HfSi_2$-RMI at 1595°C were characterized by Archimedes' method, optical microscopy, X-ray diffraction, and three-point bending tests. It was found that the open porosity of the C_f/UHTC was less than 5%. Due to the reaction between the carbon matrix and molten $HfSi_2$, a dense UHTC matrix comprising HfC, SiC, $HfSi_2$ phases were formed. The three-point bending tests resulted in a flexural strength of approximately 80 MPa at room temperature accompanied with a pseudo-ductile fracture.

Structure Stability under Extreme Environments I

Room: Tomoka B

Session Chair: Jon Binner, University of Birmingham

10:20 AM

(ICACC-S12-014-2016) High heatflux laser testing of HfB_2 cylinders

L. Larrimbe*[1]; L. Vandeperre[2]; P. Brown[3]; C. Hawkins[3]; J. DeCerbo[3]; M. Pettina'[1]; 1. Imperial College London, United Kingdom; 2. Imperial College, United Kingdom; 3. Defence Science and Technology Laboratory, United Kingdom

Hafnium diboride is one of a family of ultrahigh temperature ceramics (UHTCs) which are being considered for application in environments with a substantial heat flux such as hypersonic flight and space re-entry. In order to characterise transitions in material response with heat flux and therefore, predict the behaviour in service of UHTCs, a range of tests were conducted in which small cylindrical bars of HfB_2 were heated on end via laser heating using heat fluxes from 25 to 100 MW m^{-2} for several exposure times. After testing, the outside damage as well as damage observable in cross-sections through the cylinders was characterised using photography, optical and scanning electron microscopy (SEM). It is shown that for low heat fluxes, the damage is largely governed by thermal shock and oxidation, progressing to the onset of melting and finally extensive melt formation. Based on the results, power intensity happened to be the strongest determinant of damage in samples. The higher power densities led to much higher surface temperatures and hence much deeper melting. Finite difference/finite element modelling of the tests gives good agreement with experimental observations allowing the management of stresses and heat in the design of useful components to be predicted.

10:40 AM

(ICACC-S12-015-2016) Processing and Testing of Ultrahigh Temperature Fiber-reinforced Ceramic and Metal Matrix Composites

J. Stiglich*[1]; B. Williams[1]; J. Brockmeyer[1]; V. Arrieta[1]; 1. Ultramet, USA

Ultramet has developed innovative processing for ultrahigh temperature fiber-reinforced ceramic and metal matrix composites. Using a rapid melt infiltration process, Ultramet fabricates high strength fiber-reinforced composite structures that can operate in various hot-gas environments at temperatures above 2800°C. A low temperature process has also been developed to apply fiber interface coatings to protect the fibers during processing and to maximize composite mechanical properties during use. The processing is applicable to ceramic matrices with extremely high melting points including zirconium carbide, hafnium carbide, tantalum carbide, and ceramic alloys, as well as refractory metal matrices. Hot-gas testing of melt infiltrated composite structures in oxidizing environments has been performed at various facilities, and the components survived with low or no erosion. These composites have also been combined with conventional carbon/carbon or lightweight, ultra-high temperature, insulating foams to produce multiple-layered structures for an array of aerospace applications. Processing and testing of fiber-reinforced composite materials will be discussed.

11:00 AM

(ICACC-S12-016-2016) A diffusion-based oxidation and creep crack growth model to predict damage in ultra-high temperature ceramics

M. Pettina'*[1]; L. Vandeperre[2]; P. Brown[3]; K. Nikbin[1]; 1. Imperial College London, United Kingdom; 2. Imperial College, United Kingdom; 3. DSTL, United Kingdom

In the high temperature regime (>1600°C) ceramics can exhibit failure due to oxidation and creep in some ways similar to metals at lower temperatures. A combined creep multiaxial continuum damage diffusion-based oxidation and crack growth model is proposed for ceramic materials. The model allows for the development of an external damaged layer owing to oxidation acting from the surface and combines it with the damage due to creep under an applied load. A representative microstructure has been modelled in order to allow intergranular cracking due to enhanced diffusion and/or creep of grain boundaries. The proposed damage model is implemented in the commercial finite element software Abaqus as a user-defined subroutine and makes use of available material data for ZrB_2. Additionally, experiments on a three point bend set-up are being performed to derive basic creep properties to input into the model and validate its capability in predicting damage and cracking in ultra-high temperature ceramics.

11:20 AM

(ICACC-S12-017-2016) Composite Ceramic Thermocouples for Harsh-Environment Temperature Measurements

R. C. Pillai*[1]; G. A. Yakaboylu[1]; K. Sabolsky[1]; E. M. Sabolsky[1]; J. Bogan[2]; J. Sayre[2]; 1. West Virginia University, USA; 2. HarbisonWalker International Technology Center, USA

For temperature measurements >1200°C, a Pt-Pt/Rh thermocouple is the standard for precise measurements, but the stability of these sensors may be limited depending upon the temperature, pressure, redox environment, and presence of select corrosive species. An alternative to these precious metal thermocouples is needed which may demonstrate higher stability with lower cost. The current work investigated the development of thermocouples based on conductive silicide/oxide composites. In this work, silicide/oxide thermocouples

were fabricated by tape-casting and screen-printing techniques. The phase and microstructure of the thermocouple composites after testing were evaluated by x-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques, respectively. The thermoelectric response of the thermocouples was measured up to 1500 °C. Thermocouple with a configuration of 90 vol% $TiSi_2$-10 vol% Al_2O_3 versus 90 vol% WSi_2-10 vol% Al_2O_3 showed a peak thermoelectric voltage of 20 mV at 800 °C which is comparable or better than B-type thermocouple.

11:40 AM

(ICACC-S12-018-2016) Damage study on a refractory material operating at high temperature in an aggressive environment

A. Kallel*[1]; S. Romero Baivier[1]; 1. Vesuvius, Belgium

This work aims to qualitatively investigate damage phenomena in refractory parts used in continuous casting applications in order to increase their reliability. The material of interest consist of a mixture of alumina and graphite powders. Parts are prepared by powder compaction followed by a firing step. A homemade experimental setup is developed to test thermomechanical resistance of full scale parts. Moreover, cored samples are issued from shaped refractory with respect to their positions. Triaxiale compression trials, Brazilian tests, thermal expansion and thermal conductivity measurements are performed on cylindrical specimens from room temperature to near the operating temperature (1000°C-1550°C). Thus, a constitutive thermo-elastoplastic model issued from literature is adjusted to obtain yield and fracture surfaces. This model is then implemented into a commercial finite elements software. Failure stresses predictions are in agreement with experimental results at the range of the investigated temperatures. However, fracture path and location are not correctly reproduced. The particulate microstructure and the density distribution are under investigation to enhance our modelling approach.

S13: Advanced Materials for Sustainable Nuclear Fission and Fusion Energy

Accident Tolerant Fuels II and Fuel Ceramic Science

Room: St. John

Session Chairs: Kurt Terrani, Oak Ridge National Laboratory; Sosuke Kondo, Kyoto University

8:30 AM

(ICACC-S13-010-2016) Low Temperature Pressureless Sintering of Silicon Carbide Matrix for Fully Ceramic Microencapsulated Fuels (Invited)

Y. Kim*[1]; J. Eom[1]; Y. Seo[1]; S. Lee[2]; K. Lim[2]; 1. University of Seoul, The Republic of Korea; 2. KEPCO Nuclear Fuel, The Republic of Korea

Fully ceramic microencapsulated fuels (FCM) consist of tristructural-isotropic (TRISO) fuel particles embedded in a SiC matrix. Since the sintering temperature of SiC is usually higher than the fabrication temperature of TRISO fuel particles, UO_2 core in TRISO particles is overfired during sintering of SiC matrix. Thus, the development of a new additive composition which could densify SiC matrix at low temperatures is an important issue for the development of FCM. In the present study, SiC ceramics were fabricated by pressureless sintering at 1700-1900°C for 2 h in an argon atmosphere with a new additive system. The effect of sintering temperature on the mechanical and thermal properties of SiC ceramics was investigated. Sintered densities above 97% were obtained at a temperature as low as 1750°C without an applied pressure. Toughened microstructures, which consisted of platelet SiC grains and relatively small equiaxed grains, have been obtained when sintered at higher than 1850°C for 2 h in an argon atmosphere. Typical flexural strength, fracture toughness, and thermal conductivity of the pressureless sintered SiC ceramics with Al_2O_3-Y_2O_3-CaO were 600 MPa, 5.3 $MPam^{1/2}$, and 80 W/mK at room temperature, respectively. Preliminary data on the processing of FCM will be presented and critical issues will be suggested for further study.

9:00 AM

(ICACC-S13-011-2016) Thermodynamic Analysis of U-Si compounds from U_3Si_5 to USi_2

M. Noordhoek*[1]; T. Besmann[1]; 1. University of South Carolina, USA

Uranium silicide compounds are being considered for use in next generation nuclear fuels. For example, one possible application to create a composite fuel of primary UN with a minor secondary phase of U_3Si_5. Current analysis of these composites demonstrate that they are thermodynamically stable. However, recent experiments have shown discrepancies in the thermophysical properties of U_3Si_5 with respect to previous reports. This suggests that further study is needed for Si-rich compounds. In this work, we present the results of first principles calculations for the U_3Si_5, $USi_{1.88}$ and USi_2 phases. The thermodynamic and mechanical properties will be described with attention to possible finite temperature phase transitions. In addition, other considerations for phase stability, such as the effect of impurities or fission products, will be explored. These calculations will also aid the extension of CALPHAD (CALculation of PHAse Diagrams) models for U-Si.

9:20 AM

(ICACC-S13-012-2016) High density UN microsphere fabrication for FCM fuel development

J. W. McMurray*[1]; T. Lindemer[2]; R. Hunt[2]; J. Collins[2]; C. Silva[2]; J. Henry[1]; K. Terrani[2]; 1. Oak Ridge National Lab, USA; 2. Oak Ridge National Laboratory, USA

The internal gelation process was used to produce hydrated uranium trioxide ~1,700-μm-diameter spheres with fully dispersed carbon (UO_3-H_2O-C). Carbothermic reduction and nitriding (CTRN) of the air-dried UO_3-H_2O-C precursor in flow-through, vertical refractory-metal crucibles at temperatures up to 2123 K result in $UC_{1-y}N_y$ fuel kernels with y≈0.96 and theoretical density between 83-86%. The CTRN process is as follows. The UO_3-H_2O-C starting material is first heated in an inert, i.e. Ar, or under vacuum to drive off the H_2O molecules and reduce UO_3 to UO_2 by removal of CO_2 and/or CO to produce a biphasic UO_2-C composite. The temperature is increased such that the UO_2-C is converted to ~96% theoretical density UO_2-2UC kernels at which point N_2 is introduced. At this stage N substitutes for C in the UC phase resulting in free C that is available to further reduce the U in UO_2 by removal of CO and thus facilitating further formation of UN. The final product is an ~820-μm-diameter microsphere $UC_{1-y}N_y$ solid solution. The UN content can be enriched to a theoretical value of about 96% by removal of HCN in flowing N_2/H_2 gas at high temperatures. These microspheres form the kernel of a TRISO (tri-structural isotropic) particle for Fully Ceramic Micro-encapsulated LWR Accident Tolerant Fuel (ATF). Research supported by the US Department of Energy, Office of Nuclear Energy, Fuel Cycle Technology Program.

9:40 AM

(ICACC-S13-013-2016) Used Fuel content verification using Lead Slowing Down Spectroscopy

M. Smith*[1]; R. Kanakala[1]; 1. University of Idaho, USA

Quantification of spent fuel isotopes is a vital consideration to prevent diversion of the plutonium isotopes contained within. One of the proposed methods suitable for determining spent fuel radionuclide concentrations is the use of a Lead Slowing Down Spectrometer (LSDS). However, to be useful as an accountability verification tool, the LSDS must be able to detect the absence of pins from the center of the bundle. This paper will measure and compare the LSDS response, simulated by MCNPX, for three different scenarios: fuel bundle with no missing pins, similar bundle as in case 1, but with 5% less radionuclide concentration, homogenously

distributed, and similar bundle as in case 1, but with 5% of the pins removed and replaced with stainless steel. The removed pins will be taken from the center of the bundle. This is the "diversion attempt." The objective of this research will be to determine if the signature of the "diversion attempt" most closely resembles the used fuel bundle with no missing pins, or the bundle with 5% less radionuclide concentration, homogenously distributed. If the first case is true, then a successful diversion attempt can be made due to the self-shielding effect of the outer pins of a fuel bundle. If the second case is true, then the self-shielding effect is minimal, and the LSDS can successfully measure radionuclide concentrations, and thus detect an attempted diversion attempt

10:20 AM

(ICACC-S13-014-2016) Multi-layer Ceramic Matrix Composite Silicon Carbide Cladding for Light Water Reactors (Invited)

K. Shirvan*[1]; 1. Massachusetts Institute of Technology, USA

The multi-layer ceramic matrix composite Silicon Carbide (CMC SiC) is currently being investigated worldwide as a nuclear fuel cladding. The high temperature oxidation weakness of the current Zircaloy cladding has been highlighted in the scarce light water reactors' (LWRs) severe accident history. The CMC SiC cladding has potential to maintain its strength at high temperatures under LWR environment, while reducing the needed fissionable Uranium, when replacing the Zircaloy cladding. The latter is the key attribute that separates CMC SiC cladding concept from most other accident tolerant fuel concepts currently being investigated. This presentation focuses on discussing the current state of knowledge on performance of CMC SiC in LWR conditions as part of the experimental and simulation efforts performed at MIT for the last 15 years, including areas of neutronics, thermal hydraulics, fuel and structural performance and economics. Despite its great potential, CMC SiC cladding faces much uncertainties regarding its viability. One key challenge is CMC SiC cladding ability to overcome stress induced irradiation swelling that could lead to macro-cracking in the cladding (including end caps) during steady and transient scenarios. Such cracking would compromise CMC SiC design requirement to maintain its hermeticity. Potential areas of future R&D to address such challenges will also be presented.

10:50 AM

(ICACC-S13-015-2016) Design, Analysis, and Validation of a SiC Cladding Irradiation Experiment with High Radial Heat Flux

C. Petrie*[1]; J. McDuffee[1]; K. Terrani[2]; Y. Katoh[2]; 1. Oak Ridge National Lab, USA; 2. Oak Ridge National Laboratory, USA

SiC composite materials are a promising candidate for nuclear fuel cladding applications due to their strength at high temperatures, irradiation damage tolerance, and oxidation resistance. The accident tolerant fuels community is currently investigating a multilayered architecture incorporating a composite material and a monolith to provide hermetic containment of fission gases. There is a concern as to whether these multilayered cladding materials can survive the stresses resulting from differential swelling and thermal expansion during extended irradiation under high heat flux. In order to provide experimental validation of thermo-mechanical models of stress states in SiC cladding, an irradiation capsule design effort has been undertaken. The experimental design allows for a constant cladding outer surface temperature of ~300 °C during one cycle of irradiation in an uninstrumented "rabbit" capsule in the high flux isotope reactor. The design can accommodate clad swelling of up to 3%, while keeping the clad surface temperature constant to within ~30 °C. An engineered aluminum foil was developed to absorb the expansion of the cladding. A finite element model of the capsule performance was developed using ANSYS with custom libraries for calculating thermal contact resistance. The thermal models were validated experimentally using a sealed, instrumented testing rig.

11:10 AM

(ICACC-S13-016-2016) Quantifying radiation damage in silicon carbide with high-energy x-rays

D. Sproutster*[1]; T. Koyanagi[2]; T. Watkins[2]; R. Barabash[2]; Y. Katoh[2]; L. Ecker[1]; 1. Brookhaven National Laboratory, USA; 2. Oak Ridge National Laboratory, USA

SiC based materials display novel structural properties including resistance to radiation damage, high specific strength and retention of this strength at high temperatures. Such unique behavior has made SiC the center of many research efforts, particularly within the nuclear energy community for use as a structural material in advanced reactors *and* as an accident tolerant fuel cladding for LWR's. Here, we present recent results relating to the analysis of both the Bragg and diffuse x-ray scattering components of neutron irradiated SiC. We highlight the specific advantages of studying the diffuse scattering and the ability to capture changes that ensue with irradiation in the local atomic environment. We readily quantify several radiation-induced changes including an increase in microstrain, changes in the grain size, bondlengths, coordination numbers, lattice parameters and structural disorder. It is also possible to identify and understand the dose and irradiation temperature- dependence of specific defects attributed to radiation damage. By quantifying and linking changes in the microstructure and atomic structure, we aim to develop a more detailed understanding of the radiation response of SiC. Such studies are potentially important to build mechanistic models of material performance and to understand the susceptibility of various microstructures to radiation damage for advanced energy applications.

11:30 AM

(ICACC-S13-017-2016) Laser-Printed Ceramic Fiber Ribbons: Properties and Applications

J. Pegna[1]; S. Harrison*[1]; E. G. Vaaler[2]; J. L. Schneiter[1]; K. L. Williams[1]; R. K. Goduguchinta[1]; 1. Free Form Fibers, USA; 2. Solar Synergies, Inc., USA

The last few years have seen the emergence of a new additive manufacturing (AM) alternative to spinning for the production of ceramic fibers. This approach – called a "Digital Spinneret" (DS) – causes multiple filaments to grow in a single step using a massively parallel laser driven chemical vapor deposition process (LCVD). To date, it has been used to demonstrate the fabrication of stoichiometric Silicon Carbide fibers (SiC_f). The DS introduces a manufacturing paradigm shift with significant ramifications for the design of Ceramic Matrix Composites (CMCs), not the least of which is a potentially game-changing domestic source of SiC_f. This presentation focuses first on a presentation of state-of-the-art knowledge of SiC_f produced by the DS. Next, we discuss the anticipated impact that such fibers are expected to have on CMC fabrication, with a particular attention to nuclear applications. Finally, we explore new design opportunities afforded by additive manufacturing of fibers. We illustrate our point with an example of functional microstructures embedded within the fibers.

S14: Crystalline Materials for Electrical, Optical and Medical Applications

Semiconductor I

Room: Tomoka C

Session Chairs: Takashi Taniguchi, National Institute for Materials Science (NIMS); Takashi Matsuoka, Institute for Materials Research, Tohoku University

8:30 AM

(ICACC-S14-009-2016) Silicon carbide ceramics as source in growth of SiC for optoelectronic and energy applications (Invited)

M. Syvajarvi*[1]; V. Jokubavicius[1]; X. Liu[1]; J. Sun[1]; P. Wellmann[2]; 1. Linköping University, Sweden; 2. University of Erlangen-Nürnberg, Germany

Abrasive SiC powder is used as source material in physical vapor transport (PVT) that is used to produce hexagonal 6H- and 4H-SiC bulk crystals. Since twenty years we have applied a modified PVT approach for growth of epitaxial layers on SiC substrates using SiC ceramics plates as source. Such nominally pure plates are typically grown by CVD on graphite and is commonly used is in refractory applications. The monolithic plates enable a better uniformity of vapor species sublimation. Recently, we have initiated new research frontiers in doped silicon carbide for white LEDs and photovoltaics. In this research, we develop doped source material concepts that maintain monolithic source character and resolve growth conditions which allows to maintain a high crystal quality at various doping levels. The doping is achieved via co-doping from the monolithic source material which we have prepared in polycrystalline form by PVT with dopants, but also sintered sources have been explored. Further on, by the sublimation technique we achieved growth of cubic SiC (3C-SiC) in bulk like form using ceramic SiC sources, and now study parameter windows for bulk growth by using both monolithic and powder sources. The combination of our 3C-SiC growth approach and doped source allows us to explore this material for various semiconductor applications.

9:00 AM

(ICACC-S14-010-2016) In-situ observation of solution growth interface of SiC from Fe-Si solvent (Invited)

S. Kawanishi*[1]; T. Yoshikawa[1]; 1. The University of Tokyo, Japan

SiC has been widely applied to the high power devices from its excellent semiconducting properties to reduce energy loss. Growing high quality crystals is essential for further use of SiC devices in an upcoming sustainable society. Solution growth has attracted attentions as a method to grow high quality SiC crystals. An in-situ microscopic observation technique of high temperature crystal growth interface between a widegap crystal and a molten alloy has been established to investigate the dynamic growth behavior of SiC during the solution growth. The motion of the bunched steps during SiC growth from Fe-Si solvent at 1573 – 1973 K was monitored by the bright field observation to visualize the in-plane morphology. The growth was found to proceed via either island-type growth by the two-dimensional nucleation or spiral growth by the threading screw dislocation in the seed crystal (4H-SiC). In addition, simultaneous acquirement of interference pattern enabled to measure the step height of a few nanometers as well as the growth rate at the interface. It was clarified that the preferential growth was typically island-type growth of 3C-SiC below 1773 K and the spiral growth of 4H-SiC above 1873 K, leading to the selective growth of 4H-SiC at higher temperature. The competition of the growth domains was also detected. It was found that the interface supersaturation greatly affected to the growth morphology.

9:30 AM

(ICACC-S14-011-2016) Nitrogen incorporation during 4H-SiC bulk crystal growth (Invited)

D. Chaussende*[1]; N. Tsavdaris[1]; N. Valle[2]; E. Sarigiannidou[1]; 1. CNRS, France; 2. LIST, Luxembourg

Nitrogen is the most common n-type dopant for silicon carbide. Empirically controlled during the bulk growth by the physical vapour transport (PVT) process, the incorporation mechanism is still unclear and only a few studies deal with this topic. After a systematic experimental investigation of nitrogen incorporation as a function of different growth parameters, we could draw an incorporation mechanism at high temperature for which we pointed the significant role of incorporation on the terraces vs. the step edges. This mechanism will be discussed regarding some simple features such as dangling bond density and adsorption/desorption rate at the crystal surface.

10:20 AM

(ICACC-S14-012-2016) From Sapphire to Silicon: experimental and numerical aspects of the adaptation of the Kyropoulos process (Invited)

G. Chichignoud*[1]; A. Nouri[1]; L. Lhomond[1]; Y. Delannoy[2]; V. Brize[3]; M. Albaric[3]; F. Richard[4]; K. Zaidat[2]; 1. CNRS, France; 2. Grenoble INP, France; 3. CEA, France; 4. Cyberstar, France

Kyropoulos is a classical way to process sapphire and shall be a relevant technique applied to silicon. Crystallization is initiated from a cold region at the top of the bath whilst the hot zone is located at the bottom of the crucible. The thermal configuration is therefore intrinsically unstable from a fluid flow point of view. In addition pure liquid silicon is a semi-transparent material near its melting point, meaning that radiative properties significantly differs from sapphire. Finally difference of densities between solid and liquid phases makes the use of weight controlled process everything but obvious. Hence the adaptation of Kyropoulos process for silicon raises challenging issues, partly due to the specific properties of silicon compared to sapphire. For this reason a coupled approach between experiments and modelling is necessary. The 3D nature of the Silicon fluid flow mainly drives the shape of the grown crystal. In addition the emissivity gap between solid and liquid silicon promotes the eventual inhomogeneity in the flow distribution, making the stabilization of the growth hard to achieve. The steep evolution of radiative properties occurring during the solidification is particularly discussed, and is taken into account both in the model and experiments to achieve a controlled radial growth of the ingot.

10:50 AM

(ICACC-S14-013-2016) 3D-Mapping of Phase Distributions beneath Vickers Indentation on Silicon Wafers

S. Rogachev*[1]; 1. University of Florida, USA

Silicon, a semiconductor utilized throughout the electronics, automotive, and defense industries, exhibits complex phase transformations when subjected to high pressures. Within a hydrostatic pressure range of 10-13 GPa, silicon (Si-I) undergoes a phase change to a metallic form (Si-II). This metallic phase is unstable during unloading and gives way to various crystalline phases and an amorphous phase, all of which have different electronic and mechanical properties. The extent of the phase transformations can extend well beneath the surface of the material, leading to serious consequences for electronic applications. A single-crystal silicon (001) wafer was subjected to Vickers microindentation at varying loads. Utilizing progressive polishing and Raman spectroscopy, a nondestructive form of material characterization, three-dimensional maps of the silicon phases beneath the indent were developed. Significant levels of amorphization were found at depths 5-6 times the size of the indent. The load and loading rate dependence of various phase changes was also analyzed. The results from this research have far-reaching implications in better design of machining processes,

potential modification of the Si crystal lattice to inhibit phase transformation, and detailed data for better modeling and prediction of Si behavior and properties under high-pressure loading.

11:10 AM

(ICACC-S14-014-2016) Catalytic Combustion Type Gas Sensor With Novel Oxidation Catalysts Such Gases as Carbon Monoxide and Hydrogen (Invited)

N. Imanaka*[1]; 1. Osaka University, Japan

Unfortunately, a significant problem associated with conventional catalytic combustion-type gas sensors is that the catalysts (for example, Pt/Al_2O_3 or Pd/Al_2O_3, etc) require operating temperatures higher than 400 degree C for the complete target gas oxidation. Since other gases such as methane and volatile organic compounds (VOCs) can also burn out at such elevated temperatures, this type of sensors always lacks in selectivity for the target gas species. Recently, we have developed a low-temperature catalytic combustion-type gas sensors, by employing the novel $Pt/Ce_{0.68}Zr_{0.17}Sn_{0.15}O_{2.0}$ catalyst at moderate temperstures, which temperature is more than 300 degree C below the conventional ones. Here, novel type of catalytic combustion type gas sensors was realized, showing excellent sensing performance that demonstrated an enhanced sensivity and also drastically accelerated the response to target gases at the moderate temperatures.

11:40 AM

(ICACC-S14-015-2016) Polarity effects on the formation and physical properties of ZnO nanowires (Invited)

V. Consonni*[1]; 1. Université Grenoble Alpes, CNRS, France

Polarity effects are crucial in wurtzite compound semiconductors such as GaN and ZnO, both in the form of single crystals and thin films. They have been shown to strongly affect their formation mechanisms, the surface reactivity and stability as well as their electro-optical properties. While polarity effects have widely been investigated in ZnO single crystals and thin films, there are still important issues to address regarding their effects in the form of ZnO nanowires. In this work, the formation mechanisms of ZnO nanowires grown by wet chemistry are discussed in details. A special emphasis is made on the polarity effects due to the nucleation surfaces of ZnO nanowires such as ZnO single crystals and polycrystalline ZnO seed layers. The structural properties of these ZnO seed layers and nanowires are investigated by scanning and transmission electron microscopy (TEM) including high-resolution TEM and convergent beam electron diffraction as well as by resonant x-ray diffraction in synchrotron. The formation of O- and Zn-polar ZnO nanowires with high structural uniformity is demonstrated by combining selective area growth using electron beam lithography and etching processes with wet chemistry. The electrical and optical properties of the resulting O- and Zn-polar ZnO nanowires are further compared.

5th Global Young Investigator Forum

Applications: Ceramic Sensors and Actuators, Energy Generation and Storage and Processing

Room: Coquina Salon F

Session Chairs: Eva Hemmer, INRS; Surojit Gupta, University of North Dakota; Ken-ichi Mimura, National Institute of Advanced Industrial Science and Technology (AIST); Kathleen Shugart, UES, Inc.

8:30 AM

(ICACC-GYIF-011-2016) Non-Injection, Alkyl-thiol-Free Synthesis of $CuInS_2$ Quantum Dot (Invited)

R. Marin*[1]; A. Migliori[3]; V. Morandi[3]; F. Enrichi[4]; P. Canton[2]; 1. INRS, Canada; 2. Università Ca' Foscari, Italy; 3. CNR-IMM, Italy; 4. Veneto Nanotech, Italy

A newly developed method for the synthesis of readily silanated $CuInS_2$ quantum dots (QDs) is proposed. The synthesis of $CuInS_2$ QDs is conducted via a heat up approach. Thiolated precursors are generated in the presence of the silica precursor mercaptopropyl trimethoxysilane (MPTS) at high temperature. Diethylene glycol can be added in the reaction environment as an additional solvent beside MPTS. Heating above 180 °C leads to the production of ultrasmall luminescent QDs which can be easily dispersed in ethanol and/or acetone. The structural and morphological analyses of the so-produced nanoparticles show that they are ultrasmall in size (diameter generally below 3 nm) and copper deficient, which is a beneficial feature for this kind of emitters. The study of the optical properties allows to highlight the presence of different sizes in the reaction environment. The emission of the QDs is centered in the red region, with a profile width of more than 100 nm. The QDs display a photoluminescence quantum yield (QY) as high as 6% and the dispersions are stable for months. The developed method allows to produce heavy metal-free silane-capped quantum dots. The small size of the nanoparticles and their optical properties are promising in view of an optimization of the process via the growth of a passivating shell (ZnS) to increase the QY. Their embedding in a silica matrix for biological applications is currently under study.

9:00 AM

(ICACC-GYIF-012-2016) The Effect of Processing Conditions on the Thermal Regeneration of Fiber Bragg Gratings (FBG) for Space Applications

M. Celikin*[1]; D. Barba[1]; E. Haddad[2]; A. Ruediger[1]; F. Rosei[1]; 1. Institut National de recherche Scientifique, Canada; 2. MPB Communications Inc, Canada

High thermal stability of Fiber Bragg Gratings (FBG) is crucial for the use of optical fibers as thermal sensors in spacecrafts (above 1000°C under extreme conditions). Thermal regeneration process where a more stable but a weaker optical signal is produced was studied at a temperature range of 700 to 1000°C. In-situ high temperature stability experiments were conducted at MPB Communications Laboratories. The changes in thermal regeneration response of FBG were found to be dependent on fiber composition, grating depth and annealing process. Structural variations upon thermal regeneration process were also investigated via Transmission Electron Microscopy (TEM) analysis.

9:20 AM

(ICACC-GYIF-013-2016) Focused Ion Beam Characterization of Polycrystalline YAG Fibers

K. Shugart*[1]; H. Kim[1]; 1. UES, Inc., USA

YAG is currently being considered as a host material for high-energy fiber lasers. Researchers have produced both single crystal and polycrystalline YAG fibers, with a variety of cladding materials; the processing steps have evolved to improve fiber quality and minimize

optical propagation losses. Propagation losses are measured by injecting a 1480-nm fiber-coupled laser into the fiber. Previous characterization of these fibers includes cross-sectional scanning electron imaging, transmission electron imaging, and energy dispersive spectroscopy. However, these methods do not allow for a focused look at the areas showing greatest propagation losses. In order to improve understanding of the microstructure of these fibers, and its impact on optical propagation, another technique has been identified. Dual beam focused ion beam 3D cross sectioning coupled with energy dispersive spectroscopy have been used. This technique and its results will be discussed.

9:40 AM

(ICACC-GYIF-015-2016) Optimization of the fabrication conditions of microtubular Solid Oxide Fuel Cells by dip coating

C. I. Ramos Villegas*[1]; H. J. Avila Paredes[1]; 1. Universidad Autónoma Metropolitana, Mexico

Solid Oxide Fuel Cells (SOFCs) are electrochemical devices for converting chemical into electrical energies with efficiencies close to 60 %. Conventional SOFCs operate at temperatures near 1000 °C; however, under these conditions there are some drawbacks like components degradation and the restriction of the type of materials to be used for interconnectors and supports, which increases the cost of these devices. Therefore, there is a current trend in research to fabricate SOFCs that operate at intermediate temperatures (500-700 ° C) and with a microtubular architecture for portable applications. The present study focused on the optimization of manufacturing conditions of microtubular SOFCs. Prototypes were fabricated based on a dip coating technique on a sacrificial core; a cermet of Ni-$Ce_{0.8}Gd_{0.2}O_{2-x}$ was used as the anode, $Ce_{0.8}Gd_{0.2}O_{2-x}$ as the electrolyte, and $La_{0.8}Sr_{0.2}Co_{0.2}Fe_{0.8}O_3$ as the cathode. The electrical performance was evaluated by voltammetry in the 500-600 °C range.

10:20 AM

(ICACC-GYIF-016-2016) Sintering Kinetics of Bayer Process Alumina

T. Frueh*[1]; E. Kupp[1]; C. Compson[2]; J. Atria[2]; G. L. Messing[1]; 1. Pennsylvania State University, USA; 2. Almatis, Inc., USA

Bayer process aluminas are typically 99.0 - 99.8% pure and contain Na_2O, SiO_2, Fe_2O_3, and CaO as main impurities. In this work we report how the concentration of Na_2O and SiO_2 in particular affect densification of an MgO-free Bayer process alumina, and then how MgO affects the sintering of NaO/SiO_2 co-doped samples. We account for densification in MgO-free samples with a solution-precipitation model that strongly depends on impurity concentration and the ratio of Na_2O to SiO_2. By comparing the sintering kinetics of MgO-free and MgO-doped Bayer process alumina we were able to identify the stages at which MgO affects sintering and draw conclusions about the role of MgO in the liquid phase sintering model of Bayer process alumina.

10:40 AM

(ICACC-GYIF-017-2016) Densification and Microstructure of Hot-Pressed Boron Suboxide with Alumina and Silica Additives

P. E. O'Shannessy*[3]; E. R. Shanholtz[1]; J. LaSalvia[1]; K. D. Behler[4]; K. A. Kuwelkar[2]; 1. Army Research Laboratory, USA; 2. Rutgers University, USA; 3. Drexel University, USA; 4. TKC Global, USA

The effect of alumina and silica additives on the densification behavior and microstructure of boron suboxide has been investigated. Alumina and silica powders were added at a 5v/v% with boron suboxide powder and wet-mixed acoustically. Dried powder mixtures were hot pressed at temperatures between 1650°C – 1850°C for two hours with applied uniaxial pressure approximately 50 MPa. To minimize reaction with the graphite die and punches, boron nitride spacers and spray were utilized. Densification was monitored using an LVDT with data acquisition system. Final densities were determined by the Archimedes method. Resultant phases and microstructures were characterized by x-ray diffraction and scanning electron microscopy. X-ray diffraction of the starting boron suboxide powder suggests the presence of approximately 5-10 wt.% amorphous boron. No other secondary phases were indicated. The highest density for the starting boron suboxide powders was achieved at 1850°C, while those with additives achieved comparable density at lower temperatures (alumina slightly more effective than silica). Additionally, the onset of densification was also lower for powders with additives. Experimental procedures and results on both densification behavior and microstructures will be presented.

Young Researchers' Funding, Mobility and Networks

Room: Coquina Salon F

Session Chairs: Ken-ichi Mimura, National Institute of Advanced Industrial Science and Technology (AIST); Kathleen Shugart, UES, Inc.

11:20 AM

(ICACC-GYIF-018-2016) Science in between Fun, Funding and Fundamentals

T. Fischer*[1]; S. Mathur[1]; 1. University of Cologne, Germany

In addition to ones own scientific vision, success in the modern science business is also attributed to soft skills, like creating and maintaining peer networks, acquiring third-party funding and keeping oneself updated on the latest development in the field of expertise and related topics. Especially for emerging scientists entering the field after obtaining their PhD, science management becomes a vital point for future success. While conferences and workshops are a good place to form new contacts for collaboration, today's social media allows to maintain contacts and networks on an international basis. In addition many funding opportunities already exist targeting especially young professionals, ranging from travel support to full stipends from either national or international funding agencies. This presentation will highlight some aspects in terms of funding opportunities, networking and career planning in today's science community.

FS2: Advanced Ceramic Materials and Processing for Photonics and Energy

Solar Energy II

Room: Coquina Salon G

Session Chairs: Isabella Concina, CNR-IDASC SENSOR Laboratory & Brescia University; Giovanni Fanchini, University of Western Ontario

8:30 AM

(ICACC-FS2-010-2016) Semiconducting perovskites and their applications (Invited)

R. Nechache*[1]; 1. Ecole de Technologie Superieure, Canada

The perovskites ABO_3, with A and B cations of different valences, are multifunctional materials. Depending on their chemical composition they behave very differently, showing properties specific to metals, dielectrics, ferroelectrics and semiconductors. Most of these materials are inorganic, such as well-known ferroelectric Bi_2FeCrO_6 (BFCO). BFCO is promising because it exhibits a conversion efficiency of about 8.1% under 1 Sun illumination in thin film form. Other perovskites can be hybrid, if the cation A is replaced with an organic radical. This is the case for halide perovskite compounds ($CH_3NH_3Pb_X$), with X=Br, Cl, I, found recently to possess excellent light absorbing properties in the visible-near infrared spectrum. The use of these materials in solar cells had led to a rapid increased of the photovoltaic conversion efficiency in the last year up to about 20%. The combination of the relatively high efficiency with the low cost technologies makes perovskite photovoltaic solar cells very attractive

for future development. Here we review recent progress of our group in the exploration of perovskite materials in pursuit of two major research thrusts: Semiconducting perovskite and their applications. We will present, the controlled growth and characterization of BFCO and $CH_3NH_3PbI_3/CH_3NH_3GeI_3$ thin films via PVD techniques. The optimization of their properties and the performance of their related devices will be also discussed.

9:00 AM

(ICACC-FS2-011-2016) Photostabilty under Uv-light of organic-Inorganic Halide Perovskites

D. Benetti*[1]; H. Zhao[1]; K. Basu[1]; L. Jin[1]; F. Rosei[1]; A. Vomiero[2]; 1. INRS, Canada; 2. Institute of Metal Research, Italy

Since late 2012, organic/inorganic halides with the perovskite structure have strongly attracted the attention of the photovoltaic community when efficiencies close to 10% were first achieved in solid state cells. However the long-term stability is still an important issue that needs to be addressed. In particular, the effect of UV light on material stability is not yet well understood In this work, we investigate the photostability of the two most used perovskites materials, $MAPbI_3$ and $MAPbI_{3-x}Cl_x$ realized with different methods (one step and two steps). We focused our attention on the material itself without building a functional device. The perovskites were grown directly on fluorine-doped tin oxide-coated substrates (FTO) without using any hole-blocking layers. Recently this architecture has proved to work as photoanode to achieve high performance perovskite solar cells.. We compared the different photostability arising from the use of different materials and also from the use of different molar ratio of precursor and/or method of deposition. We found that the UV stability of the perovskite depends strongly from the material itself but also from method and precursors adopted for the synthesis. We attribute these differences to the crystalline structure of the perovskite and how it is formed due to the presence of different elements (e.g. the presence or lack of chlorine during the crystallization process).

9:20 AM

(ICACC-FS2-012-2016) Photovoltaic Properties of Multiferroic Bi_2FeCrO_6 Based p-i-n Heterojunctions with p-Type and n-Type Oxides

W. Huang*[1]; R. Nechache[1]; C. Harnagea[1]; J. Chakrabartty[1]; M. Chaker[1]; F. Rosei[1]; 1. INRS, Canada

Multiferroic materials are increasingly being studied for solar energy conversion technologies due to their efficient ferroelectric polarization-driven carrier separation and above-bandgap generated photovoltages. Recently, it reported that the power conversion efficiency of 8.1% for Bi_2FeCrO_6 (BFCO) thin-film solar cells with tunable bandgap of multiferroic oxides by engineering the cationic Fe/Cr ordering. However, the low bandgap BFCO with high cationic Fe/Cr ordering showed very weak ferroelectric properties, resulting in reduction of separation of photogenerated charge carriers, thus hindered the effective transport of photogenerated charge carriers. To enhance the internal electric field, a sandwich structure of p-i-n heterojunctions is designed. In this p-i-n junction, multiferroic material acting as intrinsic absorber is sandwiched between *p*- and *n*-type oxides as hole- and electron- collecting layer, respectively, so that the depletion regions at the p-i and i-n are added up and an internal field is formed across the entire layer of multiferroic material. In this work, we have used highly odered low bandgap BFCO as an absorber. Inorganic oxides, such as In-doped $SrTiO_3$, NiO or MoO_3 as *p*-type layer and Nb-doped $SrTiO_3$ or Al-doped ZnO as *n*-type layer, have been used along with the multiferroic BFCO to form a p-i-n heterojunctions PV device.

9:40 AM

(ICACC-FS2-013-2016) Lead-free Perovskite Solar Cells Having an Anatase TiO_2 Nanoparticle/Nanofiber Composite Electron Transport Layer

K. N. Nurpramesti*[1]; J. Ting[1]; 1. National Cheng Kung University, Taiwan

Toxicity of lead is one big concern for lead perovskite solar cells based on mesoscopic TiO_2 and has attracted many attentions to replace the Pb with Sn. We have investigated the use of TiO_2 nanoparticle/nanofiber composite, which provides a porous structure better for the pore filling, for use as an electron transport layer. Added advantages include improved electron transport and reduced recombination. To the best of our knowledge, this is the first study on Sn-based perovskite solar cells that uses such a porous layer. Titania nanofibers were fabricated by electrospinning and will be examined using the Brunauer-Emmett-Teller technique, UV-visible spectroscopy, scanning/transmission electron microscopy (SEM/TEM), X-ray diffraction (XRD). Nanofibers were then mixed with commercial P25 Titania nanoparticles and deposited by using a spin-coating technique. We have addressed the optimization of Sn-based perovskite layer deposition by investigating the growth kinetics, which critically determines the property of the layer. Also, anti-solvent additions by rapid precipitation during the spin coating were studied. Perovskite characteristics were examined using UV-Visible spectroscopy and photoluminescene spectroscopy, SEM, and XRD. Photovoltaic characterization was performed under 1 Sun AM 1.5 G simulated sunlight using Keithley 2400.

10:20 AM

(ICACC-FS2-014-2016) Pulsed laser deposition of metal-insulator transition materials for energy and photonic devices (Invited)

M. Chaker*[1]; N. Emond[1]; B. Torriss[1]; 1. INRS, Canada

Vanadium oxide (VO_2) and samarium nickelate ($SmNiO_3$) display sharp reversible metal-to-insulator transition (MIT) in response to external stimuli, such as temperature or electric field. This transition is accompanied by a dramatic variation of both electrical resistivity and infrared reflectivity. In this presentation, we overview our recent studies on the synthesis of VO_2 and $SmNiO_3$ thin films by Pulsed Laser Deposition (PLD) and the exploitation of their MIT for various applications. First, we report on the design and fabrication of a new type of high-performance variable-emittance smart coating based on VO_2 thin films. This smart coating passively switches from low emittance at low temperature to high emittance at high temperature to operate as a smart radiator device for miniaturized satellites. Second, we present a multilayer structure based on tungsten-doped VO_2 films that displays a combination of excellent characteristics (i.e. large thermal coefficient of resistivity, low resistivity and small hysteresis width). These properties are suitable for the development of high-performance uncooled microbolometers. Finally, epitaxial $SmNiO_3$ films with good MIT characteristics in the mid-infrared region were successfully grown on $SrTiO_3$ using PLD.

10:50 AM

(ICACC-FS2-015-2016) Carbon-based composite materials with applications in batteries and fuel cells (Invited)

D. H. Chua*[1]; 1. National University of Singapore, Singapore

Carbon materials have attracted much attention due to their unique properties, ranging from low dimensional effects, good structural integrity, high electrical and thermal conductivity, and chemical stability. Increasingly, carbon-based materials have progressed from thin films to the nanoscale dimensioned carbon nanotubes and graphene. In this talk, we will show that we can engineer various 1D and 2D carbon-based materials for direct applications on Li-batteries and PEM fuel cells. We will further show and compare the fuel cell properties when other 2D materials are integrated with the carbon-based materials. A series of in-situ tests are also performed which includes accelerated degradation test and electrochemical

impedance spectroscopy to validate the effectiveness and robustness of these materials. We will mention briefly other applications for these carbon based materials.

11:20 AM

(ICACC-FS2-016-2016) Investigation of the electronic structure of interface junctions in CdTe based thin film solar cells grown by pulsed laser deposition

S. Chandra*[3]; R. Nechache[1]; C. Harnagea[3]; F. Rosei[2]; 1. Ecole de Technologie Superieure, Canada; 2. INRS, Canada; 3. Institut National de la Recherche Scientifique, Canada

CdTe based solar cells have been extensively investigated because of their suitable band gap alignments, high conversion efficiency, ease of fabrication and stability leading to its commercialization. We have investigated the role of the (n-type) window layer on conversion efficiency by changing the Zn doping concentration in $Cd_{(1-x)}Zn_xS$. The interfacial electronic properties of the p-n junctions were investigated using a combination of Kelvin probe force microscopy (KPFM) and scanning electron microscopy to probe the effect of temperature annealing on the band alignment by the direct measurement of contact potential difference across the cross section of a complete cell. The junction activation effect by chloride treatment and grain boundary passivation effects were also studied at the nanoscale. Our understanding of the interfacial properties elucidates the working mechanism of such solar cells, and provides the scope for optimizing material and growth conditions for higher conversion efficiencies.

11:40 AM

(ICACC-FS2-017-2016) Effect of processing on the structure and properties of glass-ceramics materials for photonics applications

G. Gorni[2]; J. Velázquez[2]; Y. Castro[2]; A. Durán[2]; R. Balda[1]; M. Pascual*[2]; 1. Superior School of Engineering, Spain; 2. Institute of Ceramics and Glass, CSIC, Spain

Transparent oxyfluoride nano-glass-ceramics doped with RE ions are very interesting materials for photonics applications. They combine the good mechanical, chemical and thermal stability of oxide glasses with the fluoride crystals, very good host for RE ions and suitable for optical properties due to their low phonon energies. The processing route is a key issue for a suitable preparation of these materials.The typical glass processing method is the melting–quenching (MQ) but the sol-gel (SG) method is a promising alternative. MQ requires high melting temperatures with a limitation in the fluorine content. However, bulk materials and fibers can be easily obtained. SG is a cheap and low-temperature technique that allows a better control of composition and doping level. SG materials have high homogeneity and purity. Thin film can be easily obtained but bulk materials are difficult to prepare and fiber. Oxyfluoride glass-ceramics with LaF_3 nanocrystals obtained by MQ and SG will be presented as study example of the processing parameters. The crystallization process has been described using DTA taking into account the effect of the dopants. The structural properties have been studied by XRD, SAXS, HR-TEM, EXAFS and Raman Spectroscopy. Finally, the relation between processing-structure-optical properties of these materials is discussed.

40th Jubilee Symposium: Engineered Ceramics: Current Status and Future Prospects

Engineered Ceramics III

Room: Coquina Salon C

Session Chairs: Soshu Kirihara, Osaka University; Dileep Singh, Argonne National Lab

1:30 PM

(ICACC-JUB-014-2016) Silicon Nitride Ceramics (Invited)

S. Hampshire*[1]; 1. University of Limerick, Ireland

This presentation reviews one of the important engineering ceramics developed over the last forty years, silicon nitride and the related SiAlONs, a "family" of structural materials with high flexural strength, good fracture toughness, excellent creep resistance and wear resistance. Microstructure-property relationships are outlined. Oxide sintering additives, Y_2O_3 and Al_2O_3, react with silicon nitride and silica present on its particle surfaces to form an oxynitride liquid which promotes liquid phase sintering and densification by solution-diffusion-precipitation. The liquid cools to form an intergranular glass. The amount and additive ratio in silicon nitride determine glass chemistry which affects mechanical properties such as fracture toughness and strength. Thermo-mechanical properties of bulk oxynitride glasses increase with increasing nitrogen content as a result of substitution of 2-coordinated oxygen by 3-coordinated nitrogen allowing extra cross-linking of the glass network. Properties are also dependent on Y:Al ratio. Thermal expansion mismatch between the intergranular glass and the silicon nitride causes residual stresses which can be calculated from bulk Y-Si-Al-O-N glass properties (E, Tg and α). The tensile residual stresses in the glass phase increase with increasing Y:Al ratio and this correlates with increasing fracture toughness of the ceramic as a result of easier debonding at the glass/β-Si_3N_4 interface.

2:00 PM

(ICACC-JUB-015-2016) Design Silicon Nitride Ceramics with Reliability and Functionality (Invited)

H. Lin*[1]; 1. Guangdong University of Technology, China

Silicon nitride (Si_3N_4) ceramics with in-situ reinforced microstructure offer many advantages for applications as structural and functional components due to its combined properties of good mechanical strength and toughness, wear resistance, and thermal conductivity. Thus, Si_3N_4 ceramics have been designed and employed for hot-section components in turbine engines, bearing balls for high speed and precision bearing systems, and power electronic substrates. It is well known that the microstructure and thus mechanical and physical properties of Si_3N_4 ceramics could be engineered via a careful selection of oxide additives and processing conditions. The presence of glassy films at two-grain junctions would also impact the interfacial binding energy and thus debonding of reinforcing beta grains from the fine grain matrix, which ultimately determine the fracture toughness behavior of Si_3N_4 ceramics. The tailoring of the additive composition plus the microstructure is now recognized as the critical factors in obtaining both high fracture toughness and high fracture strength. This paper will provide an overview of the microstructural engineering via control of composition and processing for silicon nitride ceramics aiming for specific industrial applications components and environments.

2:30 PM

(ICACC-JUB-016-2016) Microstructural Evolution and Mechanical/Thermal Properties of Silicon Nitride Ceramics (Invited)

T. Ohji*[1]; K. Hirao[1]; 1. National Institute of Advanced Industrial Science and Technology (AIST), Japan

During the past forty years, there has been tremendous progress in mechanical and thermal performances of silicon nitride ceramics, which is one of the most important and widely used engineering ceramics, through well-organized control of the microstructure elements. For examples, both high strength and high fracture toughness can be attained by optimizing the size, morphology and alignment of the grains simultaneously, while these two properties had been believed in antagonistic relationship. In addition, adjusting the chemical phases of grain boundaries leads to further significant improvements in the fracture toughness and high-temperature properties. Even in the porous materials, markedly high mechanical properties can be realized by carefully tailoring the porous microstructure. Furthermore, significantly high thermal conductivity as well as high fracture toughness can be achieved through controlling grain size/morphology and oxygen impurities.

3:20 PM

(ICACC-JUB-017-2016) Additive Manufacturing of Silicon Carbide-Based Ceramic Matrix Composites: Technical Challenges and Opportunities (Invited)

M. Singh*[1]; M. C. Halbig[2]; J. E. Grady[2]; 1. Ohio Aerospace Institute, USA; 2. NASA Glenn Research Center, USA

Advanced SiC-based ceramic matrix composites offer significant contributions toward reducing fuel burn and emissions by enabling high overall pressure ratio (OPR) of gas turbine engines and reducing or eliminating cooling air in the hot-section components, such as shrouds, combustor liners, vanes, and blades. Additive manufacturing (AM), which allows high value, custom designed parts layer by layer, has been demonstrated for metals and polymer matrix composites. However, there has been limited activity on additive manufacturing of ceramic matrix composites (CMCs). In this presentation, laminated object manufacturing (LOM), binder jet process, and 3-D printing approaches for developing ceramic composite materials are presented. For the laminated object manufacturing (LOM), fiber prepreg laminates were cut into shape with a laser and stacked to form the desired part followed by high temperature heat treatments. For the binder jet, processing optimization was pursued through silicon carbide powder blending, infiltration with and without SiC nano powder loading, and integration of fibers into the powder bed. Scanning electron microscopy was conducted along with XRD, TGA, and mechanical testing. Various technical challenges and opportunities for additive manufacturing of ceramics and CMCs will be presented.

3:50 PM

(ICACC-JUB-018-2016) Joining and Integration of Silicon Carbide-Based Materials for High Temperature Applications (Invited)

M. C. Halbig*[1]; M. Singh[2]; 1. NASA Glenn Research Center, USA; 2. Ohio Aerospace Institute, USA

Advanced joining and integration technologies of silicon carbide-based ceramics and ceramic matrix composites are enabling for their implementation into wide scale aerospace and ground-based applications. The robust joining and integration technologies allow for large and complex shapes to be fabricated and integrated with the larger system. Potential aerospace applications include lean-direct fuel injectors, thermal actuators, turbine vanes, blades, shrouds, combustor liners and other hot section components. Ground based applications include components for energy and environmental systems. Performance requirements and processing challenges are identified for the successful implementation different joining technologies. An overview will be provided of several joining approaches which have been developed for high temperature applications. In addition, various characterization approaches were pursued to provide an understanding of the processing-microstructure-property relationships. Microstructural analysis of the joint interfaces was conducted using optical, scanning electron, and transmission electron microscopy to identify phases and evaluate the bond quality. Mechanical testing results will be presented along with the need for new standardized test methods. The critical need for tailoring interlayer compositions for optimum joint properties will also be highlighted.

4:20 PM

(ICACC-JUB-019-2016) Stereolithographic Additive Manufacturing of Ceramic Components with Functionally Modulated Geometries (Invited)

S. Kirihara*[1]; 1. Osaka University, Japan

Stereolithographic additive manufacturing has been developed to create ceramic components with functionally modulated geometries of periodic, self-similar, graded and fluctuated patterns for effective control of energy and material flows. Ceramic nanoparticles were dispersed into photo sensitive liquid resin, and the paste material was spread on a glass plate by a mechanical knife edge. Ultra violet laser beam was scanned on the top surface to create a solid cross section, and geometric structure was formed by layer stacking. The composite precursor was dewaxed and sintered to obtain a full ceramic component. Alumina photonic crystals with periodically arranged micro lattices were fabricated to diffract electromagnetic waves. Air cavities introduced into the crystals concentrate wave energies in terahertz frequency. The wave vibration can be harmonized with molecular vibrations of protein or saccharides. Yttria stabilized zirconia electrodes with ordered micro diagonals and pores were formed as solid electrolyte anodes of solid oxide fuel cell. The coordination number variations were processed to increase the specific surface areas of the cell electrode. Hydroxyapatite biological scaffolds with graded structure were created to control the distributions of micro pores. Aspect ratios of micro lattices were modulated continuously to modulate biological fluid streamlines.

S1: Mechanical Behavior and Performance of Ceramics & Composites

Processing - Microstructure - Mechanical Properties Correlation I

Room: Coquina Salon D

Session Chairs: Kevin Ewsuk, Sandia National Laboratories; Servet Turan, Anadolu University

1:30 PM

(ICACC-S1-021-2016) Strength improvements in clay-based ceramic reinforced with discontinuous basalt fiber

G. P. Kutyla[1]; P. F. Keane[1]; T. A. Carlson[2]; C. P. Marsh[2]; W. M. Kriven*[1]; 1. University of Illinois at Urbana-Champaign, USA; 2. US Army Engineer Research and Development Center, USA

Clay-based ceramics are used in a wide variety of applications and could benefit from the addition of a reinforcing fiber. The clay used was based on a powder mixture of 45% Kentucky ball clay, 40% Talc, and 15% Georgia kaolin. This powder was mixed with 28% of its own weight of 0.1 M sodium carbonate solution (for formability) and up to 30% of its weight of discontinuous basalt fibers. The basalt fibers used had a 12 μm diameter and were either chopped (6 mm long) or milled (~100 μm long). The mixture was hand rolled into cylinders which were compressed into 1x1x10 cm square-cross-section bars using plastic molds. Bars were fired to temperatures ranging from 850 to 1250 °C for 2 hours. The addition of the chopped basalt

caused warping after firing, and so was not studied further. It was concluded that chopped fibers should only be used if their orientation can be controlled. The addition of milled basalt fibers improved strength at all temperatures (up to about 40% higher strength) except for the 1250 °C firing where the basalt-reinforced samples melted. With an 1050 °C firing temperature, there was a clear distinction between fiber and matrix when viewed with SEM/EDS imaging, but this was not true for the 1150 °C fired samples. This work shows that milled basalt fibers may be used as a potentially cost-effective reinforcement for clay-based ceramics.

1:50 PM

(ICACC-S1-022-2016) Pressureless Infiltration of Al_2O_3 Preform Containing Aligned Two-Dimensional Channels with Al-Mg-Si Alloy

E. Hammel*[1]; O. Okoli[1]; 1. Florida State University, USA

Pressureless infiltration methods have been investigated in order to avoid the costs and complexities associated with pressure or vacuum assisted infiltration during the fabrication of ceramic-metal composites. The working principle behind the pressureless infiltration method is the generation of positive capillary pressure as a molten metal encounters a ceramic preform. Several important parameters need to be considered during this process including the magnesium content in the alloy, purity of the nitrogenous atmosphere, isothermal soak duration and temperature, and the ceramic preform itself. The majority of studies utilizing a pressureless infiltration process involve ceramic preforms that are of the form of packed particulate beds, fibers, foams, or other replicate templates. In this study, the focus will be on the fabrication of ceramic-matrix composite through the use of a tailorable ceramic preform. The ceramic preform will be a dense alumina body containing strategically placed channels that are exposed to the surface. A pressureless infiltration process will be used to infiltrate these channels. In this way, the reinforcement architecture can be tailored in terms of the size, shape, and orientation in order to produce the properties that befit the desired application.

2:10 PM

(ICACC-S1-023-2016) Comparison Of Dynamic Strength and Failure Mechanisms Between Boron Carbides Processed by Hot Pressing and Spark Plasma Sintering Techniques

A. K. Robinson*[1]; L. Farbaniec[1]; T. L. Munhollon[2]; K. Xie[1]; M. Shaeffer[1]; R. A. Haber[2]; K. Ramesh[1]; 1. Johns Hopkins University, USA; 2. Rutgers University, USA

Most of the processing routes for production of armor-grade boron carbide materials require processing aids for better densification. These various processing aids cause microstructural defects with different characteristics. In this work we characterize these processing-induced defects and investigate their influence on the dynamic compressive response of the material. Experiments were conducted on two groups of samples. One group is produced commercially using hot pressing and the second group is produced in smaller batches using a spark plasma sintering technique. The heterogeneity in microstructures is examined by SEM/EDS/EBSD and TEM techniques. An optical microscopy technique in conjunction with image processing is used to statistically describe the defect populations. After characterization of the materials, the failure mechanisms are investigated by loading smallsize cubic specimens in a modified compression Kolsky Bar at strain rates of $10^2 - 10^3\ s^{-1}$. A highspeed camera is used to visualize the failure process. To study the strain-rate sensitivity, the mechanical behavior is also evaluated in the quasi-static regime ($\sim 10^{-3}\ s^{-1}$). The damage evolution, differences in failure mechanisms, and the influence of geometrical characteristics of processing-induced defects on the failure process are discussed.

2:30 PM

(ICACC-S1-024-2016) Spark Plasma Sintered $4YZrO_2$-$La_2Zr_2O_7$ composites for thermal barrier applications in aeronautics

G. Chevallier*[1]; F. Aubert[1]; Y. Beynet[1]; R. Epherre[1]; A. Weibel[1]; C. Estournes[1]; 1. CIRIMAT, France

The development of new generation thermal barriers combining both high thermal stability and high mechanical properties is required to improve the efficiency of gas turbine aircraft engines. In the present work, $4YZrO_2$-$La_2Zr_2O_7$ composite powders (10-40 wt.% $4YZrO_2$) were prepared by mixing two submicronic commercial powders (4 mol.% yttria-stabilized ZrO_2, 150 nm and $La_2Zr_2O_7$, 300 nm). The specimens were fully densified by SPS at 1400°C and 100 MPa. All the specimens present a homogenous dispersion of $4YZrO_2$ and a fine microstructure. Mechanical properties increase with the $4YZrO_2$ content and the best mechanical properties (Hv = 14.6 GPa, s_f = 392 MPa; K_{Ic} = 4.1 MPa.$m^{1/2}$) are obtained for 40 wt.% $4YZrO_2$. To the best of our knowledge, these values are the highest reported up to now for such composites. These results are important guidelines for further developments of thermal barriers.

2:50 PM

(ICACC-S1-025-2016) Synthesis of high quality TiB_2 from carbon coated titanium dioxide precursor and its presureless sintering with cobalt

Z. Fu*[1]; R. Koc[1]; 1. Southern Illinois University Carbondale, USA

Titanium diboride (TiB_2) powders were successfully synthesized from carbon coated titanium dioxide (TiO_2) precursor mixing with B_4C at 1500°C for 2 hours in flowing argon at 1L/min. X-ray diffraction (XRD), transmission electron microscope (TEM), Brunauer-Emmett-Teller (BET) surface area analyzer and combustion carbon analyzer were used to characterize the produced powders. TiB_2 powders synthesized from precursor mixing with B_4C combine the advantages of single phase, high purity, fine particle size, regular shape, loos agglomeration and high surface area. Densifications were conducted for produced TiB_2 powders with cobalt content as 3 wt. %, 10 wt. % and 20 wt. % at 1500°C in argon atmosphere through presureless sintering. All samples reached higher than 98% theoretical density (TD) which would also show excellent mechanical properties including Young's modulus, Vickers hardness and fracture toughness. This is lowest temperature (lower by at least 200°C) have been reported at which TiB_2 sintered with Co and reached nearly full TD (> 98%) through presureless sintering.

3:30 PM

(ICACC-S1-026-2016) Alternative Metallic Binder Systems for High Performance Cermets

K. P. Plucknett*[1]; 1. Dalhousie University, Canada

Ceramic-metal composites, or cermets, combine the favourable properties of both constituents and are widely used in demanding tribological and corrosive environments. The most commonly used cermet system, in both bulk and coating form, is based on tungsten carbide, typically with a cobalt binder (i.e. WC-Co). However, WC-Co suffers from a number of performance limitations, including high mass, poor corrosion resistance and severe property degradation at elevated temperatures. In the present work, two new cermet systems are discussed, utilising either stainless steels or ductile nickel aluminide alloys as the binder. To minimise component mass, the two binders have been paired with either titanium carbide (TiC) or carbonitride (Ti(C,N)) ceramic phases. These materials have been assessed in terms of their fundamental mechanical behavior, sliding wear response and aqueous corrosion resistance. It is demonstrated that the new cermet systems can offer comparable sliding wear resistance to WC-Co, combined with corrosion rates that are two to three orders of magnitude lower, while being roughly half the mass. The relative performance characteristics of these new materials will be reviewed in comparison with a range of current commercial cermet systems.

3:50 PM

(ICACC-S1-027-2016) Synthesis of TiC-TiB_2 composite powders from carbon coated TiO_2 precursor with B_4C and their hot pressing properties

Z. Fu*[1]; R. Koc[1]; 1. Southern Illinois University Carbondale, USA

Submicron TiC-TiB_2 composite powders were synthesized by carbo/borothermal reduction from carbon coated precursor. Traditional mixtures were also investigated as comparison. Precursors and traditional mixtures were reacted from 1100 to 1500°C for 2 hours with argon flowing at 1L/min. Phase evolution, and surface areas were characterized by X-ray diffraction (XRD), transmission electron microscope (TEM) and Brunauer-Emmett-Teller (BET) surface area analyzer, respectively. Products synthesized from precursor had pure single phases of TiC and TiB2, fine particle size, narrow size distribution, regular shape, loose agglomeration, and high surface area. Coating precursor method had lowered reaction temperature by about 100°C. Composites with different content of TiB_2, which were controlled by changing of ratio between TiO_2, C and B_4C, can also be synthesized. Sintering properties of produced composite powders were examined by hot press. Composites reached high relative density at 1700°C under pressure of 30MPa. This is the lowest temperature at which TiC-TiB_2 composites can be sintered and reach high relative density in the literature. Mechanical and thermal properties of produced samples will also be reported.

4:10 PM

(ICACC-S1-028-2016) Laser Shock Peening of Structural Ceramics: Microstructural Evolution and Mechanical Properties

B. Cui*[1]; F. Wang[1]; C. Zhang[1]; Y. Lu[1]; M. Nastasi[1]; 1. University of Nebraska–Lincoln, USA

Applications of structural ceramics are limited by their intrinsic brittleness. The objective of this research is to improve mechanical properties of structural ceramics by laser shock peening (LSP). LSP is a novel surface-strengthening process that can prevent most failures in metallic components by inducing significant compressive stresses. However, LSP of ceramics has been challenging, particularly because of the damage induced by laser-driven shock waves in these brittle materials. It is found that when alumina are annealed at controlled temperatures and times after LSP, most of compressive stresses can still be retained while the shock wave damage is greatly reduced. The microstructural evolution in the LSP and annealing processes will be studied using focused ion beam and transmission electron microscopy. The change of mechanical properties such as the fracture toughness will be evaluated by Vickers indentation and nanoindentation methods. The microstructure-property relationship in LSP of alumina ceramics will be revealed.

4:30 PM

(ICACC-S1-029-2016) Thermal conductivity and laser processing of AlN-GPLs composites

D. Kata*[1]; P. Rutkowski[1]; J. Lis[1]; 1. AGH University of Science and Technology, Poland

Aluminum nitride is considered as versatile but challenging material for structural and functional application because very high thermal conductivity and piezoelectric feature. The AlN is applied for sensors and heat exchanger to improve their sensitivity and efficiency. The new AlN-graphene(GPLs) were prepared by hot-pressing to demonstrate anisotropic features and to find innovative applications for these polycrystals. More than 50% of anisotropy in thermal conductivity, elastic properties was obtained. The structures, morphologies, and microstructures of the hybrids were examined by X-ray diffraction, SEM and TEM methods. It is showed that graphene plays a crucial role in anisotropy and influences on microstructure. The results were correlated with thermal conductivity of the samples carried out by the laser pulse method - LFA 427 apparatus. The possibility of controlling anisotropy by graphene content and sintering conditions was showed. A fundamental interaction of laser beam and AlN-graphene(GPLs) polycrystals was examined. Thus the welding process was performed to shape different forms of heat exchanger or sensors. Laser processing parameters, microstructure, and features of joined layer, are illustrated. The different aspects of the ceramic laser processing from fundamental mechanism up to engineering applicability is discussed.

4:50 PM

(ICACC-S1-030-2016) Investigation on microstructural and mechanical properties of ceramic–reinforced aluminum matrix composites prepared by microwave sintering approach

P. R. Matli*[1]; 1. Qatar University, Qatar

Novel Aluminum metal matrix composite (AMMC's) materials were produced by reinforcing pure Al with varying volume fractions of Ni–based amorphous alloy particles (10, 15 and 20 wt%) using microwave rapid sintering approach, and subsequent hot extrusion. Microwave rapid sintering involves the heating of aluminum compacts using both microwave energy and radiant heating. Significant savings in time and energy can be achieved using the fabrication methodology. The effect of different amounts of $Ni_{50}Nb_{50}$ on the microstructure and mechanical properties of aluminum matrix was examined. The composites showed significant improvement in hardness (increment up to 130%) and compressive strength (~85% increases at 10 wt%). Comparison of mechanical properties of the developed composites with those of conventional Al-composites having ceramic/metallic reinforcements, highlight the effectiveness of using amorphous particles as promising reinforcement materials. Microwave sintered Al–MMCs are replacing conventional materials in applications such as brake rotors/drums and pushrods in automobile sectors.

S2: Advanced Ceramic Coatings for Structural, Environmental, and Functional Applications

CMAS-related TBC Degradation and Mitigation Stragegies II

Room: Coquina Salon H

Session Chair: Peter Mechnich, German Aerospace Center (DLR)

1:30 PM

(ICACC-S2-019-2016) Low Thermal Conductivity Gadolinium Zirconate/YSZ Double-layer Coatings Made by Solution Precursor Plasma Spray and Tested for CMAS Resistance

C. Jiang*[1]; E. Jordan[2]; A. Harris[2]; M. Gell[2]; 1. HiFunda LLC, USA; 2. University of Connecticut, USA

The low thermal conductivity and good CMAS resistance of gadolinium zirconate (GZO) are well documented, yet the high cost as well as low fracture toughness imposes a challenge. A widely-adopted approach for advance TBC topcoat design then is to use a double-layer structure, in which the higher temperature limit and better CMAS resistance of the GZO top layer ensure an enhanced high-temperature capability, while an inner layer of YSZ saves the cost and also avoids the damaging interaction between GZO and the thermally-grown oxide (TGO). In this study, both the GZO top layer and the low thermal conductivity (~0.63 W/mK) YSZ coatings with engineered porosity were deposited using the solution precursor plasma spray (SPPS) process, and were subsequently characterized with cyclic furnace tests, CMAS resistance tests and steam environment tests. In the cyclic furnace and high temperature steam tests, the through-thickness vertical cracks and the strong interface between both layers provided remarkable benefits to microstructural stability, while in CMAS resistance tests the GZO top layer was observed to be effective when CMAS was all put at once at the start

of furnace cycling, but appeared no better than single-layer YSZ in tests where CMAS was applied accumulatively in every cycle.

1:50 PM

(ICACC-S2-020-2016) Comparative study of the resistance of Yttrium Aluminum Garnet and Yttria Stabilized Zirconia coatings to calcium magnesium alumino- silicate

R. Kumar*[1]; E. Jordan[1]; M. Gell[1]; 1. University of Connecticut, USA

It is well known that calcium magnesium alumino- silicate (CMAS) that is ingested into gas turbines degrades thermal barrier coatings (TBCs) especially for the most widely used material; Yttria Stabilized Zirconia (YSZ). In the present work we examine the behavior of Yttrium Aluminum Garnet (YAG) as an alternative TBC material. We have previously shown that YAG with a specific microstructure (stress relieving vertical cracks) has good cyclic furnace test performance, erosion performance and competitive thermal conductivity besides having low density and high temperature stability. CMAS interaction studies have been done by making composite pellets of YAG and YSZ powders and CMAS of two compositions. These pellets after being subjected to temperatures from 1100-1500°C were characterized by X-ray Diffraction, SEM and EDS. The results show while YAG is almost inert to CMAS, YSZ shows extensive phase changes. To simulate the continuous accumulation of CMAS expected in service, a furnace test in which a diluted aqueous solution of CMAS was applied after each cycle in a cyclic furnace test. In addition, cyclic furnace tests were run in which 10 mg/cm^2 of CMAS was applied and then the samples were cycled to failure. In both types of tests YAG outperformed YSZ.

2:10 PM

(ICACC-S2-021-2016) Calcium-magnesium aluminosilicate (CMAS) interactions with advanced environmental barrier coating material

V. L. Wiesner*[1]; N. Bansal[1]; 1. NASA Glenn Research Center, USA

Development of robust environmental barrier coatings (EBCs) used to protect silicon-based ceramic matrix composite (CMC) components in next-generation air-breathing turbine engines is threatened by the ingestion of siliceous materials, like sand, dust, and volcanic ash, by aircraft turbine engines. At elevated aircraft operating temperatures (>1200°C), the ingested particulates melt, resulting in glassy deposits with compositions corresponding to calcium-magnesium aluminosilicate (CMAS). A CMAS glass was used to evaluate the high-temperature interactions between CMAS and yttrium disilicate ($Y_2Si_2O_7$), a leading EBC material. Pellets of CMAS glass and of $Y_2Si_2O_7$ were heated in air at temperatures ranging from 1200°C to 1500°C. Materials characterization techniques, including X-ray diffraction, scanning electron microscopy and X-ray energy-dispersive spectroscopy, were used to evaluate the resulting phase compositions and microstructure of reacted CMAS/EBC specimens.

2:30 PM

(ICACC-S2-022-2016) Gd_2O_3 solubility in a molten CAS: comparison between Gd-apatite precipitation kinetics and Nd-apatite as well as $Ca_3Y_2(Si_3O_9)_2$ formation kinetics

M. Vidal-Setif*[1]; F. Perrudin[1]; C. Rio[1]; O. Lavigne[1]; C. Petitjean[2]; P. Panteix[2]; M. Vilasi[2]; 1. ONERA, France; 2. IJL-UMR 7198, France

This work context is high temperature TBC degradation by molten CMAS. It aims at helping in the selection of the most effective rare earth oxide RE_2O_3 which, combined with zirconia, will limit CMAS infiltration in TBC porous microstructure by rapid formation of an apatite phase $RE_8Ca_2(SiO_4)_6O_2$ and a fluorite ZrO_2 phase containing RE and Ca in solid solution. Kinetic and thermodynamic study related to 1200°C solubility of Gd_2O_3 in a synthetic CAS melt is carried out using a standard procedure developed at the Institut Jean Lamour. The results are compared with those previously obtained with Nd_2O_3 and Y_2O_3. At the same time transport parameters of dissolved cations in CAS melt are investigated by evaluating cation diffusion coefficients. The association of SEM observations, EDS or EPMA analysis and X-ray diffraction reveals that Gd-apatite phase forms immediately after Gd_2O_3 dissolution in CAS melt, leading to anorthite precipitation in CAS. After 60min, $Ca_3Gd_2(Si_3O_9)_2$ phase is also observed disappearing after 4h. Gd-apatite precipitation is slightly slower than Nd-apatite one but quicker than $Ca_3Y_2(Si_3O_9)_2$ formation. Gd^{3+} solubility limit in CAS is about 1.3 at. %, close to Nd^{3+} one (1.4at.%) and much higher than Y^{3+}one (0.7at.%). Rare earth cations diffusion coefficients are in the same order of magnitude 10^{-13} m^2/s.

2:50 PM

(ICACC-S2-023-2016) Tailoring the EB-PVD columnar microstructure to mitigate the infiltration of CMAS in 7YSZ TBCs

R. Naraparaju*[1]; U. Schulz[1]; P. Mechnich[1]; 1. German Aerospace Center (DLR), Germany

The durability and the functionality of 7YSZ TBC is severely affected by the infiltration of molten deposits of CMAS. It infiltrates into the porous TBC at high temperatures and stiffens the TBC which ultimately loses its strain tolerance and gets delaminated. EB-PVD technique is used to coat TBCs on rotating parts such as blades and on stationary parts such as vanes. They exhibit a columnar microstructure with gaps in between them. The CMAS infiltration depth is governed by several temperature dependent factors such as viscosity, surface tension of the melt, operation temperature and shape of the columnar gaps. Variation of EB-PVD process parameters allows altering the resulting columnar morphology and porosity of the coating. In this paper, the effect of morphology and density of EB-PVD 7YSZ columns on the CMAS infiltration behavior was studied in detail. Two different TBC pore geometries were created by varying the deposition parameters and CMAS infiltration experiments were carried out at 1250°C and 1225°C for different time intervals. At 1250°C, where the viscosity of CMAS is low, it was found that the shape factor of columns has a very low influence on the overall infiltration behavior. At 1225°C (relatively high viscous regime of CMAS), the 7YSZ coating with more feathery features has proved to be CMAS resistant at least by a factor of 2 than its less feathery counterpart.

Advanced Multifunctional Coatings

Room: Coquina Salon H

Session Chair: Douglas Wolfe, Pennsylvania State University

3:30 PM

(ICACC-S2-024-2016) Zirconia Toughened Alumina Ceramic Coating by Thermal Nanoparticle Spraying

S. Kirihara*[1]; 1. Osaka University, Japan

Thermal Nanoparticle spraying can create ceramic layers with nanometer sized composite structures. As the raw material, alumina and zirconia nanoparticles of 200 and 500 nm in average diameter were dispersed into liquid acrylic resins at from 20 and 40 % in volume contents. Obtained high viscosity slurries were blown by compressed air jet of 2 atm in pressure as micro mists of 10 μm in droplet size into acetylene and oxygen gases flame for a coaxial direction. On a SUS-304 stainless steel substrate of 50×50×5 mm in size placed at 100 mm in distance from the flame gun top, the zirconia toughened alumina layers of 300 μm in thickness were formed at 50 μm/s in deposition late. Structural transitions of ceramics composite according to the nanoparticles dispersing ratios in slurry pastes were observed by digital optical and scanning electron microscopes. Vickers hardness of the coated layers was measured to optimize the gas flame spraying conditions. X-ray diffraction spectroscopy was used to analyze the residual carbon elements introduced by imperfect combustions of the liquid resin.

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(ICACC-S2-025-2016) Mo_xN Supercapcitor Electrode Fabricated by Solution Precursor Plasma Spray Deposition

Y. Gazman[1]; T. W. Coyle*[1]; 1. University of Toronto, Canada

A high surface area molybdenum nitride electrode has been developed by solution precursor plasma spraying (SPPS) which demonstrated high capacitance and stability in high cycle cyclic voltammetry testing. SPPS is a robust and controllable deposition process conducted in air that is capable of depositing a high surface area coating with nanocrystalline grains. Direct deposition of molybdenum nitride is not possible in atmospheric conditions; therefore heat treatmetn in a nitrogen environment was used to convert the as-deposited oxide coating into nitride. The initial electrode capacitance was 62.4 mF cm^{-2} measured at 100 mV sec^{-1}. The capacitance decreased by 28% over the first 5000 cycles, however after an initial surface reaction the capacitance stabilized, decreasing by only 8.5% from the 1000^{th} to the 5000^{th} cycle.

4:10 PM

(ICACC-S2-026-2016) Influence of Yb_2O_3 and Lu_2O_3 doping on microstructural and electrical characteristics of ZnO-Bi_2O_3 based varistor films

D. XU*[1]; K. He[1]; L. Jiao[1]; X. Sun[1]; Y. Yang[1]; Z. Hu[2]; N. Sun[2]; 1. Jiangsu University & Northeastern University, China; 2. Northeastern University, USA

ZnO-Bi_2O_3varistor films doped with two kinds of rare earth element oxides (Lu_2O_3, Yb_2O_3) were prepared by the sol-gel method. The effects of Lu_2O_3/Yb_2O_3 doping on microstructure and electrical characteristics of ZnO-Bi_2O_3varistor films were investigated. All samples show homogenized morphology and improved nonlinear relationship between electric field (*E*) and current density (*I*). Both Yb_2O_3 and Lu_2O_3 doping can decrease the grain size of ZnO-Bi_2O_3varistor films and improve the electrical properties, which have positive effect on the development of ZnO varistor ceramics. Yb_2O_3 doping significantly increases the dielectric constant in low frequency. 0.2 mol% Yb_2O_3 doped ZnO-Bi_2O_3varistor films exhibit the highest nonlinear coefficient (2.5) and lowest leakage current (328μA) among Lu_2O_3/Yb_2O_3 doped ZnO-Bi_2O_3 varistor films. Similarly, 0.1 mol% Lu_2O_3 doping increases the nonlinear coefficient to 1.9 and decrease the leakage current to 462 μA.

4:30 PM

(ICACC-S2-027-2016) Self-Assembled Multifunctional Nanostructured Coatings

H. Fan*[1]; 1. Sandia National Labs, USA

Conventional thin film deposition processes such as chemical vapor deposition or sputtering require severe conditions like high temperature or high vacuum, limiting their applications that need soft/mild processes on delicate substrates (e.g., plastic). Self-assembly techniques are one of the powerful and efficient methods to synthesize nanostructured materials in soft/mild conditions. Using these techniques and combination with top-down fabrication processes, materials with hierarchical feature can be produced with form and function in multiple length scales. Here, I will discuss on our recent progresses in the development of self-assembled processes for optical and electronic coatings at ambient condition. We combine self-assembly, sol-gel process, and nanocrystal colloid chemistry to produce nanostructured multifunctional films. By using functional elements, this technology enables the development of engineered coatings with tunable properties. The new processes not only meet the demanding requirements of conventional film deposition technologies but also expand the functionality of these films to deliver performance on multiple metrics concurrently. Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

4:50 PM

(ICACC-S2-028-2016) Nanotechnology for the development of functional coatings (Invited)

A. S. Khanna*[1]; 1. IIT Bombay, India

Considerable work on nanoscale or nano-modified coatings is going on globally by incorporating nanoparticles in coating formulations that enhance specific properties of coatings. The interesting properties of nanoparticles are basically due to their high surface area to volume ratio. Inorganic-organic hybrid coatings on aluminium and other substrates are being developed in our laboratory via sol-gel route by incorporation of different nano-particles to achieve hydrophobicity and self cleaning effect. HMDZ-FE sol-gel coatings, when applied on non-metallic substrates viz. cotton, wood, paper, concrete and cardboard, resulted in super-hydrophobicity with contact angle >125° and sliding angle <15°. We have also developed Nano-ZnO with flake-like morphology, which lowered discoloration and yellowing effect of epoxies by 40% when exposed to UV light. Incorporation of nano-TiO_2 also improved weathering resistance of epoxy coatings by 18% and taber abrasion by 3 times. Another coating was developed to improve the scratch resistance of automotive coatings by dispersing nano-silica particles. In the field of biomedical science, nano-structured, non-toxic, biodegradable silane based coating was developed to control the dissolution of magnesium alloy to be used as temporary body implant. Antifungal coating was also developed for leather substrates with improved scratch resistance by incorporation of nano-ZnO and nano-Ag particles.

S3: 13th International Symposium on Solid Oxide Fuel Cells (SOFC): Materials, Science and Technology

Oxygen Transport / Structure and Conductivity

Room: Crystal

Session Chairs: Kristen Brosnan, GE Global Research; Nicola Perry, Kyushu University

1:30 PM

(ICACC-S3-018-2016) Surface segregation in ceramic proton conducting niobate electrolytes (Invited)

S. Skinner*[1]; C. Li[1]; 1. Imperial College London, United Kingdom

As an alternative to high temperature oxide ion conducting ceramics proton conducting oxides have received considerable attention, with recent interest focused on the acceptor doped $LaNbO_4$ series of materials. These oxides, while showing attractive proton conducting properties, suffer from low solubility of the acceptor (typically Sr or Ca), which has limited their development. Recently we have investigated the segregation of the cation species in this family of materials in an effort to provide further information on the surface exchange kinetics of these materials. In this work we report our findings obtained from low energy ion scattering studies of the $La_{1-x}Sr_xNbO_{4-d}$ materials, highlighting significant enrichment of Sr in the outermost layers of the ceramics. These findings have implications for the defect chemistry of teh outermost surface and in turn will affect the transport of protons through the ceramics. This also questions the bulk composition of the nominally acceptor doped phases.

2:00 PM

(ICACC-S3-019-2016) Application of Bilayer MIECs in Low Temperature SOFCs

A. Jaiswal*[1]; K. Duncan[1]; A. Hussain[1]; E. D. Wachsman[1]; L. Wang[2]; D. Ding[2]; B. Blackburn[2]; 1. University of Maryland, USA; 2. Redox Power Systems, USA

Mixed ionic electronic conductors (MIECs) are critical components for a number of applications including SOFCs, batteries and permeation membranes. For SOFCs, MIECs are useful as cathode and anode materials ($La_{1-x}Sr_xCo_{1-y}Fe_yO_3$, $Ba_{1-x}Sr_xCo_{1-y}Fe_yO_3$, $La_{1-x}Sr_xCr_{1-y}V_yO_3$). Application of MIECs as electrolytes in SOFCs is limited due to their electronic conductivity, which results in reduced cell open circuit voltage. An interesting approach to alleviate this problem is a combination of two MIECs in a bilayer form like doped-CeO_2/stabilized-Bi_2O_3 and doped-CeO_2/stabilized-ZrO_2. Stabilized-ZrO_2 is a pure ionic conductor under fuel cell conditions, while doped-CeO_2 becomes an n-type conductor under reducing conditions. On the other hand, stabilized-Bi_2O_3 has been reported to be a p-type conductor under oxidizing conditions. A theory has been proposed in the past for a bilayer electrolyte with n-type and p-type MIEC architecture that provides performance enhancements over single-layer MIEC. However, the theory has never been experimentally explored/validated. In this paper, we look at bilayer MIEC electrolytes, based on doped-CeO_2/stabilized-Bi_2O_3, in terms of defect chemistry and transport properties. The analysis will be supported by electrochemical cell test results under fuel cell operating conditions and application of a continuum-level electrochemical model.

2:20 PM

(ICACC-S3-020-2016) Effects of fast elemental interdiffusion in highly defective Gd-doped ceria

V. Esposito*[1]; D. W. Ni[1]; F. Teocoli[1]; D. Marani[1]; D. Z. de Florio[2]; F. C. Fonseca[3]; 1. Technical University of Denmark, Denmark; 2. Universidade Federal do ABC, Brazil; 3. IPEN - CNEN / SP, Brazil

Highly doped ceria presents fast mass diffusion effects at low oxygen partial pressure ($pO_2 < 10^{-12}$ atm) and relatively low temperatures (T > 800 °C). Such effects are promoted by high content of oxygen defects and the chemical reduction of Ce^{4+} cations to Ce^{3+}. In this work, the densification, viscosity and the microstructural evolution of several ceria based compounds and composites are characterized during sintering under low pO_2 and compared with conventional sintering in air. Treatments at controlled pO_2 conditions and temperatures result in unforeseen mass diffusion driven effects with low viscosity flows and high reactivity between the component materials. Polycrystalline ceria-based compounds formed in such tuned chemo-thermal conditions show enhanced electrochemical properties.

2:40 PM

(ICACC-S3-021-2016) Mechanical Damping and Dielectric Relaxation of 8 mol% YSZ

P. Gao*[1]; K. An[2]; D. Yu[3]; E. Lara-Curzio[2]; A. Payzant[2]; G. Brankovic[4]; Z. Brankovic[4]; M. Radovic[1]; 1. Texas A&M University, USA; 2. Oak Ridge National Laboratory, USA; 3. Tianjin University, China; 4. University of Belgrade, Serbia

8 mol% Yittria Stabilized Zirconia (YSZ) with high ionic conductivity is currently essential material for highly-efficient and environmentally-friendly energy technologies, such as solid oxide fuel cells (SOFCs). Mechanical properties, as well as electrochemical properties, of 8YSZ are significant to reliability and durability of SOFCs which work under harsh environment including high temperature, mechanical stress, electrical field, etc. In this study, mechanical behaviors of 8YSZ were studied by cycling compression testing and Dynamic Mechanical Analysis (DMA) in the 25–600°C temperature range. Both testing methods demonstrate significant frequency dependent damping in the 50–500°C temperature range that can be attributed to reorientation of oxygen vacancy-dopant clusters. In-situ neutron diffraction test was used to verify the change of oxygen vacancy complexes under stress. In addition, electro-mechanical coupling tests were carried on in the same temperature range. The coupling between electrical and mechanical behavior of 8YSZ in 25 – 600°C temperature range is discussed in details in this paper.

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(ICACC-S3-022-2016) Elastic Properties and Mechanical Loss of SOFC Materials under Electric Field and Low Oxygen Partial Pressure by Resonant Ultrasound Spectroscopy

A. M. Bolon*[1]; M. Radovic[1]; 1. Texas A&M University, USA

Yttria Stabilized Zirconia and doped cerias are excellent ionic conductors that are commonly used as electrolyte materials for Solid Oxide Fuel Cells. Mechanical loss and activation energy of defect motion was determined using Resonant Ultrasound Spectroscopy (RUS) in the 25 – 600 °C temperature range. Yttria Stabilized Zirconia (YSZ) was tested under an electric field of either 300 V, 500 V or 1000V, while pure ceria was studied at different reduction amounts. The mechanical loss, Q^{-1} was determined as a full with at the half maximum of the resonant peak at different frequencies and temperatures. In addition, shear and elastic moduli were determined with temperature. It was found that the electric field decreases the mechanical loss in YSZ, but does not affect the activation energy of defect motion. In ceria, the reduced ions acted like dopants, resulting in an increase in mechanical damping at low temperatures.

3:40 PM

(ICACC-S3-023-2016) Phase Interaction and distribution in Mixed Ionic Electronic Conducting Ceria-Spinel Composites

M. Ramasamy*[1]; S. Baumann[1]; F. Schulze-Kuppers[1]; A. Opitz[2]; R. Iskander[3]; J. Mayer[3]; M. Bram[1]; O. Guillon[1]; 1. Forschungszentrum Juelich GmbH, Germany; 2. Vienna University of Technology, Austria; 3. Gemeinschaftslabor für Elektronenmikroskopie (GFE), Germany

Mixed Ionic electronic conductors find various applications as SOFC cathodes and oxygen transport membranes. Dual phase composites are a promising class of thermochemical stable materials, in which two ceramic phases are coupled to provide a pure electronic and ionic conducting pathway, respectively. Composites of 20 mol% Gadolinia doped ceria (GDC) and $FeCo_2O_4$ spinel (FCO) are investigated. GDC-FCO 60:40 wt-% ratio showed reasonable oxygen permeation with ionic conductivity as the limiting factor. Spinel content was reduced to as low as 10 wt-% in the composite and their corresponding electrical conductivity and oxygen permeation were measured from which ambipolar conductivity was calculated. GDC-FCO 85:15 wt-% ratio show high ambipolar conductivity comparable to standard single phase $La_{0.58}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$ (LSCF) at 850°C. The Microstructure analysis showed reversible and thus temporary spinel decomposition at sintering temperature as well as phase interaction forming a Gd- and Fe-rich orthorhombic perovskite with traces of Ce and Co. To further investigate the phase interaction and secondary phase formation, Pulsed Layer Deposition of FCO layer (~400nm) over polycrystalline GDC substrate and annealing at varying temperatures and times from 1000 to 1200°C were carried out. These samples were analyzed by XRD, TEM, etc., to understand the interlayer interaction of the phases.

4:00 PM

(ICACC-S3-024-2016) Structural and Conductivity Study of ZrO_2 doped with Yb_2O_3 and Sc_2O_3

V. Shukla[1]; A. Rai[1]; I. L. B.[1]; K. Balani[1]; A. Subramaniam[1]; S. Omar*[1]; 1. Indian Institute of Technology Kanpur, India

High conductivity of ScSZ has attracted significant research attention for the electrolyte application in SOFCs. However, due to high cost of Sc_2O_3 and the presence of complex phase assembly in ScSZ, limits its applicability. At higher Sc_2O_3 content in ZrO_2 (>10 mol.%), it is well known that the highly conductive cubic (*c*) phase

transforms to rhombohedral phases around 600°C, which leads to concomitant drop in conductivity on cooling. The presence of rhombohedral phases, which form due to oxygen vacancy ordering, can be suppressed by adding a slight amount co-dopant oxides. The present work aims to study the structure and conductivity in ScSZ co-doped with Yb_2O_3. Yb_2O_3 addition not only stabilizes the *c*-phase, but also reduces the cost. Powders of $(Yb_2O_3)_x(Sc_2O_3)_{0.12-x}(ZrO_2)_{0.88}$ (x= 0, 0.01, 0.03 & 0.05) compositions were synthesized using solution combustion citric method. The bulk samples were prepared using spark plasma sintering method, which allow fabrication at relatively low temperature and short time. Both XRD and Raman spectroscopy techniques were used to analyze the phases present in bulk samples. On adding Yb_2O_3, both techniques suggest the presence of dominant *c*-phase. We will discuss the conductivity and correlate it with phases observed in these samples. Also, the results of long-term conductivity ageing studies performed on co-doped samples (kept under external dc current) will be presented.

4:20 PM

(ICACC-S3-025-2016) High-Temperature ^{57}Fe Mössbauer Study of Mixed Ionic–Electronic Conducting $(Ba_{0.5}Sr_{0.5})(Co_{0.8}Fe_{0.2})O_{3-\delta}$

P. Gaczynski[1]; A. Harpf[2]; J. Boer[2]; R. Kircheisen[2]; R. Kriegel[2]; K. D. Becker*[1]; 1. TU Braunschweig, Germany; 2. Fraunhofer IKTS, Germany

An in-situ ^{57}Fe Mössbauer study of $(Ba_{0.5}Sr_{0.5})(Co_{0.8}{}^{57}Fe_{0.08}Fe_{0.12})O_{3-\delta}$ (BSCF) has been undertaken in order to obtain insight into local coordination and valence of iron in the material and into the magnetic properties of BSCF. The room-temperature Mössbauer spectra of BSCF were found to depend strongly on oxygen stoichiometry. Their magnetic six-line patterns clearly reflect two magnetically and chemically distinct environmens of iron. In the paramagnetic high-temperature phase (T ≥ 320 °C), the quadrupole-split signals demonstrate that local symmetry at iron sites is lower than cubic. At 700, 850, and 1000°C, the spectra have been collected as a function of oxygen partial pressure, P_{O2} ($5\bullet10^{-5} \le P_{O2}$/bar ≤ 1). Isomer shifts (IS) and quadrupole splittings (QS) were found independent of P_{O2}. Results are discussed in respect to average valence and local coordination of the iron probes. The isothermal decrease of signal intensity observed with increasing oxygen deficit is attributed to changes in the vibrational properties of BSCF.

S4: Armor Ceramics

Developments in Materials and Process Modeling II

Room: Coquina Salon E

Session Chair: Nitin Daphalapurkar, The Johns Hopkins University

1:20 PM

(ICACC-S4-022-2016) The Origin of Brittle Failure of Boron Carbide from First Principles Based Multiscale Simulations

Q. An[1]; W. A. Goddard*[1]; 1. Caltech, USA

Boron carbide (B_4C), the third hardest material in nature, has not been incorporated into commercial applications because it exhibits anomalous failure due to amorphous band formation when subjected to hypervelocity impact. Based on the DFT study, we found that the (01)/< 101> slip system is the most plausible slip system and that this slip leads to a unique plastic deformation in which a boron-carbon bond between neighboring icosahedral clusters breaks to form a carbon lone pair on the C within the icosahedron. Further shear then leads this C to form a new bond with the B in the middle of a CBC chain. This then initiates destruction of this icosahedron, result in the amorphous band. To determine the atomistic origin of this brittle failure, we performed large-scale reactive-molecular-dynamics simulations on shear deformation of B_4C, using the reactive force field. We examined the (0001)/<10 0> slip system related to twinning and the (01)/< 101> slip system related to amorphous band formation. We find that brittle failure in B_4C arises from formation of higher density amorphous bands due to fracture of the icosahedra. This leads to negative pressure and cavitation resulting in crack opening. Thus, to design ductile materials based on B_4C we will propose specific microalloying aimed at promoting shear relaxation through inter-icosahedral slip that avoids icosahedral fracture.

Developments in Materials Characterization, Properties, and Response I

Room: Coquina Salon E

Session Chair: Jerry LaSalvia, Army Research Laboratory

1:40 PM

(ICACC-S4-023-2016) Investigation of the Structural and Physical Properties of Boron Carbide Across the Solubility Range

K. A. Kuwelkar*[1]; K. Behler[2]; V. Domnich[1]; R. A. Haber[1]; 1. Rutgers University, USA; 2. US Army Research Laboratory, USA

Boron carbide is the material of choice for lightweight armor applications due to its extreme hardness, high Young's modulus and low specific weight. The homogeneity range in boron carbide extends from ~9 to ~20 at.% C via substitution of boron atoms for carbons and vice versa, with the solubility limits not uniquely defined in the literature. It was previously established that a strong correlation exists between the B:C ratio and the width and height of the unit cell. But the exact nature of this relationship is debated. Evaluating the stoichiometry from the lattice parameters provides a convenient and non-destructive technique to calculate the final composition of boron carbide. This work focusses on hot pressing boron carbide with controlled stoichiometries across the solubility range. These samples were investigated using X-ray diffraction, chemical analysis and Raman spectroscopy to determine the precise compositions. Lattice parameter measurements from whole pattern fitting and Rietveld refinement were correlated to the respective B:C ratios and an improved calibration curve for future stoichiometric measurements is proposed. Due to the variance of mechanical properties and ballistic response with the stoichiometry, the effect of the stoichiometry on the physical properties was evaluated in conjunction with the structural properties.

2:00 PM

(ICACC-S4-024-2016) Transmission Electron Microscopy of Amorphization Band Structure due to Rate-Dependent Indentation on Micro- and Nano-Grained Boron Carbide

G. Subhash*[1]; P. Jannotti[1]; M. DeVries[1]; J. Pittari[1]; 1. University of Florida, USA

Pressure-induced amorphization (or localized collapse of crystal structure) in boron carbide has been identified as a major weakening mechanism. However, the different structural features that evolve within the amorphized regions has not been investigated in the literature. In this study extensive transmission electron microscopy (TEM) has been conducted in the regions beneath static and dynamic Vickers indentations on 5 micron and 250 nm grain size boron carbide to identify various structural features of the amorphized zones. It was observed that amorphized bands appear sporadically in the indentation-influenced zone as white streaks of different size and shape. TEM lattice images reveal dislocations (missing lattice planes) in narrow amorphous bands of 1-2nm but large irregular shaped bands of several tens of nanometers are also observed in these regions. In general, there was a large discrepancy in the density of amorphized bands between micro-grained and nano-grained B_4C. In large grained B_4C a significantly higher number of amorphized bands were observed compared to nano-grained B4C. The rationale for the observed differences and the rate dependence on the density of amorphous bands is being investigated and will be discussed during the presentation.

2:20 PM

(ICACC-S4-025-2016) Analysis of mechanical properties distribution in a hot-pressed boron carbide

L. Farbaniec[1]; J. D. Hogan[2]; M. Shaeffer[1]; K. Ramesh*[1]; 1. Johns Hopkins University, USA; 2. University of Alberta, Edmonton, Canada

In this work, chemical and mechanical studies were carried out in order to perform micromechanical characterization on a commercially available hot-pressed boron carbide. A combined SEM/EDS/EBSD analysis is used to determine its characteristic chemical composition and crystal structure. Nanoindentation using a Berkovich indenter is performed to determine local mechanical properties of the boron carbide matrix and inclusions of significant size. Subsequently, the fracture behavior is studied in dynamic compression at strain-rates of $10^2 - 10^3\ s^{-1}$. The microstructure characterization showed that boron carbide has a microstructure composed of submicron crystals, preferentially oriented carbon inclusions and others, such AlN and BN. Nanoindentation conducted in three principal directions of the material plate showed lower hardness and elastic moduli of the matrix material in the hot-pressing direction. The elastic moduli of the inclusions was 3–4 times lower as compared to boron carbide grains, and hardness differ by one order of magnitude. Based on the SEM/EDS analysis of post-mortem fragments, it appears that the larger carbon inclusions are key factors contributing to the failure. The influence of microstructure heterogeneity on the mechanical response of the material is discussed.

2:40 PM

(ICACC-S4-026-2016) The effect of grain size on the indentation size effect in boron carbide and silicon carbide

C. Besnard*[1]; N. Al Nasiri[1]; W. Montague[1]; P. Brown[2]; F. Giuliani[1]; L. Vandeperre[1]; 1. Imperial College London, United Kingdom; 2. Defence Science and Technology Laboratory Porton Down, United Kingdom

Light weight ballistic protection materials are attractive and essential for a number of applications. Boron carbide and silicon carbide are good armour ceramics because of their excellent properties: they are among the hardest materials in the world, have a low density, a high melting point and a high Young's modulus. In this paper, the indentation size effect of boron carbide and silicon carbide with different grain size will be investigated. Indentations were made with instrumented nano- and micro Berkovich indenters. It is found that the decay in hardness correlates well with a change in the dependence of unloading compliance with load and the onset of cracking. A back calculation of the hardness from the additional compliance due to cracking gives values consistent with the experiments confirming that the size effect is due to cracking. The grain size was found not to influence the hardness in the nano regime nor did the grain size influence the size effect strongly.

3:20 PM

(ICACC-S4-027-2016) Compression strength of boron carbide

J. Swab*[1]; 1. Army Research Laboratory, USA

Boron carbide is a ceramic under consideration for a number of impact resistant applications. The numerous models and simulation packages that predict impact resistance commonly include compression strength as an input parameter. In many instances compressive strength of a ceramic is inferred from a hardness value. This can be misleading as the hardness of most ceramics varies with the test method and the indentation load. A test methodology using a dumbbell-shaped specimen was designed and successfully evaluated several decades ago. This design ensured that compressive fracture occurred in the reduced gage section and minimized stress concentrations at the specimen fillets. Even though it was shown to be the best manner to determine the compression strength of advanced ceramics few researchers use this specimen due to the specimen machining cost and instead use straight right-circular cylinders or cuboidal specimens. The compressive strength of boron carbide under quasi-static loading as well as the higher rate load available in a split Hopkinson bar test will be determined using this dumbbell-shaped specimen.

3:40 PM

(ICACC-S4-028-2016) TEM Characterization of the Deformed Region Beneath Knoop Indents in Boron Carbide

J. LaSalvia*[1]; S. D. Walck[2]; K. D. Behler[2]; 1. Army Research Laboratory, USA; 2. TKC Global, USA

In an effort to better understand the mechanistic response of polycrystalline boron carbide to large contact stresses, transmission electron microscopy (TEM) methods were used to examine thin cross-sections of the inelastically deformed regions beneath Knoop indents of various loads and load-dwell times. TEM cross-sections were prepared from 0.3, 1, and 2 kgf Knoop indents in a hot-pressed polycrystalline boron carbide. Due to excessive spallation of material surrounding 2 kgf indents, load-dwell times of 15 and 45 s were only used for the 0.3 and 1 kgf indent loads. TEM specimen preparation involved masked-ion milling (MIM), epoxy infiltration, and focused-ion beam (FIB) milling. Details of this method are presented in a companion talk. TEM characterization of the inelastically deformed regions show extensive stress-induced amorphization, microcracking, and macrocracking. Observations clearly show that these deformation mechanisms are related. Stress-induced amorphization predominately occurred in discrete slip bands that were nanoscale in width and microscale in length. Microcracks were observed at slip band intersections, while macrocracking appeared to be a consequence of both mechanisms. The trajectory of slip bands appeared similar to slip lines for blunt-wedge indentation, indicating the importance of shear stress on their formation. Experimental procedures and results will be presented.

4:00 PM

(ICACC-S4-029-2016) Characterizing Armor Ceramic Microstructures Non-Destructively Through Their Electrical Properties

M. Golt*[1]; K. Strawhecker[2]; M. Bratcher[2]; E. Warner[3]; 1. TKC Global Solutions, USA; 2. U.S. Army Research Laboratory, USA; 3. Bowhead Science and Technology, LLC, USA

The electrical properties of a ceramic material, which are directly related to the composition and microstructure, can be characterized rapidly, non-destructively, and through the entire sample volume. Impedance spectroscopy is a method used to measure the frequency dependent electrical properties of materials and provides the ability to isolate and quantify the electrical response of each constituent of the ceramic microstructure (grains, grain boundaries). This presentation will discuss how impedance spectroscopy, which is supported by other electrical characterization methods such as conductive atomic force microscopy (C-AFM) and scanning microwave impedance microscopy (sMIM), can be used to non-destructively evaluate the microstructures of bulk silicon and boron carbides. Particular focus will be placed on what information is obtained from electrical measurements on the grain boundary properties (structure and composition) and the level of doping resulting from the sintering additives.

4:20 PM

(ICACC-S4-030-2016) Comparison of Amorphized Zones Beneath Static and Dynamic Indentations in Boron Carbide

G. Parsard*[1]; G. Subhash[1]; 1. University of Florida, USA

When exposed to high pressure, boron carbide exhibits a localized loss of crystallinity (amorphization) which may cause structural weakening of the material. In this study, the load- and rate-dependence of amorphization in boron carbide is investigated in the quasistatic and dynamic strain rate regimes. To induce amorphization, specimens were indented using a Vickers indenter across a range of loads at quasistatic and dynamic strain rates. Successive

mechanical polishing steps were used to expose subsurface material so that Raman spectroscopy could be performed on each of those surfaces to detect evidence of amorphization. The resulting data was analyzed and assembled into three-dimensional representations of the amorphized volumes beneath the indentations. A dynamic expanding cavity model is being utilized to model the data and extract measures of the growth rate of amorphization. The results indicate that the ratio of the amorphized zone depth to the indentation depth appears to remain constant irrespective of the load for static indentations. Similar results are being compiled for dynamic indentations which will be presented at the conference.

4:40 PM

(ICACC-S4-031-2016) Dynamic Electromechanical Behavior of Ferroelectric Ceramics in the Morphotropic Phase Boundary

L. E. Lamberson*[1]; L. Shannahan[1]; 1. Drexel University, USA

Ferroelectric ceramics are exploited for their large dielectric and piezoelectric response with tunable capacitance in sensors and actuators. These materials are traditionally used in their linear, reversible piezoelectric regime, but in this work we explore their electromechanical performance under dynamic compressive loads. Large mechanical loading induces time-dependent microstructural changes via domain switching, and domain wall motion from the electromechanical coupling (if understood) could be used to create more damage tolerant materials with optimized capacitance for a given applications which include smart armor and triggering devices. This study investigates the dynamic compressive direct longitudinal piezoelectric response of Nb-doped fully dense commercially available zirconate titanate (PZT) in the MPB where elctromechanical properties are maximized. A modified Kolsky bar (split-Hopkinson pressure bar) is used to compress the samples at 10^3 s^{-1} and the in-situ electromechanical response and damage evolution is measured. Results suggest that the domain structure (dipole line-up) can be altered with the application of rapid mechanical loading to fragmentation. These results are discussed in the context of micromechanics predictions utilizing an effective electroelastic moduli as a function of increasing crack density.

5:00 PM

(ICACC-S4-032-2016) The Influence of Impurities on Alumina Microstructure

R. Moshe*[1]; W. D. Kaplan[1]; 1. Technion - Israel Institute of Technology, Israel

The main goal of the present research is to study the influence of impurities, at concentrations below the solubility limit, on the evolving microstructure of alumina. The macroscopic properties of alumina strongly depend on the composition of the powder used for the sintering process, and the microstructure of the sintered body, where dopants and impurities are known to affect sintering rates and grain growth. In this study, the impurity content was varied by doping alumina with different amounts of CaO, below the solubility limit. The amount of cation in the alumina was determined by conducting fully standardized wavelength dispersive spectroscopy (WDS) and the change in grain boundary mobility as a function of the amount of dopant was characterized using scanning electron microscopy. Unlike segregating dopants which reduce grain boundary mobility by solute-drag, CaO increases the rate of grain growth. Possible mechanisms by which CaO increases grain boundary mobility will be discussed.

S6: Advanced Materials and Technologies for Direct Thermal Energy Conversion and Rechargeable Energy Storage

Recent Developments on Lithium Batteries

Room: Tomoka A

Session Chairs: Naoaki Yabuuchi, Tokyo Denki University; Prabeer Barpanda, Indian Institute of Science

1:30 PM

(ICACC-S6-016-2016) Insights into the Structure and Performance of NMC Cathode Materials for Li-Ion Batteries (Invited)

M. Doeff*[1]; 1. Lawrence Berkeley National Lab, USA

NMC cathode materials (Li[NixMnyCoz]O2; x+y+z ≈1) are currently used in some Li-ion batteries. They are particularly attractive for traction applications based on cost and performance considerations. In particular, there is the possibility of raising energy density by charging to higher potentials in these devices, and thereby utilizing more of the theoretical capacities (~280 mAh/g) of the NMCs. Charging to potentials significantly above about 4.3V vs. Li+/Li often results in rapid capacity fading upon cycling due to formation of a cathode-electrolyte interface (CEI) layer and particle surface reconstruction to a rock salt structure, resulting in impedance rise. Surface reconstruction occurs even upon prolonged exposure to electrolytic solutions prior to electrochemical cycling, and may account for the first cycle coulombic inefficiencies that are observed even in NMCs charged to conservative voltage limits. The negative effects of surface reconstruction may be ameliorated by preparing materials with reduced surface reactivities, which result in better first cycle coulombic efficiencies, higher practical capacities and better cycling characteristics. The principles that have been discovered during our studies of these materials can be used to design robust, safe, high capacity NMC materials that can be incorporated into the next generation of electric vehicle batteries.

2:00 PM

(ICACC-S6-017-2016) High Energy Density Li-rich Layered Oxides as Positive Electrode Materials for Li-ion Batteries (Invited)

L. Croguennec*[1]; H. Koga[3]; S. Pajot[2]; C. Genevois[4]; F. Weill[1]; P. Feydi[6]; M. Ménétrier[1]; C. Delmas[1]; L. Simonin[5]; 1. ICMCB-CNRS, France; 2. ICMCB-CNRS and CEA Tech Aquitaine, France; 3. ICMCB-CNRS and Toyota Motor Europe, France; 4. CEMHTI, France; 5. CEA Liten, France; 6. CEA Tech Aquitaine, France

The materials currently attracting most interest as positive electrodes for Lithium-ion batteries are Li and Mn-rich layered oxides as they exhibit outstanding energy densities at an affordable cost. A common feature for all these layered oxides is a high capacity "plateau", observed only at the end of the first charge, once all the transition metal ions are already at the tetravalent state. That behavior has been explained by the reversible participation of oxygen anions in the redox processes, thanks to hybridization between their *p* levels and the *d* levels of the transition metals. We will show that this reaction is reversible within the bulk, occurring without any major structural modification, while at the surface oxidized oxygen ions are lost causing irreversible structural reorganizations at the outer part of the particles, those being at the origin of a continuous voltage decay upon cycling. We will show that we are currently trying to stabilize reversible anion participation to the redox processes through the formation of concentration gradients within the particles (aggregates). The goal here is to promote the formation of Li and Mn-rich layered oxides in the bulk and of stoichiometric layered oxides $LiMO_2$ at the outer part of the aggregates, and thus to combine high energy density and chemical stability.

2:30 PM

(ICACC-S6-018-2016) High-capacity electrode materials for rechargeable lithium batteries: Li_3NbO_4-based system with cation-disordered rocksalt structure (Invited)

N. Yabuuchi*[1]; 1. Tokyo Denki University, Japan

Lithium-excess compounds, Li_2MeO_3 (Me = Mn^{4+}, Ru^{4+}, etc.), have been extensively studied as highcapacity positive electrode materials. Although the origin as the high reversible capacity has been a debatable subject for a long time, recently it has been confirmed that charge compensation is partly achieved by solid-state redox of nonmetal anions (i.e., oxide ions), coupled with solid-state redox of transition metals, which is the basic theory used for classic lithium insertion materials, such as $LiMeO_2$ (Me = Co^{3+}, Ni^{3+}, etc.). Herein, as a compound with further excess lithium contents, a cation-ordered rocksalt phase with lithium and pentavalent niobium ions, Li_3NbO_4, is examined as the host structure of a new series of high-capacity positive electrode materials for rechargeable lithium batteries. Approximately 300 $mAhg^{-1}$ of high-reversible capacity at 50 °C is experimentally observed, which partly originates from charge compensation by solid-state redox of oxide ions. It is proposed that such a charge compensation process by oxide ions is effectively stabilized by the presence of electrochemically inactive niobium ions.

3:20 PM

(ICACC-S6-019-2016) Recent advances in positive electrode materials for Li-ion batteries (Invited)

G. Rousse*[1]; 1. College de France/UPMC, France

Li-ion batteries have empowered consumer electronics and are now seen as the best choice to propel forward the development of eco-friendly electric vehicles. To enhance the energy density of the positive electrode materials, two ways can be explored: 1) enhancing the capacity by taking advantage of the anionic redox activity coming in addition to the well-known cationic one; this occurs in layered-type materials Li_2MO_3 (M=Mn, Ni, Co..); 2) increasing the voltage by deviating from commercialized polyanionic compound $LiFePO_4$. A key tool to do this relies in exploiting the *inductive effect* of polyanions PO_4^{3-}. It is now well established that modifying the electronegativity of the polyanions provides as an important way to tune redox potentials in a wide variety of systems. $LiFeSO_4F$ constitutes a textbook example as replacing PO_4^{3-} in the well-known $LiFePO_4$ by SO_4^{2-} and F^- resulted in an increase of the voltage from 3.45V to 3.6V and 3.9V for the tavorite and triplite polymorphs, respectively. However, a major drawback lays in the moisture sensitivity of these sulfate based compounds. Therefore we recently moved to oxy-sulfates: we could synthetize and fully characterize $Fe_2O(SO_4)_2$ and $Li_2Cu_2O(SO_4)_2$, that offer new directions in the quest for new polyanionic electrode materials.

3:50 PM

(ICACC-S6-020-2016) Amorphous lithium manganate, a new matrix for high density Li ion batteries

M. Freire[2]; N. Kosova[4]; C. Jordy[5]; O. I. Lebedev[3]; D. Chateigner[3]; A. Maignan[3]; V. Pralong*[1]; 1. CNRS ENSICAEN, France; 2. cnrs saft, France; 3. CNRS CRISMAT, France; 4. Institute of Solid State Chemistry and Mechanochemistry, Russian Federation; 5. SAFT, France

Due to their low weight, high energy densities and long cycle life, the development of rechargeable Li-ions batteries is a major scientific challenge. For many applications requiring energy storage, the need to increase the energy density of storage devices is of first importance, this is the reason why the battery scientific community is studying intensively and worldwide new high capacity cathodes materials. After a composition screening, a new material family has been discovered in the Li-Mn-O system and has been investigated as potential new material for Li-ion batteries to replace conventional NMC materials ($LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$). In this study we report for the first time the synthesis, structural and electrochemical characterizations of a new non-lamellar oxide with the highest capacity observed ever before in the Li-Mn-O system. This new patented material is prepared at the nano-scale (5-10 nm) by mechanical alloying at room temperature, which shows a discharge capacity of 300 mAh/g. It is a rock-salt type nanostructured material, prepared by a direct mechanochemical synthesis. In this work are reported the first structural and electrochemical characterizations of a new active compound as positive electrode for Li-ion batteries.

4:10 PM

(ICACC-S6-021-2016) Facile route to develop CNT reinforced $LiFePO_4$ and Co_3O_4 with uniform CNT distribution, as superior electrode materials for Li-ion batteries

M. K. Satam*[1]; R. Natarajan[1]; A. Chatterjee[1]; Y. Krishnan[1]; M. Jangid[1]; S. Kobi[1]; A. Mukhopadhyay[1]; 1. IIT Bombay, India

Poor electronic conductivities, as well as mechanical degradation upon lithiation/delithiation, are some of the issues associated with the ceramic electrode materials for Li-ion battery. Efficient reinforcement with strong and electronically conducting nanofibers (viz. CNTs) is expected to address these issues. However, challenges associated with obtaining uniform dispersion of CNTs suppress the achievable improvements. Against this backdrop, using an engineered but facile sol-gel based synthesis route, we demonstrate the development of electrode materials characterized by the presence of uniformly distributed CNTs, reinforcing the interiors of the ceramic crystallites, along with those present around the periphery of particles. In this route, the CNTs are directly incorporated into the $LiFePO_4$ and Co_3O_4 matrix sols, instead of physically mixing the electrode powders and CNTs. $LiFePO_4$ (cathode) and Co_3O_4 (anode) have been separately prepared and used as the electrode (matrix) materials in the present work. Both the types of the CNT-reinforced electrode materials, developed using the engineered sol-gel based route, possess considerably improved cycle life, rate capability and reduced potential hysteresis, as compared to the unreinforced electrode materials and the CNT-containing electrodes in which the CNTs were added via physical mixing.

4:30 PM

(ICACC-S6-022-2016) Preparation and battery performance of lithium-iron-fluorosilicate glass cathode

T. Togashi*[1]; K. Shinozaki[1]; T. Honma[1]; T. Komatsu[1]; 1. Nagaoka University of Technology, Japan

Lithium ion battery (LIB) has many problems, which are caused by using $LiCoO_2$ as a cathode material in LIBs. Therefore, it is of importance to develop new cathode materials. In recent years, our laboratory demonstrated that lithium-iron-silicate glasses work as a cathode material in LIB. However, the battery performance is not good in the actual capacity and the discharge voltage. Therefore, to improve the battery performance of lithium-iron-silicate glass cathodes, we tried to prepare lithium-iron-fluorosilicate glasses in which a part of Li_2O was substituted with LiF. We also examined the electrochemical properties of the glasses in this work. (40-x) Li_2O-2xLiF-10Fe_2O_3-50SiO_2 (x=0-20, mol%) glasses, *i.e.* fluorosilicate glasses, were prepared by using a conventional melt-quenching method. The quenched samples were measured by DTA and XRD to confirm the vitrification. We also examined AC impedance, battery performance test, XPS measurement, and Raman spectroscopy. In this work, we obtained the glass samples at x=0-15, but the sample at x=20 was not vitrified by a melt-quenching method. The electrochemical conductivity was increased with x, *e.g.*, $\sigma = 2.1\times10^{-9}$ Scm^{-1} at x =0 to $\sigma = 2.4\times10^{-8}$ Scm^{-1} at x=10. Also, the battery performance such as actual discharge capacity and discharge voltage was improved by the substitution of LiF, *e.g.,* 29 $mAhg^{-1}$ (1.93 V) at x=0 to 69 $mAhg^{-1}$ (2.32 V) at x=*15.*

4:50 PM

(ICACC-S6-023-2016) Unravelling the interplay of particle size and lithium ion transport in $LiFePO_4$

R. Shahid*[1]; S. Murugavel[1]; B. Roling[2]; 1. University of Delhi, India; 2. Fachbereich Chemie Physikalische Chemie, Germany

For the first time, intrinsic lithium ion conductivity in olivine phosphates (LFP) with different particle sizes is obtained by using the broad band ac impedance spectroscopic technique. The measured Li^+ conductivity strongly varies with particle size but in a non-monotonous manner. The obtained frequency dependent conductivity spectra provide unambiguously the dimensionality of Li^+ motion, where we find parallel shift of Li^+ diffusion mechanism from 1D to either 2D or 3D and exclusively determined by the presence of anti-site defects and is a unique property of LFP. The present study emphasizes the significance of atomic level observations of lithium ion diffusivity with particle size, which is strongly depends on the dimensionality, concentration of anti-site defects, diffusion length and surface energy kinetics. Here, we identify that there is a particle size regime (150 nm) where the Li^+ diffusion transition from the nanoregime to the bulk. The present results could explain why the nano sized LFP has better discharge capacity and high rate capability than the bulk counterpart

S7: 10th International Symposium on Nanostructured Materials: Functional Nanomaterials and Thin Films for Sustainable Energy Harvesting, Environmental and Health Applications

Advanced Processing and Characterization of Nanomaterials I

Room: Coquina Salon A

Session Chairs: Lisong Xiao, University of Duisburg-Essen; Theodor Schneller, RWTH Aachen University

1:30 PM

(ICACC-S7-020-2016) Microcrystalline Sodium Tungsten Bronze Materials Applied in Photocatalysis (Invited)

B. Tang*[1]; 1. Shandong Normal University, China

Sodium tungsten bronze is a kind of nonstoichiometric compound Na_xWO_3 ($0<x<1$). Their physical properties can vary dramatically with the x value. Herein, we present the production of microcrystalline hexagonal semiconductor Na_xWO_3 ($X<0.25$) nanowire bundles via a facile hydrothermal synthesis, and studied its structure and physical properties changing with the high-temperature reduction process. We found that when it was calcined under high temperature with the presence of reductive agents such as carbon or H_2, both reductive process and electronic conductivity transfer process occurred in a result of forming conductor materials. The as-prepared materials showed amazing photocatalysis even under Visible and IR light irradiation.

2:00 PM

(ICACC-S7-021-2016) Carbon nanotube thin films for flexible electronics applications (Invited)

E. I. Kauppinen*[1]; 1. Aalto University School of Science, Finland

Indium is used as ITO (indium-tin oxide) transparent conducting films (TCF) for touch screens of mobile phones and portable computers. Polycrystalline silicon is the semiconductor material used in thin film field effect transistors (TFT-FET) of display back planes. Introduction of flexible devices requires new materials to replace ITO and silicon, due to their rigid nature. We have developed single-walled carbon nanotube (SWNT) thin films to manufacture touch sensors with electrical properties on par with those of ITO-on-PET, and with optical properties better than those of ITO, metal nanowire and metal mesh. SWNTs were used to manufacture TFT-FETs with properties comparable to those made from silicon. We show that SWNT networks consisting of long, clean and highly individualized SWNTs exhibit improved TCF performance. We introduce the novel FC-CVD reactor based on spark discharge catalyst generation to experimentally study the effect of bundling on the performance of TCF and TFT-FETs. TCFs made from individual tubes with 4 micron mean length show 60 ohms/sq sheet resistance at 90 % transparency.

2:20 PM

(ICACC-S7-022-2016) Smart Powder Processing for Advanced Materials (Invited)

M. Naito*[1]; T. Kozawa[1]; A. Kondo[1]; M. Matsuoka[1]; 1. JWRI, Osaka University, Japan

Smart powder processing stands for novel powder processing techniques that create advanced materials with minimal energy consumption and environmental impacts. Particle bonding technology is a typical smart powder processing technique to make advanced composites. This mechanical process can directly synthesize the cathode powders from their starting materials and make the composite granules with another kind of particles without any heat assistance. In this paper, its application for lithium ion batteries (LIBs) will be explained. Recently, we have demonstrated the synthesis of $LiCoO_2$, $LiFePO_4$ and $LiNi_{0.5}Mn_{1.5}O_4$ powder granules as cathode materials by applying this technology. Besides, concentration-gradient cathode particles were favorably created using the combination of this technology and additional heating process. The electrochemical performances of the coin cells made by the cathode powders will be also explained.

2:40 PM

(ICACC-S7-023-2016) Atomic scale STEM analysis of structure and dopant effects on grain boundary in oxide ceramics (Invited)

T. Tohei*[1]; M. Sakai[1]; N. Shibata[1]; Y. Ikuhara[1]; 1. The University of Tokyo, Japan

Recent advances in transmission electron microscopy (TEM) enable us to obtain information about structure and chemical composition of materials even at a scale of one atomic column. High angle annular dark field (HAADF) image using atomic-size STEM probe combined with EDS or EELS analysis is a powerful tool for the investigation of microscopic modification of materials such as defects or dopants. In this work, we investigated the atomic structure and dopant effects on grain boundary (GB) in α-Al_2O_3 (alumina) by employing atomic scale STEM observations on bicrystal samples. Structural properties of alumina ceramics are drastically changed by adding small amount of dopants and dopant segregation on GB is considered to be responsible for the properties. Based on the bicrystal approach we can conduct systematic studies using well controlled and characterised sets of GBs and dopants. From a series of observations on doped $\sum$13 GBs in alumina, it was found that divalent dopants do not segregate solely but tend to co-segregate with accompanying aliovalent elements, while tetravalent dopants can segregate into GB without co-dopants. Among these dopant species, Si-doped GB was found to show an interesting behaviour causing nano-faceting upon heavy doping. These results give an intriguing demonstration of dopant induced change in grain boundary morphology and atomistic structures.

Advanced Processing and Characterization of Nanomaterials II

Room: Coquina Salon A

Session Chairs: Esko Kauppinen, Aalto University School of Science; Makio Naito, JWRI, Osaka University

3:20 PM

(ICACC-S7-024-2016) Time dependent dispersion and gelation phenomena of fine alumina powder aqueous suspension for advanced gel casting process by using poly-isobutylene-alt-maleic anhydride (Invited)

H. Kamiya*[1]; Y. Okada[1]; S. Shimai[1]; 1. Tokyo University of Agriculture and Technology, Japan

For advanced new gel casting process of inorganic ceramics fine powder green bodies from concentrated aqueous suspension, we had discovered that commercial poly-isobutylene-alt-maleic anhydride acted as a dispersant, firstly, and then generated a time dependent gelation of concentrated fine alumina aqueous suspension. In order to investigate the action mechanism of this polymer among primary alumina particles during dispersion and gelation process, time-dependent surface interaction change between alumina particle and sapphire substrate were characterized in aqueous solution with this polymer by using colloid probe atomic force microscope. Based on time dependent surface interaction change, such as repulsive and long range attractive force generation, and other data, such as functional groups behaviors after polymer adsorption on alumina particles by FT-IR, the amount of adsorbed polymer, macroscopic suspension viscosity, the action mechanism of this polymer between alumina particles was discussed. The effects of molecular structure and additive content, the relationship between molecular weight and primary particle size on dispersion and gelation behavior of concentrated alumina suspension were also discussed.

3:50 PM

(ICACC-S7-025-2016) Controlled Formation of Nanoparticles from Gas-Phase Reactions for Energy Storage (Invited)

L. Xiao*[1]; Y. Sehlleier[1]; C. Schulz[2]; H. Wiggers[2]; 1. University of Duisburg-Essen, Germany; 2. Center for Nanointegration Duisburg-Essen (CENIDE), Germany

Materials for energy applications e.g., heterogeneous catalysis and electrochemical energy storage require materials with specific properties such as high surface area and short diffusion length. Nanoparticles (NPs) can fulfill these requirements; however, they can only provide the desired functions if they are tailored in terms of chemical/phase composition, particle size, surface properties and morphology. The rapid increase of commercial interest with respect to energy applications requires specific nanomaterials that are available in large scale. Up to now, the desired NPs produced by established chemical and physical routes are often only obtainable in small quantities that limit their practical applications. Gas-phase synthesis of NPs is a particularly suitable method since it enables the continuous production of nanoscaled powders of high purity with controlled properties. In addition, scalable production rates promote the industrial viability of nanomaterials. In this talk, three kinds of gas-phase reactors namely hot-wall, flame, and microwave-plasma reactors will be introduced. The tailored synthesis of NPs using these three rectors will be illustrated, and the formation processes and mechanisms will be presented in detail. Using the examples of gas-phase-made Fe_2O_3 and Si NPs, the utilization of nanomaterials in respect of energy storage applications will be demonstrated.

4:10 PM

(ICACC-S7-026-2016) Nanostructured complex metal oxide thin films for energy applications manufactured and compositionally engineered by chemical solution deposition (Invited)

T. Schneller*[1]; 1. RWTH Aachen University, Germany

Complex metal oxide thin films represent an intriguing class of materials for a plethora of applications in electronic devices such as capacitors, coated conductors, solid oxide fuel cells (SOFC), electrolyzers, and other components in energy technology. Among the available deposition technologies chemical solution deposition (CSD) offers a unique potential for the economic fabrication of such thin films in high quality due to its high flexibility with regard to composition and coating method, and without the need for complex and size limiting vacuum apparatuses. Precursor chemistry, thermal processing conditions, and substrate represent the key parameters to control the phase-, texture-, and microstructure development and thus the electrical properties. After a brief overview on the corresponding established principles by means of frequently investigated ferroelectric perovskites, the attention is drawn to advanced deposition methods such as ink-jet printing and microemulsion mediated synthesis to generate nanocomposite films with tailored heterogeneity. Proton conducting electrolyte and oxide electrode thin films for intermediate temperature operating SOFCs and other electrochemical devices will serve as illustrative examples for the application of these modern methods and the use of the gained know-how for morphology engineering.

4:30 PM

(ICACC-S7-027-2016) Investigation of Magnetic Iron Oxide Nanosheets Synthesized by Hydrothermal Method

Y. Kamei*[1]; Y. Makinose[1]; K. Wakayama[1]; K. Katsumata[2]; N. Matsushita[1]; 1. Tokyo Institute of Technology, Japan; 2. Tokyo University of Science, Japan

Magnetic nanomaterials have attracted much attention for their potential applications in the magnetic recording media and biomedical fields, and so on. Among these nanomaterials, Fe_3O_4 and γ-Fe_2O_3 nanocrystals with a variety of shapes (e.g. nanoparticles, nanorods, nanospheres, nanosheets) and size have been successfully synthesized in order to obtain chemical and physical properties. In particular, magnetic iron oxide nanosheets are expected to have interesting magnetic properties derived from their 2D anisotropic structures due to the 2D quantum and surface effects. Several syntheses of iron oxide nanosheets have been reported, including solvothermal synthesis, thermal decomposition. Herein, we report hydrothermal synthesis of Fe_3O_4/γ-Fe_2O_3 nanosheets with high aspect of ratio lateral size to thickness (> 50), and investigate their magnetic property by using magnetic force microscopy (MFM) for the first time. The results showed that the as synthesized Fe_3O_4/γ-Fe_2O_3 nanosheets were (111) plane orientation having hexagonal shape with 10-500 nm in lateral size and 7.0-10.5 nm in thickness. The macroscopic magnetic property of the nanosheets was ferromagnetic at room temperature. The local magnetic response observations of the nanosheet by MFM suggested that the magnetizations in nanosheet were different at the edge and in the center.

5:10 PM

(ICACC-S7-028-2016) 2-D carbon/NiO for use in supercapacitors

X. Nguyen Thi*[1]; J. Ting[1]; 1. National Cheng Kung University, Taiwan

Supercapacitors attract a huge interest in recent years due to their high specific power and long cycle stability. Carbon based nanomaterials have unique outstanding properties such as high surface area and good mechanical stability, suitable for applications in supercapacitors. There are various allotropes of carbon have been considered for electrode materials in supercapacitors such as activated carbon, graphene, and carbon nanotubes. In this study, we have investigated the use of a new form of 2-D carbon derived from commercial carbon fibers and NiO as the electrode materials. The

2-D carbon was synthesized by electrochemical exfoliation of pitch based carbon fibers in hydrofluoric acid solution at room temperature under various conditions and followed by further sonication. By mean of microwave-assisted hydrothermal method, the growth of nickel oxide on the 2D carbon was performed. The NiO not only provide pseudo reaction but also prevents the stacking of the 2-D carbon. The obtained materials were first characterized for the material properties and then made into electrodes for supercapacitor assembly. The resulting supercapacitor was evaluated using cyclic voltammetry, electrochemical impedance spectroscopy and charge – discharge technique. We show that the inexpensive, non-toxic 2-D carbon/NiO composite material is a promising advanced electrode material for supercapacitors.

5:30 PM

(ICACC-S7-029-2016) Synthesis and characterization of V_2O_5-HfO_{2-x} core shell nanoparticles by precipitation method for visible light photodegradation

S. Lu*[1]; J. Ting[1]; 1. National Cheng Kung University, Taiwan

A novel V_2O_5-HfO_2 core-shell nanoparticles have been fabricated using a precipitation method. V_2O_5 has a band gap of 2.0 eV, which absorbs visible light. However electron-hole pairs recombine very rapidly, making pure V_2O_5 undesirable for photodegradation. On the other hand, HfO_2 has a band gap of 6.0 eV, not appropriate for light absorption. However, in this study, HfO_2 was annealed in different atmospheres to generate oxygen vacancies, which forms acceptor levels below the conduction band of HfO_2 and also below that of V_2O_5. This, coupled with the HfO_{2-x}-V_2O_5 core-shell structure, allows the photoelectrons in the conduction band of V_2O_5be transferred to the defect donor levels, thus reducing the recombination. Degradation of methylene blue was examined under visible light and UV light. We demonstrate that degradation using V_2O_5-HfO_2 is much better than that using pure V_2O_5. The effects of the defect structures in HfO_2 and V_2O_5-HfO_2 composition are discussed and reported.

5:50 PM

(ICACC-S7-030-2016) Latest Developments Organometallic Hybrid Perovskite Solar Cells

D. M. Gedamu*[2]; R. Nechache[3]; F. Rosei[1]; 1. INRS, Canada; 2. INRS-EMT, Canada; 3. Ecole de technologie supérieure, Canada

Organometallic perovskite photo absorbers recently emerged as one of the promising potential substitutes for silicon based solar cells because of a cost effective synthesis technique and the rapid progress in the power conversion efficiency after a pioneering work of Miyaska et al.. Already efficiency of over 20% has been achieved for planar geometry asprepared perovskite based solar cells fabricated in two step solid or chemical synthesis routes. Stability at ambient condition, better efficiency and the presence of toxic substance lead (Pb) in the microstructure of perovskites however pose challenges for the application of the material. Planar geometry solar cell devices could be fabricated using standard process: a two-step spin coating process on FTO or ITO coated glass substrates. Employing various techniques, the aforementioned problems will be addressed and latest results from various synthesis techniques will be presented. Using hybrid chemical vapor deposition (HCVD) and spin coating or combination of the two technologies, results from various solar cells will also be presented. The recently introduced HCVD technique offered new route resulting in a smooth, compact and high crystalline quality of perovskite. Both lead based and lead-free perovskite solar cell synthesized in different blocking layers such as ZnO and TiO_2 and the effect of mesoporous TiO_2 film on the solar cell will also be discussed.

6:10 PM

(ICACC-S7-031-2016) Solution synthesis of Al doped ZnO transparent electrodes: mission impossible or need for more insight

M. K. Van Bael*[1]; A. Hardy[1]; K. Elen[1]; 1. Hasselt University & imec, Belgium

Transparent conducting oxides (TCO) are gaining increasing importance, not only in solar panels, but also in various new thin film based technologies. The herewith increasing demand of TCO's is associated with immense scientific and economic challenges: First, reliable synthesis routes have to be developed that allow mass production at justifiable cost. Solution based deposition is in this respect an appealing alternative to standard physical deposition methods, as they often require (high) vacuum conditions. Second, the vastly increasing demands for TCO materials motivate the search for cost-effective alternatives to Indium doped Tin Oxide (ITO). (Doped) zinc oxide (ZnO) is among such promising alternatives. Although the proposed routes and materials have important advantages, some crucial challenges jeopardize their success in e.g. energy applications. We investigate and compare various approaches to synthesize Aluminium doped ZnO. A first route is based on precursor *solutions* comprising the dissolution of molecular precursors followed by solution deposition on a substrate. A thermal treatment is then needed to transform the molecular precursor into the desired (crystalline) oxide. A second route starts with the preparation of TCO *nanoparticles*, which are consecutively dispersed in a liquid before deposition and thermal treatment.

S8: 10th International Symposium on Advanced Processing and Manufacturing Technologies for Structural and Multifunctional Materials and Systems (APMT10)

Novel Ceramic Processing I

Room: Coquina Salon B

Session Chairs: Tohru Suzuki, National Institute for Materials Science; Ralf Riedel, TU Darmstadt

1:30 PM

(ICACC-S8-020-2016) *In situ* formed SiC nano-inclusions in Si_3N_4 based ceramics - thermal shock resistance, wear behavior and oxidation resistance (Invited)

P. Sajgalik*[1]; 1. Institute of Inorganic Chemistry, Slovak Academy of Sciences, Slovakia

Six different sintering aids (Lu_2O_3, Yb_2O_3, Y_2O_3, Sm_2O_3, Nd_2O_3 and La_2O_3) were used for the processing of dense Si_3N_4/SiC micro/nano composites. Thermal shock resistance: A critical temperature difference increased with an increasing ionic radius of RE^{3+} for both the composites and the monoliths. Wear behavior: The friction coefficient as well as the specific wear rate decreased with a decreasing ionic radius of rare-earth elements in both the monoliths and the composites. High bonding strength and the high fracture toughness are the reasons why the ceramics doped by Lu exhibited the best wear resistance. Oxidation resistance: Composites exhibited predominately parabolic oxidation behaviour indicated diffusion as the rate limiting mechanism. Exception was only the Si_3N_4-SiC composite sintered with Lu_2O_3. In this case diffusion of cation has been strongly suppressed because of the beneficial effect of stable grain boundary phase and the presence of the SiC particles predominately located at the grain boundaries of Si_3N_4. The first principle calculations were used for the explanation of the fracture behaviour of the composites depending on the rare earth additive. The energy of fracture was calculated with respect to the chemical composition of GB. The experimental and theoretical results will be discussed.

2:00 PM

(ICACC-S8-021-2016) Development of silicon nitride / multilayered graphene nanocomposites (Invited)

C. Balazsi*[1]; 1. Bay Zoltan Nonprofit Ltd. for Applied Research, Hungary

Silicon nitride is a promising structural ceramic material that was developed in a search for high strength and high toughness ceramics that could replace metals in advanced turbine and reciprocating engines to give higher operating temperatures and efficiencies. During the last few years new cost effective, high quality carbon based filamentous was developed in the form of graphene platelets (GPLs), also called graphene nanoplatelets (GNP), multilayer graphene nanosheets (MGN) or graphene nanosheets (GNS). These platelets demonstrate exceptional high thermal and electrical conductivity and an exceptional combination of mechanical properties. The aim of the present work is to investigate the influence of the addition of various kinds of graphene nanoplatelets on the structure and other properties of Si3N4 based composites prepared by high efficient attritor milling. Acknowledgement Authors thanks to M-ERANET Grace" Graphene-ceramics composits for tribological application in aqueous environments.

2:30 PM

(ICACC-S8-022-2016) Fracture-induced amorphization of polycrystalline SiO_2 stishovite: nanoscale transformation toughening in the hardest oxide

N. Nishiyama*[1]; F. Wakai[2]; H. Ohfuji[3]; Y. Tamenori[4]; H. Murata[5]; T. Taniguchi[5]; M. Matsushita[3]; E. Kulik[1]; K. Yoshida[2]; T. Irifune[3]; 1. Deutsches Elektronen-Synchrotron DESY, Germany; 2. Tokyo Institute of Technology, Japan; 3. Ehime University, Japan; 4. Japan Synchrotron Radiation Research Institute, Japan; 5. National Institute for Materials Science (NIMS), Japan

Silicon dioxide (silica) is the most abundant oxide component on the Earth's surface and has been widely used in industry. Stishovite is a high-pressure polymorph of silica stable above 9 GPa. This material has been known as the hardest oxide at ambient conditions (H_V ~ 30 GPa). A previous study reported synthesis of nanocrystalline bulk stishovite from a bulk silica glass rod. Fracture toughness of this material was reported to be ~10 MPa $m^{1/2}$, whereas single crystal stishovite is known as a very brittle material (K_{1c} = 1.6 MPa $m^{1/2}$). Nanocrystalline bulk sithovite is a very hard and toughed material. In order to understand an active toughening mechanism in this material, we performed Si-K XANES measurements and TEM observations for fracture surfaces of nanocrystalline bulk stishovite. Our experimental results show that amorphous silica exists on the outermost fracture surfaces. These results indicate that huge tensile stress at the crack tip induces solid-state amorphization from stishovite to amorphous silica. This transformation accompanies a huge volume expansion of 95%. This volume expansion causes transformation toughening. In addition, this volume expansion is much larger than that of tetragonal to monoclinic transition in zirconia (4%), resulting in a thinner transformed region whose thickness is several tens of nanometers.

2:50 PM

(ICACC-S8-023-2016) Mechanical and Thermal Properties of Pressureless Sintered Silicon Carbide Ceramics with Alumina-Yttria-Calcia-Strontia

Y. Seo*[1]; J. Eom[1]; Y. Kim[1]; 1. University of Seoul, The Republic of Korea

Development of a new composition which could densify SiC ceramics at low temperatures is an important issue for widening the industrial applications of SiC ceramics. In the present work, SiC ceramics were fabricated by pressureless sintering at 1750-1950ºC for 2 h in an argon atmosphere with a new quaternary additive system (Al_2O_3-Y_2O_3-CaO-SrO). The effect of sintering temperature on the mechanical and thermal properties of SiC ceramics was investigated. Sintered densities above 95% were obtained at a temperature as low as 1800ºC without an applied pressure. Toughened microstructures, which consisted of platelet SiC grains and relatively small matrix grains, have been obtained when sintered at equal to or higher than 1900°C for 2 h in an argon atmosphere. The self-reinforced microstructures are the results of the beneficial effects of the new quaternary additive system and the acceleration of the $\beta \rightarrow \alpha$ phase transformation of SiC grains by adding 1 vol% α-SiC into β-SiC as a seed. Typical flexural strength and fracture toughness of the pressureless sintered SiC ceramics with Al_2O_3-Y_2O_3-CaO-SrO at 1850ºC were 454 MPa and 4.9 $MPam^{1/2}$ at room temperature, respectively.

3:30 PM

(ICACC-S8-024-2016) Silicate ceramic materials with improved properties for technical applications prepared by controlled mullite cristallisation (Invited)

J. Lis*[1]; J. Partyka[1]; M. Grandys[1]; A. Tajdus[1]; 1. AGH University of Science and Technology, Poland

Silicate ceramic material made from natural and processed minerals are still the basic volume of ceramics produced for market application. Despite significant progress in the modernization of traditional products and development of new silicate ceramics, there are still potential opportunities to improve the properties of such materials by controlling their phase composition and microstructure. A known primary mechanism for increasing the mechanical properties of these materials is the crystallization process of forming of mullite phase in the composite microstructures of the silicates. In the paper, new possibilities of control of mullitisation process are discussed for creation an appropriate microstructure. The basic method is to use a raw material with nano and micron size and/or control of sintering phenomena. The silicate materials with high mechanical properties close alumina ceramics are obtained, which can be used as structural ceramic materials for different technical applications, and it can provide a new offer for ceramic tiles or electroceramics. The examples of new materials and their applications are discussed in detail.

3:50 PM

(ICACC-S8-025-2016) Fabrication of c-axis oriented Si_3N_4 ceramics by molding under low and static magnetic field using graphene / Si_3N_4 nanocomposite particles as seed particles (Invited)

J. Tatami*[1]; N. Sugimoto[1]; T. Takahashi[3]; M. Iijima[1]; S. Tanaka[2]; 1. Yokohama National University, Japan; 2. Nagaoka University of Technology, Japan; 3. Kanagawa Academy of Science and Technology, Japan

Si_3N_4 ceramics are expected to be used as a substrate for SiC power modules. Because thermal conductivity of c-axis of b-Si_3N_4 has much higher than that of a-axis, alignment of c-axis of Si_3N_4 is effective in the improvement of the thermal conductivity of the Si_3N_4 ceramics. In this study, graphene / Si_3N_4 nanocomposite particles was used to fabricate c-axis oriented Si_3N_4 ceramics by molding in low and static magnetic field. The graphene / Si_3N_4 nanocomposite particles were prepared by mechanical treatment. SEM and SPM observation showed that graphene particles were successfully fixed on an elongated Si_3N_4 particle. A slurry of the seed particles, α-Si_3N_4 and sintering aid powder was prepared, and then it was molded in the low and static magnetic field. As a result, it was confirmed that c-axis of b-Si_3N_4 seeds were oriented under the magnetic field of 0.4 T. After firing at high temperature, dense Si_3N_4 ceramics in which c-axis of elongated β-Si_3N_4 grains were well oriented were obtained. In this process, it was also found that the aspect ratio of the seed particles were also important.

4:10 PM

(ICACC-S8-026-2016) Manufacturing Complex-Shaped Silicon Nitride Components through Room-Temperature Injection Molding of Ceramic Suspension Gels (CeraSGels)

L. Rueschhoff*[1]; J. Youngblood[1]; R. Trice[1]; 1. Purdue University, USA

A novel processing technique of injection molding silicon nitride suspension gels (CeraSGels) at room temperature is proposed to

overcome common forming difficulties associated with silicon nitride and other ceramic systems. CeraSGels are a combination of a ceramic powder, water-soluble polymer (used for rheology optimization and green body strength) and water. CeraSGels have recently been shown to be desirable for injection molding due to their rheological properties at room temperature, which can be tailored through polymer type, molecular weight, and ceramic loading. Injection molding is a promising processing method for silicon nitride since near-net complex shapes can be easily formed, with the possibility of alignment of high aspect ratio microstructural features through exploiting the shear stresses that arise during forming. In the present work, highly loaded aqueous silicon nitride (>45vol.%) CeraSGels have quickly and easily been formed using commercially available water reducing admixtures (WRAs), commonly used in cementitious mixtures. Preliminary rheology, forming, and sintering studies will be presented to prove this a viable process for forming near-net and complex shapes of advanced silicon nitride parts.

4:30 PM

(ICACC-S8-027-2016) TEM Analysis of Interfaces in Diffusion-Bonded Silicon Carbide Ceramics Joined Using Metallic Interlayers

T. Ozaki*[2]; Y. Hasegawa[2]; H. Tsuda[3]; S. Mori[3]; M. C. Halbig[4]; M. Singh[1]; R. Asthana[5]; 1. Ohio Aerospace Institute, USA; 2. Technology Research Institute of Osaka Prefecture, Japan; 3. Osaka Prefecture University, Japan; 4. NASA Glenn Research Center, USA; 5. University of Wisconsin-Stout, USA

Silicon Carbide (SiC) is a promising material for thermostructural applications due to its excellent high-temperature mechanical properties, oxidation resistance, and thermal stability. However, joining and integration technologies are indispensable for this material in order to fabricate large size and complex shape components with desired functionalities. Although diffusion bonding techniques using metallic interlayers have been commonly utilized to bond various SiC ceramics, detailed microstructural observation by Transmission Electron Microscopy (TEM) of the bonded area has not been carried out due to difficulty in preparing TEM samples. In this study, we tried to prepare TEM samples from joints of diffusion bonded SiC ceramics by Focused Ion Beam (FIB) system and carefully investigated the interfacial microstructure by TEM analysis. The samples used in this study were SiC fiber bonded ceramics (SA-Tyrannohex™: SA-THX) diffusion bonded with metallic interlayers such as Ti, Ti/Mo, and Mo-B. In this presentation, the result of microstructural analysis obtained by TEM observations and the influence of metallic interlayers and fiber orientation of SA-THX on the joint microstructure will be discussed.

4:50 PM

(ICACC-S8-028-2016) Large-scale Fabrication of Nitrogen Vacancy Embedded Diamond Nanostructure Arrays: Method and Mechanism

C. Gu*[1]; W. Li[1]; Q. Jiang[1]; 1. Beijing National Lab for Condensed Matter Physics, China

Sources of single photons are of fundamental importance in many applications as to provide quantum states for quantum communication and quantum information processing. Color centers in diamond are prominent candidates to generate and manipulate quantum states of light, even at room temperature. However, the efficiency of photon collection of the color centers in bulk diamond is greatly reduced by refraction at the diamond/air interface. To address this issue, in this work, we explored a combined technique of electron beam lithography nano-patterning and reacted ion etching to fabricate periodically-positioned nanoscale nitrogen vacancy color center embedded diamond nanopillars from bulk diamond structure in larger scale. The influence of the shape, size, period and material type of the mask pattern as well as the processing conditions, on the shape evolution of the resulted free-standing structure, have all been investigated systematically. The underlying mechanism is discussed. Furthermore, the fabrication conditions are optimized and various parameters were used to tune the characteristics of the structures. Single photon property measurement indicate that compared with the film counterpart, an enhancement of about ten folds in single photon collection efficiency was achieved with greatly improved signal to noise ratio.

S10: Virtual Materials (Computational) Design and Ceramic Genome

Modeling of Innovative Ceramics for Functional Applications III

Room: Ponce DeLeon
Session Chair: Sean Smith, University of New South Wales

1:30 PM

(ICACC-S10-017-2016) Computational Design of SiCO Ceramics for Novel Li Batteries (Invited)

P. Kroll*[1]; 1. UT Arlington, USA

Combining extensive structure modeling and density functional calculations we explore Li insertion in SiCO ceramics. In a first step, we rationalize experimental evidence of the high Li storage capacity of these novel anode materials. A large variety of atomistic models of amorphous SiCO are analyzed in detail to locate the origin of favorable Li insertion. A fortuitous balance exists between bonding of the Li-cation and promotion of electrons into low-lying orbitals located within the "free" carbon phase embedded in SiCO. However, defects inside the "free" carbon phase are also responsible for the observed significant loss of Li during the initial loading cycle of the material. Consequently, in a second step we design new SiCO materials without defects, which, therefore, provide an optimum amount of sites available for Li storage within the embedded carbon phase. We screen a manifold of hypothetical crystalline SiCO structures and compare them to amorphous models of SiCO to outline the basic necessities for materials synthesis. We will show that the interface between embedded carbon and surrounding oxide phase is crucial for Li storage, and that amorphous SiCO ceramics have the potential of providing a 3-4 times higher Li storage capacity than graphite.

2:00 PM

(ICACC-S10-018-2016) Comparison of Oxygen Diffusion Mechanisms in Ytterbium Disilicate from Kinetic Monte Carlo Simulation

B. S. Good*[1]; 1. NASA Glenn Research Center, USA

Ytterbium disilicate is of interest as a potential environmental barrier coating for aerospace applications, notably for use in next generation jet turbine engines. In such an extreme environment, the transport of oxygen through these coatings is undesirable if high temperature corrosion is to be avoided. Oxygen diffusion can occur through a number of mechanisms. In this work we compare vacancy-mediated and interstitial diffusivities using kinetic Monte Carlo simulation, with migration barrier energies, vacancy formation energies and heats of solution computed using density functional theory. We have found that, in the case of vacancy-mediated diffusion, many of the potential diffusion paths involve large barrier energies, though some paths have barrier energies smaller than one electron volt, with the result that the vacancy-mediated diffusivity is small, as long as only intrinsic vacancies are present. In the case of interstitial diffusion, migration barrier energies are typically less than one electron volt, indicating that interstitial diffusivity may be large. However, the heat of solution is positive, indicating that the concentration of interstitial oxygen is likely to be small. It is therefore expected that the material is unlikely to exhibit significant oxygen permeability via either mechanism.

2:20 PM

(ICACC-S10-019-2016) Complex defects study in Ga-, In-based skutterudites CoSb3

L. Xi*[2]; J. Yang[1]; W. Zhang[1]; 1. Shanghai University, China; 2. Shanghai Institute of Ceramics, Chinese Academy of Sciences, China

Complex defect is one of the challenging problems to be understood in doping and associated structure tuning in materials science. Thermoelectrics are generally heavily doped semiconductors for which optimization of doping is critical. This goes beyond optimization of the carrier concentration. For example, doping n-type skutterudites by alkali metal (AM), alkaline earth (AE), and rare-earth (RE) filling strongly affects the thermal conductivity, the carrier mobility, and the thermopower, all of which play central roles in the performance of the material, and additionally modifies the band structure. In this work, we investigated the complex doping behavior of Ga and In, and their co-doping with AM, AE, RE in $CoSb_3$ using ab initio total-energy calculations and thermodynamic. The formation energies of void filling, Sb substitution and complex dual-site occupancy defects with different charge states, and their dependence on chemical potentials of species, were studied. This work can design novel filled $CoSb_3$ skutterudite phases based on a combination of filling and Sb-substituted Ga/In defects and demonstrate that there may be more space to optimize electrical and thermal transport properties of skutterudites and even other TE materials by utilizing complex doping.

Modeling of Innovative Ceramics for Functional Applications IV

Room: Ponce DeLeon

Session Chair: Peter Kroll, UT Arlington

3:00 PM

(ICACC-S10-020-2016) Computational studies on the stability of $SrCoO_{3-\delta}$ phases for electrocatalytic oxygen evolution (Invited)

H. Tahini[1]; X. Tan[1]; J. Zhu[2]; W. Zhou[2]; F. Kurnia[1]; J. Hart[1]; S. Smith*[1]; 1. UNSW, Australia; 2. The University of Queensland, Australia

We report computational studies of oxygen evolution reactions (OER) by strontium coboltate, a theoretically ideal catalyst. Experimentally, $SrCoO_{3-\delta}$ always exhibits deviation from ideal stoichiometry due to the presence of O vacancies. Here, using first-principles calculations based on GGA+U and applying energy corrections to reduce errors due to O overbinding we investigate the O defect chemistry and the stability of different $SrCoO_{3-\delta}$ phases. The role of various surface active centres consisting of Co^{3+} and Co^{4+} and how these can influence the rate of OER will be discussed. The discussion will be extended to the recently synthesised Sc and Nb doped $SrCoO_3$ which exhibits an enhanced catalytic activity. Understanding the variations these defects introduce into the electronic density of states of the active Co centres under various electrode potentials together with the non-stoichiometry of $SrCoO_3$ will provide a more detailed understanding of the OER activity and conditions for optimum yields.

3:30 PM

(ICACC-S10-021-2016) Computational Materials Design of Novel Functional Oxides (Invited)

V. R. Cooper*[1]; 1. Oak Ridge National Laboratory, USA

Theory and computation have become critical aspects of the materials discovery process. Electronic structure methods, such as density functional theory, excel at the characterization of macroscopic properties in materials that have yet to be grown. However, predicting synthesizability and operability is less straightforward. Temperature, pressure and the stability of competing phases are among the many factors that determine whether a material can be made or will exhibit favorable properties under the required operating conditions. Our efforts have focused on the use of first principles methods to predict materials with enhanced properties that *can be synthesized* and *remain active* under device relevant conditions. In this presentation, I will discuss our three-pronged approach which emphasizes synergies between (i) electronic structure calculations for properties predictions, (ii) phenomenological/empirical models for examining phase stability and (iii) experimental validation. As an example, I will discuss our recent work towards the discovery of Pb-free piezoelectrics and mulitferroics and applications of superlattices for the design of a new class of transparent conducting oxides. Together, these examples illustrate a framework for accelerating the design and experimental realization of novel functional materials. Research was sponsored by the US DOE, Office of Science, BES, MSED and Early Career Research Programs.

4:00 PM

(ICACC-S10-022-2016) Microstructure Design For Fast Oxygen Conduction (Invited)

D. S. Aidhy*[1]; W. J. Weber[2]; 1. University of Wyoming, USA; 2. University of Tennessee, USA

In the past decade, the research in designing fast oxygen conducting materials for electrochemical applications has largely shifted to microstructural features, in contrast to materials-bulk. In particular, understanding oxygen energetics in heterointerface materials is currently at the forefront, where interfacial tensile strain is being considered as the key parameter in lowering oxygen migration barriers. Nanocrystalline materials with high densities of grain boundaries have also gathered interest that could possibly allow leverage over *excess volume* at grain boundaries, providing fast oxygen diffusion channels similar to those previously widely observed in metals. In addition, near-interface phase transformations and misfit dislocations are other microstructural phenomenon/features that are being explored to provide faster diffusion. In this work, the current understanding on oxygen energetics, i.e., thermodynamics and kinetics, originating from these microstructural features will be discussed. Experimental observations, theoretical predictions and novel atomistic mechanisms relevant to oxygen transport will be highlighted.

4:20 PM

(ICACC-S10-023-2016) Molecular Mechanisms of dissolution and absorption in Alkaline and Acid Treatment of Zeolite (Invited)

Y. Liu*[1]; 1. Shanghai University, China

With the aim to optimize alkaline and acid treatment of zeolites to obtain hierarchical mesoporous zeolites, dissolution and absorption mechanisms relevant to mesopore formation were investigated at a molecular level by density functional calculations. In the alkaline dissolution processes, dealumination is energetically more favorable than desilication, though both processes can occur. This theoretical results supports the recent experimental hypothesis and clarifies the misunderstandings of "alkaline dissolves Si" lasting for decades. On the other hand, the dissolved Al species prefer to be absorbed back onto zeolite surfaces whereas the dissolved Si species tend to aggregate in alkaline solution. Our study of acid treatment confirms that "acid dissolves Al" as commonly believed. The dissolution process promotes but the absorption process hampers the mesopore formation, laying foundation for understanding the mesoporosity influenced by the variations of zeolite framework and solution in alkaline and acid treatment.

S12: Materials for Extreme Environments: Ultrahigh Temperature Ceramics (UHTCs) and Nano-laminated Ternary Carbides and Nitrides (MAX Phases)

Novel Processing Methods I

Room: Tomoka B
Session Chair: Zhengming Sun, Southeast University

1:30 PM

(ICACC-S12-019-2016) Synthesis and densification of nano-UHTC powders and UHTC-SiC nano composites (Invited)

S. Lee*[1]; L. Feng[1]; H. Kim[1]; 1. Korea Institute of Materials Science, The Republic of Korea

We wanted to synthesize ultra-fine UHTC powders by the carbothermal reduction of oxides and wanted to fabricate UHTC-SiC nano composites using the powder. The powder was synthesized at 1500-1600°C using a modified spark plasma sintering (SPS) apparatus. UHTC-SiC composites were prepared by high-energy ball-milling and reactive spark plasma sintering (R-SPS) at 1550-1750°C under 40MPa pressure using silicides ($ZrSi_2$, $HfSi_2$, $TaSi_2$), B_4C and C as the starting materials. The synthesized powders had a fine particle size of about 100nm and a low oxygen content of ~ 0.5wt%. The metal basis purity of the powder was 99.9% excluding Zr impurity. The intermediate reactions and particle growth were minimized due to the low synthesis temperature and fast heating/cooling during the modified SPS process. Ultra-fine (200-300nm) and homogeneously distributed UHTC and SiC grains were obtained in the dense composites due to the molecular-level homogeneity of Si and Zr, Hf, Ta in the silicides, the high-energy ball-milling of raw powders and low sintering temperature by R-SPS. We could synthesize fine UHTC powders and nano-UHTC-SiC composites by using modified SPS and reactive SPS process.

2:00 PM

(ICACC-S12-020-2016) Melt Formed Hafnium Carbide-Carbon Eutectics for Ultrahigh Temperature Applications

L. Bracamonte*[1]; S. Pickard[1]; J. Withers[1]; 1. Materials & Electrochemical Research Corporation, USA

There is a need to improve the oxidation resistance of materials used for hypersonic vehicles which experience temperatures of 1500-3000°C. Carbon-carbon (C-C) composites can provide structural stability at these temperatures, but graphite fibers and matrices oxidize above ~450°C, thus requiring an oxidation protective coating. MER has demonstrated that hafnium carbide (HfC)-carbon (C) eutectic coatings can be produced by plasma transferred arc (PTA) additive metal manufacturing wherein HfC and C powders are introduced into the plasma and melted, which requires temperatures >4000°C. Thus, PTA heating of materials offers the advantage of being able to achieve extreme temperatures not possible by conventional furnace heating processes. The plasma melt forming approach can produce coatings on flat or complex shaped pieces, which is not possible by standard ultra-high temperature ceramic (UHTC) processing techniques such as hot pressing. HfC-C eutectic coatings on C-C composites were evaluated by multiple heating methods in air that provided up to 30 minutes protection at 2600°C. It is also possible to produce a matrix of HfC-C that further enhances oxidation performance. Additionally incorporating HfC fibers results in a near 100% HfC composite that could provide even higher temperature oxidation resistance.

2:20 PM

(ICACC-S12-021-2016) Preparation and optimization of ultra-refractory ZrB_2-$MoSi_2$-based dual composite ceramics for high temperature structural use

F. Monteverde*[1]; D. Sciti[1]; S. Failla[1]; R. J. Grohsmeyer[2]; G. Hilmas[2]; W. Fahrenholtz[2]; 1. CNR-ISTEC, Italy; 2. Missouri University of Science and Technology, USA

Dual Composite (DC) ceramics of ultra-refractory zirconium diboride (ZrB_2) and molybdenum disilicide ($MoSi_2$) are being investigated as candidates for high-temperature structural use in corrosive environments, due to the high-temperature ductility of $MoSi_2$ coupled to high strength and oxidation resistance. The DC architecture concept has been shown to increase wear resistance while maintaining or increasing fracture toughness in WC-Co composite inserts for RT applications by the microstructure engineering of discretely segregated sub-composites at different length scales. Various ZrB_2-$MoSi_2$ based DC composites were prepared by synthesizing discrete granules of various dimensions, dispersing them in a continuous matrix of another sub-composite composition with different properties and consolidating them by hot-pressing. The research investigated the co-active densification of multi-scale microstructures, and the effects of differing properties of (strong) granules and (tough) matrices sub-composites, differing oxidation resistance of the two compositions, as well as granule size and relative volume fraction between sub-composites. Mechanical properties (elastic modulus, 4-pt flexure strength and fracture toughness) at room temperature and at 1500°C of various DC composites will be reported and compared to corresponding conventional particulate composites.

2:40 PM

(ICACC-S12-022-2016) Fabrication and Characterization of Thermal Protection Systems with Hybrid Ceramic-Polymer Matrix Composites

H. Yang[1]; J. Gou[1]; C. Harris*[1]; 1. University of Central Florida, USA

Since Thermal Protection System (TPS) was developed for the Apollo missions 40 years ago, the TPS for space probes entering planetary atmospheres at very high velocities still relies on the ablative systems. A high temperature, light weight, cost effective hybrid TPS has been designed and fabricated via ceramic foaming technique and phenolic resin infiltration process. The SiCO foams were produced via two different routes: 1). a mixture of chopped carbon fibers reinforced polysiloxanes and PLA microfibers, served as sacrificial fibers was decomposed at higher temperature to produce microchambers; 2) the liquid ceramic precursor was mixed with blowing agent and the blend was cured and foamed, leading to a one-step ceramic foam process. After the pyrolysis, the ceramic foams were infiltrated with phenolic resin followed by the resin cross-linking in order to protect the ceramic skeleton at high temperature and to enhance mechanical properties. The materials of both routes were characterized via SEM, three point bending testing, oxyacetylene ablation torch testing and shock tube testing to investigate the microscopic morphology, mechanical properties and thermal behaviors of composites TPS.

New Precusors for Powders, Coatings, and Matrix or Fibers of Composites

Room: Tomoka B

Session Chair: Sea-Hoon Lee, Korea Institute of Materials Science

3:20 PM

(ICACC-S12-023-2016) Spontaneous metal whisker growth on MAX phases, the phenomenon, the mechanism (Invited)

Z. Sun*[1]; P. Zhang[1]; Y. Zhang[1]; Y. Liu[1]; B. An[2]; T. Iijima[2]; 1. Southeast University, China; 2. National Institute of Advanced Industrial Science and Technology (AIST), Japan

Understanding the spontaneous metal whisker growth has been a challenge for decades, that will be briefly reviewed. And the whiskering phenomenon on the surface of MAX phase materials, which is relatively new, poses a potential barrier to their application, since it casts doubts about their stability. Mainly with Cr_2GaC as an example, we found the elemental source for spontaneous growth of Ga whiskers to be the free Ga contained in the MAX phase material, which exists in different forms. A catalyst-based model, with cleavage planes of MAX phase grain involved as catalyzing sites, is proposed to understand the formation of Ga whiskers. This model explains and predicts well the growth behavior of the whiskers. Due to the unusual similarity of the morphologies between the Ga whiskers and the general metal whiskers, such as tin whiskers which haunted the electronics industry for roughly 70 years, the significance of the catalyst-based model on uncovering the myth of the general metal whiskers is obvious.

3:50 PM

(ICACC-S12-024-2016) *In-situ* borothermic route to Group 4 nanosized metal borides particles

L. Zoli*[1]; P. Pinasco[1]; D. Sciti[1]; 1. ISTEC-CNR, Italy

An *in-situ* borothermal synthesis was investigated to achieve submicron sized ZrB_2 particles at temperature <1000°C in flowing of Ar/H_2 atmosphere. We propose the use of sodium borohydride ($NaBH_4$) as a boron source as an alternative to elemental boron or boron carbide. Advantages of sodium borohydride with respect to the latters are a lower price, higher purity and lower melting point. Furthermore, the reaction byproducts are easily removed by washing with cold diluted HCl solution. The powders, e.g. ZrO_2 and $NaBH_4$, were dry mixed and thermally treated at increasing temperatures (600, 900, 1100°C) and B:Zr ratio (4:1, 3:1, 2:1) to study the reaction yield. X-Ray diffraction and FE-SEM and STEM techniques were used to analyses reagents and products before and after synthesis. For the sake of comparison, parallel experiments were also conducted with elemental boron using the classical borothermal reaction in the same conditions. It was found that the reaction of ZrO_2 with $NaBH_4$ was completed after 30 min at 900°C, with a 4:1 B:Zr ratio, e.g. at 200°C lower than typical synthesis temperature via the borothermal reaction. Microstructural observation revealed ZrB_2 particles with dimensions around 100 nm. After successful synthesis of ZrB_2, work is in progress to extend the reaction to other refractory metal oxides, such as HfO_2 and TiO_2.

4:10 PM

(ICACC-S12-025-2016) Single-Source-Precursor Synthesis and Properties of Hf-Containing Ultrahigh-Temperature Ceramic Nanocomposites (UHTC-NCs)

J. Yuan[1]; Q. Wen[1]; E. Ionescu*[1]; 1. Technical University Darmstadt, Germany

Polymer-derived ceramic nanocomposites (PDC-NCs) can be synthesized via thermal conversion of suitable single-source precursors, leading in a first step to amorphous single-phase ceramics, which subsequently undergo phase separation processes to furnish bi- or multiphase ceramic nanocomposites. PDC-NCs have been shown to be excellent candidate materials suitable for applications at ultrahigh-temperatures and under harsh environments. In the present work, amorphous SiHfCN- and SiHfBCN-based materials were synthesized via cross-linking and ceramization of tailor-made single-source precursors. High-temperature annealing of the obtained amorphous ceramics led to UHTC-NCs with promising compositions, such as SiC/HfC, HfN/Si_3N_4/SiBCN or HfC/HfB_2/SiC. The presented results emphasize a convenient preparative approach to nano-structured ultrahigh-temperature stable materials starting from greatly compliant single-source precursors. Additionally, recent results concerning the stability of the prepared UHTC-NCs in ultraharsh environments (i.e., oxidative atmosphere, combustion atmosphere, hydrothermal environment) will be presented and discussed.

4:30 PM

(ICACC-S12-026-2016) Synthesis of Sinterable Titanium Diboride (TiB_2) powders

A. M. Celik*[1]; R. A. Haber[1]; 1. Rutgers University, USA

Titanium diboride powders were synthesized by using borothermic reduction reactions from titania, boron carbide and carbon powder mixtures. Starting powders were mixed and reacted at 1800 °C for 30 min to form phase-pure, fine TiB_2 powders. Spark Plasma Sintering method was used to manufacture dense samples with no sintering additives. Chemical analysis, phase determination, morphology imaging, and mechanical property measurements were performed on both powders and bulk samples. Production of dense monolithic TiB_2 ceramics with good mechanical properties was achieved.

S13: Advanced Materials for Sustainable Nuclear Fission and Fusion Energy

Accident Tolerant Fuels III and Nuclear Graphite

Room: St. John

Session Chairs: Koroush Shirvan, Massachusetts Institute of Technology; Takaaki Koyanagi, Oak Ridge National Laboratory

1:30 PM

(ICACC-S13-018-2016) Fabrication and Characterization of SiC-SiC Composite-based Accident Tolerant Cladding for Light Water Reactor (Invited)

C. Deck*[1]; H. Khalifa[1]; G. Jacobsen[1]; J. Sheeder[1]; J. Zhang[1]; O. Gutierrez[1]; J. Stone[1]; C. A. Back[1]; 1. General Atomics, USA

Silicon carbide (SiC) offers high temperature strength, low gas permeability, and stable behavior under neutron irradiation. When reinforced with SiC fibers (as a SiC-SiC composite), significant toughness improvements are obtained and pseudo-ductility is observed. A multi-layered cladding design shows promise to couple the hermetic properties of monolithic SiC with the toughness of the composite, and has potential to offer improved performance and enhanced accident tolerance in light water reactor applications. Current work has focused on scaling up fabrication capabilities while meeting straightness, uniformity, and roughness requirements. Non-destructive x-ray computed tomography (XCT) examination has been applied to evaluate microstructure and geometric tolerances. An analytic model has been developed to predict cladding behavior under reactor operating conditions, and a large set of SiC-SiC data was obtained in order to provide statistically significant mechanical behavior results as input to this model. Thermal conductivity and permeability of cylindrical SiC-based fuel cladding specimens were also measured to assess cladding performance in the as-fabricated and stressed conditions. An overview of these results is presented to show the progress in fabrication, characterization, and modeling of SiC-based structures for nuclear fuel cladding applications.

2:00 PM

(ICACC-S13-019-2016) Characterization of Strength and Toughness of Complex TEP SiC-SiC Composites Structures

H. Zhao[1]; W. Housley[1]; K. Shapovalov[1]; H. Khalifa[2]; X. Huang*[1]; 1. University of South Carolina, USA; 2. General Atomics, USA

The fabrication of high strength, nuclear-grade silicon carbide (SiC) fiber reinforced SiC matrix composite structures for reactor core components is key technology for implementation of these materials in advanced reactor designs. SiC/SiC composite plates were fabricated at General Atomics by a transient eutectic-phase (TEP) high pressure sintering method. Characterizations of mechanical strength and toughness were conducted on small coupon sized samples cut off from different locations of the SiC/SiC structural components with hole features. Several methods were applied to quantify the mechanical strength and toughness of SiC/SiC composite plates. Single edge notched beam (SENB) and double torsion (DT) testing methods were adapted to quantify the fracture toughness of pre-notched SiC composite samples. Crack-mouth-opening and surface displacement field were tracked with digital image correlation (DIC) technique. The measured deformation information capture the growth of a damage zone which is used to quantify the size of an equivalent "crack". Acoustic emission (AE) was applied to detect the onset of microscopic cracking and sliding events, and correlated to the measured macroscopic stress-strain behavior. The study on the TEP SiC composites indicated excellent strength, prominent pseudo-ductile failure behavior and much improved toughness in comparison with monolithic SiC materials.

2:20 PM

(ICACC-S13-020-2016) Performance evaluation of SiC/SiC Cladding for LWR Applications

G. Singh*[1]; K. Terrani[2]; Y. Katoh[2]; 1. Oak Ridge National Lab, USA; 2. Oak Ridge National Laboratory, USA

Fukushima events shifted the focus of nuclear research towards development of accident tolerant fuel cladding system. SiC/SiC cladding is one of the concepts being considered for the improved cladding integrity. To evaluate the performance of SiC/SiC cladding under operating conditions a thermo-mechanical analysis of the cladding has been performed. State of the art properties of SiC/SiC composites were employed to accurately determine the thermo-mechanical behavior of the cladding. The dependence of various properties on irradiation and temperature were incorporated into the analysis for predicting the in-reactor performance. Results shed light on the viability of the SiC/SiC composite cladding concept for LWR systems.

2:40 PM

(ICACC-S13-021-2016) Effort Towards Correlation Between SiC-SiC Composite Mechanical Strength and Architecture and Microstructure Measured using X-Ray Computed Tomography

J. Sheeder*[1]; C. Deck[1]; H. Khalifa[1]; G. Jacobsen[1]; J. Zhang[1]; C. Back[1]; 1. General Atomics, USA

As the development of silicon carbide fiber reinforced silicon carbide matrix (SiC-SiC) composites continues with an end goal of use as nuclear fuel cladding and other reactor components, a need arises for non-destructive evaluation (NDE) techniques to act as a quality control tool. This work describes the characterization of composite void distribution, detailed surface dimensions, and fiber architecture using X-Ray Computed Tomography (X-Ray CT). Initial efforts to correlate this data with mechanical testing (hoop strength via elastomeric insert) are discussed. The ultimate goal of this effort is to use the data provided from X-Ray CT to help predict estimated failure locations and strengths on SiC/SiC composite tubes with no destructive test requirements. To help reach this goal, a variety of architectural features (sample volume, void size/location/volume, surface roughness, fiber/braid angle, wall thickness, roundness and cylindricity) are measured. Techniques used on CT reconstructions are discussed along with common challenges faced when measuring said features.

3:20 PM

(ICACC-S13-022-2016) Hot water corrosion behavior of ion irradiated high purity SiC (Invited)

S. Kondo*[1]; M. Lee[1]; T. Hinoki[1]; 1. Kyoto University, Japan

SiC and SiC/SiC are attracting attention as alternative materials for fuel cladding because of the conceivable better chemical stability and strength under LOCA. We have focused on the effect of irradiation damage on the hydrothermal corrosion of SiC, because the irradiation significantly modified the microstructure and create the defect levels within the band gap. In this study, the corrosion behavior following the ion irradiation was studied for high purity SiC, such as two types of CVD-SiC and sintered SiC. Samples were irradiated with Si ions up to 10 dpa at 400 or 800 °C in DuET facility, Kyoto University. The irradiated surface subjected to 320 or 360 °C water (20 MPa) was studied by scanning and transmission electron microscopy. The electrode potential was measured for both the irradiated and unirradiated regions. Selective corrosion was observed at crystallographic boundaries such as grain boundaries, twin boundaries, and stacking faults regardless of the irradiation. It is clear that the regions ion-irradiated were preferentially damaged, indicating the operation of the irradiation accelerated corrosion in SiC. This work was performed under contract with Toshiba Corporation in "Research and Development of Innovative Technologies for Nuclear Reactor Core Material with Enhanced Safety" entrusted to Toshiba by the Ministry of Education, Culture, Sports, Science and Technology of Japan (MEXT).

3:50 PM

(ICACC-S13-023-2016) Proton irradiation of joints of silicon carbide

M. Gentile*[1]; T. Abram[1]; 1. The University of Manchester, United Kingdom

The development of joints of silicon carbide tubes is a key issue in the deployment of accident tolerant nuclear fuels. This research work studies the microstructure and the properties of joints of silicon carbide tubes after proton irradiation. Joints made of calcia-alumina glass were proton irradiated to 10 dpa at 400°C. The joints were produced through laser brazing. The microstructure and the properties of the glass were characterised before and after proton irradiation through secondary electron microscopy, x-ray diffraction analysis and nano-indentation. The data shows that the alumina – calcia glass have good performance under irradiation.

4:10 PM

(ICACC-S13-024-2016) Property evaluation and microstructure characterization of the A3-3 matrix graphite for the Chinese HTR-PM pebble-style fuel elements

X. Zhou*[1]; A. A. Campbell[2]; Y. Katoh[2]; B. Liu[1]; 1. Tsinghua University, Beijing, China, China; 2. Oak Ridge National Laboratory, USA

The Chinese High Temperature gas-cooled Reactor, Pebble-bed Module (HTR-PM), will utilize TRISO fuel, centrally loaded into spherical fuel elements, and surrounded by a shell of matrix graphite. The matrix graphite provides structural support to the fuel, prevents fuel damage, and allows heat transfer from the fuel to the coolant. The A3-3 matrix graphite being investigated was prepared at the Institute of Nuclear and New Energy Technology, Tsinghua University of China. A3-3 contains 64wt% natural flake graphite, 16wt% artificial graphite, and 20wt% phenol resin binder, which reduces to 71wt% natural graphite, 18wt% artificial graphite, and 11wt% phenol resin-derived coke carbon, after the final heat treatment. The material sources for this A3-3 are different then historical A3-3, which is why microstructure characterization and the evaluation of mechanical properties of this new composition A3-3 is required. This presentation will discuss microstructure features, such as the porosity, pore size and distribution, and multiple

physical, mechanical, and thermal properties of this material, such as strength, elastic modulus, and coefficient of thermal expansion.

4:30 PM

(ICACC-S13-025-2016) Microstructural Evolution in Neutron Irradiated Fine-Grained Graphite

A. A. Campbell*[1]; Y. Katoh[1]; 1. Oak Ridge National Laboratory, USA

Two next-generation nuclear reactors, the Very-High Temperature Reactor and the Molten Salt Reactor, will utilize graphite as the primary core structural material. From a safety standpoint, it is necessary to understand how the graphite will perform to estimate the lifetime of the core internals, including how various mechanical and thermal properties change in the high-temperature and neutron irradiation environments. The current limitation is that predicting the behavior of a new graphite grade is limited because the dependencies of property changes on the evolving microstructure are still unknown. Therefore, each new graphite grade requires a multi-year irradiation program in a test reactor to measure these changes. This lack of the understanding is because graphite is a composed of microstructure features that range from angstroms to meters, and some techniques necessary to investigate these features have only been developed in the last few years. This presentation will discuss the current investigations at Oak Ridge National Laboratory into the microstructure changes of different graphites that have been irradiated in the High Flux Isotope Reactor including: pore size (optical microscopy, μ-CT, porosimetry), crystallite dimensional change, anisotropy (ellipsometry), and Raman spectroscopy. Lastly these changes will be compared to the property changes to suggest possible controlling mechanisms.

S14: Crystalline Materials for Electrical, Optical and Medical Applications

Optical Material II

Room: Tomoka C

Session Chair: Edith Bourret, Lawrence Berkeley National Laboratory

1:30 PM

(ICACC-S14-016-2016) Single-crystal fiber optics: a review (Invited)

J. A. Harrington*[1]; 1. Rutgers University, USA

Single-crystal (SC) fiber optics made from oxide crystals such as sapphire and YAG have promising applications as both passive and active fibers. Most SC fibers such as sapphire are transmissive up to about 3 mm and, therefore, are potentially excellent fibers for the transmission of high-power Er:YAG lasers operating near 3 mm. As an active fiber, SC fibers grown from rare-earth doped YAG and other garnets could provide an excellent alternative to conventional glass fiber lasers and amplifiers for the generation of extremely high laser powers. In general, the optical and physical properties of SC fibers, including reduced non-linear effects such a stimulated Brillouin scattering (SBS) and high thermal conductivity, often exceed those of glass fiber optics. The methods to grow SC oxide fibers, which include laser heated pedestal growth (LHPG), will be reviewed along with their optical and laser properties.

2:00 PM

(ICACC-S14-017-2016) Cladded Doped Single Crystals Fibers for High Power Laser and Amplifier Applications (Invited)

G. Maxwell*[1]; 1. Shasta Crystals Inc, USA

Single crystal fibers are an intermediate between laser crystals and doped glass fibers. They have the advantages of guiding laser light and matching the efficiencies found in bulk crystals, which makes them ideal candidates for high-power laser and amplifier applications. One major challenge has been to clad the core doped fibers with transparent cladding, thick enough to allow optimum transmission and guiding throughout the fiber. This work focuses on the growth of a flexible fiber with a core of dopant (Er, Nd, Yb, etc…) and a polycrystalline clad of suitable material to enable tailoring of the numerical aperture of the fiber. The core of the fiber can be made of YAG or CaAlGdO4 (CALGO) and the clad can be made of YAG, alumina, silica or CALGO. A combination of growth and cladding experiments are described. Several ways of achieving thicker claddings are envisioned and explored. Scattering loss measurements at visible wavelengths along with dopant profile characterization are also presented.

2:30 PM

(ICACC-S14-018-2016) Some aspects of the growth of borate-based crystals by the micro-pulling down technique (Invited)

M. Ferriol*[1]; F. Assi[1]; M. Cochez[1]; M. Aillerie[1]; 1. Université de Lorraine, France

Since a few years, we are involved in the search of efficient non-linear optical materials for V-UV laser beam generation. Presently, we are working on borate-based crystals grown by the micro-pulling down technique in order to take advantage of the fiber shape for the making of integrated devices. The crystallographic structure of borates is based on arrangements and associations of $[BO_3]^{3-}$ and $[BO_4]^{5-}$ groups with a triangular and tetrahedral geometry. The presence of $[BO_4]^{5-}$ groups undergo the existence of $[B_3O_6]^{3-}$ and $[B_3O_7]^{5-}$ structures. All of them are at the origin of nonlinear optical properties of borate-based compounds. As several borate melts are often very viscous, it is necessary to use a flux for growing crystals. The search of a convenient flux requires the study of the corresponding phase diagrams which is a part of our activities. The originality of our research is that very few works have been devoted to the growth of crystal fibers by the micro-pulling down technique using a flux. The purpose of this talk is to present our latest results and state of the art on the growth and characterization of crystal fibers of different materials: $Ca_5(BO_3)_3F$, $Bi_2ZnB_2O_7$, $LaBGeO_5$ and $BaCaBO_3F$.

New Direction II

Room: Tomoka C

Session Chair: Qiang Li, Tsinghua University

3:20 PM

(ICACC-S14-019-2016) A new mechanism of piezoresponse in ferrielectric single crystals: Polarization Twist (Invited)

Y. Noguchi*[1]; Y. Kitanaka[1]; M. Miyayama[1]; 1. The University of Tokyo, Japan

The electro-mechano property of ferroelectrics governs the performance of the piezoelectric devices such as sensors, actuators and ultrasonic imagings. It has recently been understood that a phase transition (including polarization rotaion) by applying an electric field (E) is the origin of the superior electro-mechano property. Here, we report a piezoresponse up to 1000 pm/V originating from a new mechanism in ferrielectric single crystals. $(1–x)Bi_{0.5}Na_{0.5}TiO_3–xBaTiO_3$ [BNT–BT] ferrielectric single crystals were grown by the TSSG method at a high oxygen pressure (Po_2) of 0.9 MPa. Single-crystal structural analysis under electric fields demonstrate that BNT–7% BT crystals exhibited an extremely high piezoelectric strain constant d_{33} up to 1000 pm/V. The structural analyses based on neutron powder diffraction and single-crystal XRD reveale that the high d_{33} originates from a polarizaiton enhancement accompanied by octahedral rotation in the *P*4*bm* ferrielectric phase.

3:50 PM

(ICACC-S14-020-2016) Crystal growth methods as a tool for manufacturing metamaterials and plasmonic materials (Invited)

D. A. Pawlak*[1]; M. Gajc[1]; K. Sadecka[1]; P. Osewski[1]; B. Surma[1]; K. Wysmulek[1]; J. Sar[1]; 1. Institute of Electronic Materials Technology, Poland

Novel research areas have been developed in the field of photonics: metamaterials and nanoplasmonics. By utilizing the ideas developed in these research areas and using specially-designed materials, unusual electromagnetic properties such as artificial magnetism, negative refractive index, cloaking and squeezing photons through subwavelength holes have been demonstrated. These novel fields need new material fabrication techniques, especially bottom-up approaches such as self-organization. Two novel bottom-up manufacturing methods will be presented: (i) method based on directionally-grown self-organized eutectic structures; and (ii) NanoParticles Direct Doping method (NPDD) based on directional solidification of dielectric matrices doped with various nanoparticles. In both cases we apply one of the crystal growth methods - the micro-pulling down method - to create the material. We demonstrated (i) volumetric materials with localized surface plasmon resonance at visible and IR wavelengths; (ii) materials with enhanced luminescence eg. at 1.5 um wavelength, and up-conversion processes due to plasmonic resonances; (iii) material with subwavelength transmission at IR frequencies; (iv) materials with enhanced Faraday effect; and (v) materials for phonoanodes in photoelectrochemical cells for generation of hydrogen.

4:20 PM

(ICACC-S14-021-2016) Preparation of Transparent Phosphors using Melt Synthesis Method

K. Toda*[1]; 1. Niigat University, Japan

Recently, transparent phosphors such as glass, glass-ceramic and single crystal have been extensively investigated as a promising materials for high power white LEDs due to their excellent thermal and chemical stabilities. In this study, we are synthesized the transparent phosphors by the melt synthesis method using are-imaging furnace and the optical properties of the glass phosphors obtained in this study are characterized. The reaction of melt synthesis method is similar to that of liquid phase reaction method, as a result, this method is more suitable to obtain the homogeneous samples compared with a conventional solid-state reaction method. Furthermore, arc-imaging furnace can be rapidly heated up to high temperature and also rapidly cooled by removing the sample stage or shutdown the light source. Therefore, the melt synthesis method using arcimaging furnace is suitable for rapid screening of novel phosphors and for synthesizing the metastable oxide materials or glass phosphors. From this point of view, we have successfully synthesized some of the novel oxide powder phosphors and oxide glass phosphors for white LEDs. In this study, we mainly discusses on the optical properties of the novel glass phosphors prepared by this method and the availability of the melt synthesis method using arc-imaging furnace for developing the novel glass, glass-ceramic and single crystal phosphors are also discussed.

5th Global Young Investigator Forum

Advanced Ceramic Materials Prediction, Design and Novel Processing

Room: Coquina Salon F

Session Chairs: David Poerschke, University of California Santa Barbara; Erica Corral, The University of Arizona; Jesse Angle, Exponent Inc.

1:30 PM

(ICACC-GYIF-019-2016) Microstructure and Mechanical Properties of Ultra-High Purity ZrB_2 Using Thermodynamic Assisted Models and Spark Plasma Sintering (Invited)

E. L. Corral*[1]; 1. The University of Arizona, USA

Zirconium diboride is an ultra-high temperature ceramic (UHTC) with attractive material properties for use in extreme hypersonic flight environments and energy applications. The diboride phase is the basis for high temperature oxidation resistant UHTC composites using secondary phase reinforcements that also enhance high temperature properties of ZrB_2-based composites. However, the mechanical properties are limited by the impurity content found in the diboride source powder. Thus our work focuses on developing a methodology to process the highest purity ZrB_2 using spark plasma sintering (SPS) and computational thermodynamics analysis coupled with high-resolution atomic scale electron microscopy. A clear path towards processing ultra-high purity ZrB_2 ceramics is presented using a combined experimental and thermodynamically assisted processing method through thermal treatments and oxide reducing agents carbon and boron carbide (B_4C). Computational thermodynamic phase diagrams consisting of the Zr-O-C ternary and Zr-B-C-O quaternary are developed to predict and explain the microstructures found after SPS. Scanning electron microscopy (SEM) and scanning transmission electron microscopy (STEM) analysis shows evidence of SPS-unique grain boundary cleaning and the potential to use current to further improve ZrB_2+B_4C purity.

2:00 PM

(ICACC-GYIF-020-2016) Investigation of the role of carbon ZrO2 mixing in ZrN powder synthesis

S. Naim Katea*[1]; 1. Uppsala University, Sweden

ZrN is of great interest due to its hardness, durability, thermal conductivity. Lately the need for a nano-phase powder has emerged as ZrN is chosen as the matrix for U, Pu and Am in the Gen IV Pb and Pb-Bi cooled reactors. A problem is the present micron sized and impure ZrN produced through carbothermal nitridation is the very high sintering temperatures required even with SPS, which is not suitable for production. Present carbothermal nitridation use milling/mixing of ZrO2 and carbon black, but even with long time milling poor mixing is obtained which leads to mixed Zr(O,N), ZrN and ZrC phase and coarse grain sizes. Here three routes with different degrees of mixing of the carbon and ZrO2 source are compared in the carbothermal nitridation; (i) ZrO2 and carbon black, (ii) ZrO2 and sucrose added from solution and (iii) an all solution process using a sucrose-Zr alkoxide mixture. A range of techniques were used to describe the processes; TG-DTA, XRD, IR and Raman spectroscopy SEM-EDS and TEM-EDS. It was found that the all solution based process providing an extremely good mixing of the carbon and ZrO2 in the 4 nm sized ZrO2 surrounded by a graphenic carbon provided the best materials after heating to 1500C, with phase pure ZrN in 20-30 nm size according to XRD, but detailed studies with TEM revealed a 4-5 nm thick shell of an almost amorphous phase and that there was probably some carbon in the material.

2:20 PM

(ICACC-GYIF-021-2016) The Use of Concrete Admixtures to Disperse Highly Loaded Silicon Nitride Ceramic Suspension Gels (CeraSGels) for Room-Temperature Processing

L. Rueschhoff*[1]; J. Youngblood[1]; R. Trice[1]; 1. Purdue University, USA

The mechanical strength and workability of modern cements have improved with the development of a variety of advanced chemical admixtures. Commercially available water reducing admixtures (WRAs) are used in cement mixtures to decrease the water content needed through steric stabilization of cementitious particles. These WRAs are composed of polycarboxylates containing a charged backbone that adhere to the particle surface, with polymer side chains that repel each other to stabilize the particles to gain increased solid loading. While these WRAs are used most commonly in cement mixtures, this research focuses on using a variety of commercially available compositions to stabilize highly-loaded aqueous silicon nitride suspensions. The unique rheology obtained from the use of these WRAs allows for forming at room temperature via injection molding, with unprecedented solid loadings (>45 vol%). Preliminary rheology, forming, and sintering studies will be presented to prove this a viable process for forming near-net and complex shapes of advanced silicon nitride parts.

2:40 PM

(ICACC-GYIF-022-2016) Wet oxidation behavior of silicide and SiC-fiber-reinforced composites fabricated by melt infiltration using Si-Hf and Si-Ti alloy

T. Tsunoura*[2]; Y. Okubo[2]; K. Yoshida[2]; T. Yano[2]; T. Aoki[1]; T. Ogasawara[1]; 1. Japan Aerospace Exploration Agency, Japan; 2. Tokyo Institute of Technology, Japan

SiC fiber-reinforced composites are one of the promising materials for high temperature structural materials such as thermal protection system of hypersonic aircraft and jet engine components due to their excellent properties under extreme condition. In our previous work, SiC fiber-reinforced composites were successfully fabricated by melt-infiltration method using Si-8.5at%Hf and Si-16 at%Ti eutectic alloy below 1400°C. In this study, their oxidation behavior was evaluated. Three-dimensional preforms consisting of amorphous SiC fibers were used as the reinforcement, and the fibers were coated with CVI-C as an interphase and CVI-SiC for protecting the CVI-C and the matrix. Then, the preform covered with Si-8.5at%Hf or Si-16at%Ti alloy was heated up to 1375-1390°C, and the SiC fiber-reinforced composites were obtained. Oxidation tests were carried out at 800-1200°C for 100 hours in gas-flow mixed air with steam. The composites using Si-Hf alloy showed catastrophic oxidation behavior after wet oxidation test at 800-1000°C. On the other hand, in the composites using Si-Ti alloy, thin oxidation layer with the thickness of about 10 mm was formed after wet oxidation test at 1000°, and catastrophic oxidation behavior did not occur in any condition.

3:20 PM

(ICACC-GYIF-023-2016) Mixing and thermal decomposition investigations in blend of preceramic polymers

K. Kita*[1]; M. Fukushima[1]; Y. Yoshizawa[1]; N. Kondo[1]; 1. National Institute of Advanced Industrial Science and Technology (AIST), Japan

Preceramic polymers, including organic and inorganic polymers with a continuous Si–R network (R =O, C, N and B), can provide ceramic materials as residue through their decomposition at elevated temperature In this study, we will try to make silicon based ceramic products by using polymer blend containing polycarbosilane (PCS) and polysiloxanes with strategically selected mixing ratio, in order to achieve the shape stability and improved specific surface area with nano-size porosities. Molten viscosity, oxidation curing and thermal decomposition of preceramic polymer blend were significantly affected by the mixing ratio of polysiloxanes to PCS, leading to the shape tolerance and thermal stability of pyrolyzed blends. Microstructure and mechanical properties of pyrolyzed products will be also discussed, in terms of mixing ratio of polymer blend.

3:40 PM

(ICACC-GYIF-024-2016) Formation of micro-textured alumina bodies under applied magnetic field using novel, water-soluble polymer gelling system

C. A. Moorehead*[1]; V. L. Blair[1]; R. E. Brennan[1]; 1. US Army Research Laboratory, USA

Alumina is an excellent candidate as an optical material for laser gain media due to its high thermal conductivity. However, it is challenging to make transparent because of its anisotropic crystal structure. To combat the anisotropy, we aim to magnetically align the particles such that the change in index of refraction is minimized from grain to grain, thus reducing light scattering. In order to do that, a processing method that provides a liquid medium in which the particles can rotate during alignment then freezes them in place after alignment is necessary. This work describes a gel-casting method using a water-soluble gelling system of isobutylene and maleic anhydride co-polymer that provides such a mobile liquid medium necessary for magnetic alignment. It then forms a network *in-situ,* at very low concentrations (0.3-0.5 wt%), that traps the particles in place and prevents miss-alignment prior to sintering. The product is a dense, near-net shaped green body with high solids loading, low organic content, low shrinkage, and moderately high strength. This presentation will focus on the adaptation of this gelling system to variously sized particles, investigation of the gel formation mechanism, and analysis of the micro-texture, via XRD, of magnetically aligned bodies cast in a magnetic field.

4:00 PM

(ICACC-GYIF-025-2016) Morphology and engineering properties of cellular ceramics prepared by gelation and freezing method

M. Fukushima*[1]; C. Matsunaga[1]; T. Ohji[1]; Y. Yoshizawa[1]; 1. National Institute of Advanced Industrial Science and Technology (AIST), Japan

Tailored cellular architectures composed of unidirectional oriented micrometer-sized cylindrical pores with very high potrosities above 90vol%, nearly honeycomb-like shape, could be controlled by gelation of ceramic raw powder dispersed slurry and its freezing. This paper will focus on the advanced processing methodology to modulate pore morphologies such as size, shape and orienation varied by gelation freezing approach, that can improve various functionalities such as mechanical properties, machinability, fluid permeability, thermal conductivity and electrochemical response. This gelation freezing processing is simple, ecofriendly and versatile way to control pore architectures and yield large monoliths with improved characteristics.

4:20 PM

(ICACC-GYIF-026-2016) Direct ink-writing of a preceramic polymer and fillers to produce hardystonite ($Ca_2ZnSi_2O_7$) bioceramic scaffolds

G. Franchin*[1]; A. Zocca[1]; H. Elsayed[1]; E. Gioffredi[2]; P. Colombo[1]; 1. University of Padova, Italy; 2. Turin Polytechnic, Italy

A novel approach for the production of porous polymer-derived ceramics will be presented, which is the application of direct ink-writing process to a system comprising a preceramic polymer and fillers followed by pyrolysis and thus ceramization. The incorporation of active fillers to a preceramic polymer opens the possibility of generating complex ceramic phases with a controlled and pure composition upon pyrolysis. The latest developments on the 3D-printing of an ink based on a preceramic polymer and fillers will be presented, focusing on a novel composition for developing hardystonite ($Ca_2ZnSi_2O_7$) from a preceramic mixture containing zinc oxide and calcium oxide precursors as active fillers. Suitable formulations were investigated for the extrusion of fine filaments

(350 μm diameter) through a nozzle. The conditions and requirements for the production of highly porous lattices with spanning features will be discussed in detail, focusing on the rheology of the inks (flow curves, dynamic oscillation tests and viscosity recovery tests). The importance of gel formation and the double role of the preceramic polymer as silica precursor and viscosity increasing agent will be examined as well. The influence of the heat treatment atmosphere (air or nitrogen) on the morphology, phase formation and crushing strength of the highly porous scaffolds produced will be debated.

4:40 PM

(ICACC-GYIF-027-2016) Manufacture of complex-shaped ceramic components with highly oriented reinforcing phase by horizontal dip-spin casting

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A novel ceramic processing method, called Horizontal Dip Spin Casting (HDSC), enabled fabrication of tubular ceramic parts with a highly aligned reinforcing chopped fiber phase. In HDSC, highly loaded (>50 vol.%) aqueous ceramic suspensions with a minimal amount (≤5 vol.%) of water-soluble polymer, employed as a rheological modifier, were produced with carbon whisker contents up to 30 vol.%. During forming, cylindrical foam molds were dipped into the suspension and rotated uniaxially to align the reinforcing phase. Rheological study of suspensions containing alumina powder and alumina powder/carbon whiskers, which were used as model material systems, showed that the suspensions followed a yield-pseudoplastic flow behavior. The degree of alignment of the carbon whisker phase in the green bodies was characterized for various suspension formulations, carbon whisker content and forming speeds. Characterization indicated high alignment for all cases, confirming the effectiveness of HDSC for aligning high aspect ratio phases in curved ceramic specimens.

5:00 PM

(ICACC-GYIF-028-2016) Micro/nano-indentation and scratching of Si_3N_4 based nanocomposites

C. Lee*[1]; H. Lu[2]; J. Huang[1]; 1. National Cheng Kung University, Taiwan; 2. National Chin-Yi University of Technology, Taiwan

In our previous work, $Si_3N_4/TiC_{0.37}N_{0.63}$ nanocomposites were consolidated by spark plasma sintering, and the average grain width of Si_3N_4 and $TiC_{0.37}N_{0.63}$ are about 85 nm and 90 nm, respectively. The wear resistance of $Si_3N_4/TiC_{0.37}N_{0.67}$ is increased by 30%, primarily due to the effects of nanostructured grains. Thus, it is essential to understand the mechanical responses and micro-fracturing behavior under low stress environment. First, a brittleness index of the nanocomposites is used to predict the micro-fracturing behavior. All of the as-sintered specimens demonstrate similar quasi-plastic fracturing modes with brittleness index of ~0.6, regardless of $TiC_{0.37}N_{0.63}$ content. Secondly, the indentation deformation and micro-cracking is evaluated by micro/nano-indentation. The micro-hardness, young's modulus, and elastic work ratio of Si_3N_4 based nanocomposites proportionally decrease with increasing $TiC_{0.37}N_{0.63}$ content. Finally, single-grid-scratching tests were conducted. Damage occurred predominantly in the form of intergranular fracture with lateral crack propagation resulting in the majority of material removal. The decreasing micro/nano-indentation properties and scratching resistance are attributed to the decline of relative density of the nanocomposites. However, the distributed nano-$TiC_{0.37}N_{0.63}$ in Si_3N_4 matrix enhance the fragment when a low stress is applied.

5:20 PM

(ICACC-GYIF-029-2016) Nitridation behavior of silicon powder compacts doped with Y_2O_3 and MgO additives

C. Matsunaga*[1]; Y. Zhou[1]; D. Kusano[2]; H. Hyuga[1]; Y. Yoshizawa[1]; K. Hirao[1]; 1. National Institute of Advanced Industrial Science and Technology (AIST), Japan; 2. Japan Fine Ceramics Co., Ltd.,, Japan

Silicon nitride ceramics with high thermal conductivity are expected to be used as promising substrate materials for the next-generation power devices. Our recent studies found that silicon nitride with both high thermal conductivity and good mechanical properties could be fabricated by a route of sintering of reaction-bonded silicon nitride (SRBSN), and nitridation was a key process for the SRBSN method. In the present study, a high purity silicon powder doped with 2 mol% of Y_2O_3 and 5 mol% of MgO additives was formed into pellets with a diameter of 15 mm and thicknesses ranging from 3 mm to 9 mm by die-pressing and cold isostatic pressing. Nitridation of the pellets were conducted in a nitrogen atmosphere. Effects of a variety of parameters such as nitriding temperature and holding time and thickness of the pellet specimens on the nitridation behavior of silicon were studied through examining the nitridation rates, analyzing the phase compositions and observing the microstructures of the nitrided compacts.

FS2: Advanced Ceramic Materials and Processing for Photonics and Energy

Multi-functional Materials

Room: Coquina Salon G

Session Chairs: Clara Santato, Ecole Polytechnque de Montreal; Oussama Moutanabbir, Ecole Polytechnque de Montreal

1:30 PM

(ICACC-FS2-018-2016) Solution processing of thin- and ultra-thin Fe-containing oxide and nano-composite films (Invited)

G. Westin*[1]; 1. Uppsala University, Sweden

Solution based synthesis routes using metal alkoxides and organically coordinated metal salts have been used to prepare Fe-oxide based thin and ultra-thin films on flat and nano-structured surfaces such as wire arrays of porous nano-particulate films. The systems prepared were of varying complexities from Ti-doped and non-doped a-Fe2O3 via Fe-containing heterometallic spinel and perovskite phases to metal – oxide nano composites with PtNi metal particles in ultra-thin Fe2O3. The syntheses and products were studied with a wide array of analytical techniques including; SEM, TEM, XRD, TGA, DSC/DTA, IR and Raman spectroscopy. Such simple low cost synthesis routes to highly complex nano-materials are required for practical application in many areas of sustainable energy conversion and storage, catalysis and magneto-electric applications

2:00 PM

(ICACC-FS2-019-2016) Observation of in-plane charge transport in monolayer hexagonal boron nitride (Invited)

M. Siaj*[1]; F. Mahvash[1]; T. Szkopek[2]; 1. UQAM, Canada; 2. McGill University, Canada

Hexagonal boron nitride (hBN), also known as white graphite, is a wide bandgap semiconductor that has found use as a high quality dielectric in van der Waals heterostructures incorporating other 2D materials such as graphene. We report the chemical vapor deposition (CVD) growth and characterization of monolayer h-BN. The growth was performed in a tube furnace on Cu foils using an ammonia borane (NH_3-BH_3) precursor. Scanning electron microscopy was used to study the morphology of the as-grown films and optimize growth conditions to yield high coverage of monolayer h-BN. Chemical analysis was performed X-ray photoelectron

spectroscopy. The h-BN structure was investigated by electron diffraction of suspended films. The optical properties of our h-BN films were probed by cathodoluminescence and UV-Vis absorption spectroscopy. In-plane electron transport studies were performed on h-BN films transferred to SiO_2/Si substrates using a variety of electrode geometries. Ni electrodes were used to provide electrical contact. We have observed quadratic scaling of current with voltage, consistent with space-charge limited transport with a mobility of up to ~ 0.01 cm^2/Vs. Our observation of in-plane charge transport suggests that h-BN can function as a semiconductor with appropriately chosen contact electrodes.

2:30 PM

(ICACC-FS2-020-2016) Solution-based Bio-inspired Growth of Photocatalytically Active Nanoporous Membranes and Oriented Nanowires for Water Purification and Splitting (Invited)

D. Kisailus*[1]; 1. UC Riverside, USA

Nanowire arrays were produced on polycrystalline TiO_2 templates via hydrothermal reactions. Wires grow in an epitaxial manner, with their orientation dependent on the underlying TiO_2 grain. The diameter and the number density of the nanowires were tuned by controlling the surface properties of the templates, while the tip sharpness of nanowires was influenced by precursor solubility and diffusivity. Photoelectrochemical (PEC) performance of resultant TiO_2 nanowires for water splitting demonstrated the photocatalytic activity was dependent on the length and areal density of the nanowires, which was controlled by the synthesis conditions and the surface chemistry of the templates. Bio-inspired nanoporous membranes were synthesized using biologically-inspired scaffolds to template the nucleation and growth of TiO_2 with controlled size and phase. By modifying solution conditions, we have produced a self-supporting porous, high surface area TiO_2 nanoparticle membrane with controlled crystallite size, phase, and porosity. These bulk porous TiO_2 membranes can be utilized in photocatalytic applications, eliminating the need for nanoparticle recovery systems, thereby reducing processing costs and increasing amount of viable applications of photocatalytic systems.

3:20 PM

(ICACC-FS2-021-2016) From Thin Films to Nanocrystals: Assorted WO_3 Gas-Sensing Materials from Multifaceted Wet Chemical Processing (Invited)

M. Epifani*[1]; 1. CNR-IMM, Italy

Wet chemical processing of materials is inherently characterized by flexibility features, by controlling the precursor reactivity. These general considerations hold in principle, and of course the term "reactivity" first needs being better defined. From this point of view, hydrolytic processing allows 3D development of the material structure, through progressive inorganic cross-linking. Then, by controlling the spatial cross-linking extent, different materials typologies can be obtained. In this work, hydrolytic processing of tungsten chloroalkoxide precursor in different conditions will be illustrated for the synthesis of WO_3 nanostructures. The chloroalkoxide is less prone to uncontrolled hydrolysis and precipitation, and can be processed in progressively demanding conditions. Simple precursor drying results in classical WO_3 powders, while thin films can be prepared by spin-coating. More advanced processing is possible. Tiny (2-3 nm) monoclinic WO_3 quantum dots can be prepared by solvothermal processing in narrow range of conditions. Finally, layers of WO_x species can be deposited onto TiO_2 nanocrystals, resulting in radical modification of the naked anatase nanostructures. The gas-sensing properties of these materials will be reviewed, further showing the importance of suitable processing for lowering the dimensionality of the final product.

3:50 PM

(ICACC-FS2-022-2016) Structuring of Nanoporous Powders into Hierarchically Porous Nanostructured Adsorbents for Clean Energy (Invited)

F. Akhtar*[1]; 1. Division of Materials Science, Sweden

Nanoporous materials such as zeolites, metal organic frameworks, activated carbons and aluminum phosphates are suitable for catalysis, gas separation, biogas upgrading and storage applications. These high surface area materials are invariably produced in particulate form and need to be assembled into mechanically strong hierarchically porous macroscopic structures such as structured monoliths, honeycombs and laminates for industrially important catalysis and gaseous fuel upgrading and storage applications. Structuring of nanoporous powders enables an optimized structure with high mass transfer, low pressure drop, efficient heat management, and high mechanical and chemical stability. Important properties of the nanostructured adsorbents structures will be discussed with a focus on biogas upgrading, decarbunization of fuels and safe fuel storage. A versatile nanostructurization approach to process nanoporous powders into hierarchically porous monoliths with high CO_2 capture capacity, CO_2 over CH_4 and CO_2 over N_2 selectivity, rapid uptake and release kinetics and high mechanical strength will be discussed. Finally, the concepts of adsorption and diffusion, mass and heat transfer will be combined in a discussion of the optimal porous architecture and geometry of nanostructured adsorbents to fulfill future demands of safe storage and handling of gaseous fuels.

4:20 PM

(ICACC-FS2-023-2016) Stretchable organic bioelectronics (Invited)

F. Cicoira*[1]; 1. Polytechnique Montreal, Canada

Organic electronic devices have attracted particular attention in the last decades for applications in bioelectronics. Besides low-temperature processes, low-cost and ease of processing, another significant advantage of organic devices is their mechanical flexibility. A flexible or stretchable organic device can be plastered on skin to monitor e.g. body movements. A combination of flexible/stretchable architectures with organic bioelectronics could lead to a mechanical compliance device, which will be a promising candidate for future e-skin or e-health applications. However, device development on such materials presents several challenges. Flexible and stretchable substrates are not compatible with conventional photolithography, which renders the fabrication of micro-scale devices difficult. In addition, all the processes involved in the flexible/stretchable bioelectronics device development should be environmentally friendly and the materials used should not contain any toxic ingredients. In this talk I will discuss flexible and stretchable micro-scale electrode arrays and transistors based on the conducting polymer poly-(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonic acid) (PEDOT:PSS) on poly(dimethylsiloxane) (PDMS) substrates.

4:50 PM

(ICACC-FS2-024-2016) Conductive Ceramic Composites for Fabricating High Temperature and Harsh Environment Sensors: Thermal Processing, Stability and Properties

G. A. Yakaboylu*[1]; R. Chockalingam[1]; B. Armour[1]; K. Sabolsky[1]; E. M. Sabolsky[1]; 1. West Virginia University, USA

There is a need for solid-state temperature and pressure sensors to provide real-time measurements within industrial processes such as power generation, coal gasification, and steel and glass manufacturing. Unfortunately, most common electrical materials suffer from structural/functional issues caused by the high operating temperatures (750°-1600°C), alternating reducing/oxidizing environment, high pressure (1000 psi) and corrosive environment. In this study, thermal processing of conductive ceramic composites composed of metal silicides ($MoSi_2$, WSi_2, etc.) and refractory oxides (Al_2O_3,

ZrO_2, Cr_2O_3, etc.) were investigated. After sintering the composites up to 1600°C in argon, densification, microstructure, phase development, short-term/long-term stability and grain growth studies were performed. Quantitative scanning electron microscopy (SEM) image analysis was performed to determine the level of homogeneity of the composites, which has a significant effect on the physical properties. Their 4-point DC conductivities and coefficients of thermal expansion (CTE) were measured between 1000°-1200°C to study their thermal and electrical performance at high temperatures as a function of the composition and processing.

Posters

Poster Session A

Room: Ocean Center Arena

(ICACC-FS2-P001-2016) Consolidation and characterization of calcium lanthanum sulfide infrared optical materials

Y. Li*[1]; Y. Wu[1]; 1. Alfred University, USA

Due to its favorable optical and mechanical properties, calcium lanthanum sulfide ($CaLa_2S_4$) has been studied as a promising candidate for infrared optical material. In this study, calcium lanthanum sulfide materials were prepared through the pressure assisted sintering techniques. XRD and SEM were applied to characterize the as-sintered materials to correlate the phase compositions and microstructures to different processing conditions. The optical and mechanical properties of as-sintered $CaLa_2S_4$ materials were also investigated. The sintering mechanisms of $CaLa_2S_4$ materials were studied for different consolidation methods. In addition, a preliminary study on adding ZnS as the second phase into the $CaLa_2S_4$ materials was performed to understand the influences of ZnS on phases, microstructures and properties of the $CaLa_2S_4$ optical materials.

(ICACC-FS2-P002-2016) Effects of Oxygen Partial Pressure on the Structural and Electrical Properties of Sputtered SnO_X Thin Films

S. Han*[1]; H. Kim[1]; 1. Seoul National University, The Republic of Korea

Transparent conducting oxides (TCOs) are widely used for opto-electrical devices due to high electrical conductivity and high optical transparency in visible light. Up to now mostly commercialized TCOs are n-type, while few p-type TCOs are available due to their poor performances. Recently simple binary oxides such as ZnO, NiO, Cu_2O and SnO have received attentions as promising p-type oxide. In this study the changes of structural and electrical properties of tin oxide films deposited by DC reactive sputtering with various oxygen partial pressure (P_O 3.3~23.1%) were investigated and the proper process conditions for p-type SnO films were also successfully established. The results of XRD and XPS shows that the SnO phase was gradually transformed to SnO_2 with increasing P_O. Especially the films have dominantly SnO phase in P_O under 4.8% and SnO_2 phase in P_O over 9.0%. These structural changes from SnO to SnO_2 cause remarkable changes in electrical properties. The films sputtered in P_O under 3.3% exhibit stable p-type behavior (hole concentration N_h ~10^{18}/cm^3, Hall mobility μ_h 0.8~5.1 $cm^2V^{-1}s^{-1}$). Whereas the films formed in P_O over 16.7% exhibit stable n-type behavior (Nb ~10^{19}/cm^3, μ_h 0.9~1.5$cm^2V^{-1}s^{-1}$). The p-type conduction behavior were also confirmed with TFTs (P_O 3.3%), which shows clear p-type conduction behavior with on/off ratio ~10^3 and linear mobility ~0.7 $cm^2V^{-1}s^{-1}$.

(ICACC-FS2-P003-2016) Development of Low Temperature Glass Systems for High Efficiency Lighting Devices

J. Liao[1]; Y. Chung[1]; F. Wu*[1]; 1. National United University, Taiwan

The development in high power output and advanced optical performance devices is one of the demands for the next generation lighting. The low temperature glass systems, including borosilicates and phosphates with functional element addition, were developed to replace the frequently used polymer materials in lighting packages. The incorporation of Li and Na decreased the characteristic temperatures of the glasses significantly. A lowest forming temperature down to 440°C was found for the phosphate glass. With adequate Bi addition in the borosilicate glasses, a stable structure and enhanced optical performance, including a refractive index upto 1.9 and an 85% transmittance in the visible range, were obtained. The phosphor-containing light conversion layers applied in LED lighting devices were fabricated by gravitational condensation of phosphors into the developed glasses. The control on treatment temperature and time during the condensation process allowed the formation of a homogeneous and stable phosphor-containing glass layer. The phosphor-containing glass layer was successfully applied in high performance white light LED packages.

(ICACC-FS2-P004-2016) Stability of Semiconductor Core Optical Fibers

J. Guo[1]; M. Ordu[1]; J. Bird[1]; S. Ramachandran[1]; S. Basu*[1]; 1. Boston University, USA

Semiconductor core optical fibers allow low loss mid-IR transmission enabling various applications such as remote IR laser delivery and chemical sensing. Ge/Si alloy core optical fibers with borosilicate glass cladding were fabricated by fiber drawing. Ge/Si rods are placed in borosilicate glass tubes and placing additional borosilicate glass tubes concentrically increases the cladding diameter. This study examines the Rayleigh instability of the Si/Ge cores as a function of core diameter, draw temperature and draw velocity, as well as the resulting optical properties of the fibers.

(ICACC-S1-P005-2016) Shear/tensile tests on joined glass-to-steel components

M. Ferraris*[1]; S. Delapierre[1]; T. Scalici[2]; A. Valenza[2]; C. Fichera[1]; M. Avalle[1]; 1. Politecnico di Torino, Italy; 2. Universita' di Palermo, Italy

Results of an experimental investigation on several adhesive joined glass-to-steel components in tensile and torsion mode will be presented. Surface modification of glass by etching and ionic exchange will be done to improve the joined components mechanical strength. Advantages and disadvantages of these tests are discussed and compared with models, with particular focus on the measurement of pure or apparent shear strength of the joints.

(ICACC-S1-P006-2016) Joining of Cf/SiC ceramic composite to itself and TI64 for aerospace applications

P. Gianchandani[1]; M. Bangash[1]; V. Casalegno[1]; M. Ferraris*[1]; 1. Politecnico di Torino, Italy

Silicon carbide based composites (C/SiC and SiC/SiC) are robust materials able to satisfy the high tech requirements needed in mechanical, chemical and electrical applications. They are now used in aerospace industry for hypersonic aircrafts thermal structures rocket propulsion thrust chambers, high temperature burner environments. Ti6Al4V is used in jet aircraft structures and engines for its high strength-to-weight ratios. This work presents the joining of C/SiC composites to itself and to Ti6Al4V by utilizing innovative pressure-less brazing. The joint process is based on silicon and molybdenum as joining materials: Mo3Si, MoSi2 and Mo5Si3 have been found at the joining interface. Joined samples are characterized in term of morphology and mechanical strength.

(ICACC-S1-P007-2016) Long Term Durability Results From Ceramic Matrix Composites: Comparison Across Multiple Material Systems

G. Ojard*[1]; A. Calomino[2]; B. Flandermeyer[3]; J. Brennan[1]; D. Jarmon[1]; D. Brewer[2]; 1. United Technologies Research Center, USA; 2. NASA Langley, USA; 3. Pratt & Whitney, USA

As ceramic matrix composites are being considered for aggressive engineering applications such as in gas turbine engines, an understanding of how the material class performs in the long term needs

to be understood (creep testing). Insight into this can be gained by looking at past performance across multiple material systems. Some ceramic matrix composites have been tested to 10,000 hours and beyond. This has been done for two different composites systems: Melt Infiltrated SiC/SiC and a glass ceramic matrix composite. In addition, creep tests out to 2,000 hours have been performed on a polymer infiltrated pyrolysis manufactured composite. Shorter term tests (500 hours) have been accomplished in a chemical vapor infiltrated composite. For all of these systems, a range of stresses, temperature and times were achieved. Based on this, a comparison can be made between the systems looking at both short term and long term capability and recommendations made based on performance and microstructure.

(ICACC-S1-P008-2016) Influence of Curvature on High Velocity Impact of SiC/SiC Composites

R. Mansour*[1]; M. Kannan[1]; M. Presby[1]; G. Morscher[1]; F. Abdi[2]; C. Godines[2]; J. Shi[3]; S. Choi[4]; 1. The University of Akron, USA; 2. AlphaSTAR Corporation, USA; 3. Rolls Royce Corporation, USA; 4. NAVAIR, USA

As the aerospace industry leans towards using ceramic matrix composites (CMCs) in jet engines, a closer attention must be given in order to understand the damage caused by foreign object impact. To address this issue, several samples of liquid silicon infiltrated fiber reinforced SiC/SiC composites were impacted by high speed projectiles with velocities near the speed of sound at room temperature and pressure. The major objective of this work was to evaluate the influence of curvature and thickness of the samples on damage profiles when impacted by a steel projectile. The post impact fracture surfaces were analyzed using non-destructive evaluation (NDE) techniques. The results were compared between curved and straight specimens with various thicknesses. Ultimately, it was found that the damage profile and the energy absorbed by the specimens were highly affected by curvature and thickness.

(ICACC-S1-P009-2016) Si_3N_4-based Ceramics Fabricated with a Mixture of Si_3N_4-Si Powders

R. Huang*[1]; Y. Wu[1]; S. Ye[1]; Y. Long[1]; H. Lin[1]; 1. Guangdong University of Technology, China

Advanced silicon nitride (Si_3N_4) ceramics were fabricated using a mixture of Si_3N_4 and Si powders via conventional solid process. These Si_3N_4 ceramics with sintering additives of ZrO_2+Gd_2O_3+MgO were sintered at 1835°C and 0.1 MPa in N_2 atmosphere for 2h. The effects of Si adding content on phase structure, density, flexural strength, and thermal conductivity of the sintered samples were investigated. The results showed that with increase of added Si content, the density of the samples decreased from 3.39 g/cm^3 to 2.92g/cm^3 except for the sample without Si addition, while the thermal conductivity of the samples decreased slightly. On the other hand, with the addition of Si, the flexural strength reach maximum values at Si content of 25%, and then decrease with increasing Si content. Results demonstrated that the Si_3N_4 ceramics with the flexural strength and thermal conductivity of 1146MPa and 59.2W m^{-1} K^{-1} could be obtained via the proper control of the Si and initial Si_3N_4 powder content. This study suggested that addition of Si powder in the starting materials might provide a promising route to fabricate cost-effective Si_3N_4 ceramics with excellent properties.

(ICACC-S1-P010-2016) High temperature electrical behavior of melt-infiltrated SiC/SiC composites

M. P. Appleby*[2]; G. Morscher[2]; D. Zhu[3]; E. Maillet[1]; 1. GE Global Research, USA; 2. The University of Akron, USA; 3. NASA Glenn Research Center, USA

Recent work has been presented suggesting the use of electrical resistance (ER) monitoring as a tool for monitoring high temperature tensile damage accumulation in melt-infiltrated (MI) SiC/SiC ceramic matrix composites (CMCs). However, because of the convoluted electrical response of these materials under complex high temperature loading conditions, it becomes necessary to understand the contribution to change in ER from thermal and mechanical loading respectively. To that end, the present work characterizes the temperature-dependent electrical responses of several MI SiC/SiC CMC systems using both an isothermal and high heat-flux laser-based approach. The resistivity data is used to describe the electrical contributions of the constituent materials and thermal gradient induced by non-uniform heating. The resulting ER data is then used along with high temperature mechanical data as inputs in a micro-mechanics-based electro-mechanical model in order to characterize damage of CMCs under thermo-mechanical testing conditions.

(ICACC-S1-P011-2016) Creep Properties of Lutetium Oxide Containing SiAlON Ceramics

D. Turan*[1]; 1. Anadolu University, Turkey

Silicon nitride (Si_3N_4) and SiAlON ceramics are generally used at high temperatures requiring high creep resistance. Out of Si_3N_4 based materials, the best creep resistance was obtained with the addition of lutetium oxide (Lu_2O_3) into Si_3N_4. These materials owe their superior properties to the microstructure and the formation of secondary phases. Although it is known that Lu_2O_3 effect the properties of Si_3N_4 in a positive way, there is no study on the determination of creep properties of Lu_2O_3 containing alpha, beta or alpha/beta SiAlON ceramics. Therefore, in this study, 45×3×4 mm bar shaped samples were prepared with different SiAlON compositions containing Yb_2O_3, Er_2O_3 and Lu_2O_3 and gas pressure sintered. After surface preparation by grinding and polishing, creep tests were applied to the sintered samples in atmospheric environment at 1400 °C for 72 hours under 100 MPa pressure. Each composition were investigated by using x-ray diffractometer and scanning electron microscopy techniques before and after creep tests. Creep test results showed that Lu_2O_3 composition has the best creep resistance as expected while Yb_2O_3 composition has the worst creep resistance. However, creep resistance for Er_2O_3 composition was very close to Lu_2O_3 containing composition. After determining the best sintering and heat treatment conditions creep mechanism were determined by applying creep tests at different temperatures.

(ICACC-S1-P012-2016) The effect of BN volume fraction on BN particle dispersion SiC composites

S. Yanagawa*[1]; T. Hinoki[1]; K. Shimoda[2]; 1. Kyoto University, Japan; 2. National Institute for Materials Science (NIMS), Japan

SiC fiber-reinforced BN particle dispersion SiC (SiC/SiC+BN) composites show high oxidation resistance. And their strength doesn't degrade even after high temperature exposure in air up to 1500°C. The mechanical properties of the composites are determined by the properties of fiber, matrix and interface between fiber and matrix. And the matrix and interface properties are strongly affected by the volume fraction of BN in the matrix. So the object of this research is to optimize BN volume fraction of the composites for high temperature use. The SiC/SiC+BN composites were fabricated by varying BN volume fraction and microstructure and mechanical properties were evaluated. In order to understand fundamental properties of matrix, the SiC+BN monolithic ceramics were also fabricated with the same BN volume fraction of the composites. It turned out that the strength of the SiC+BN monolithic ceramics degraded with BN volume fraction increment. And BN distribution and matrix density were quite fine among the 10~70 range of BN volume fraction according to the microstructure observation and density measurement. The mechanical properties and microstructure of the composites will be also reported.

(ICACC-S1-P013-2016) Experimental verification of continuum damage mechanics model for SiC/SiC composites using digital image correlation technique

S. Ogihara[2]; T. Kikuta*[3]; R. Maeno[3]; T. Aoki[1]; T. Ogasawara[1]; R. Kitamura[2]; 1. Japan Aerospace Exploration Agency, Japan; 2. Tokyo University of Science, Japan; 3. Tokyo University of Science undergraduate school, Japan

SiC fiber reinforced SiC matrix (SiC/SiC) composites are excellent in heat resistance, and also lightweight. SiC/SiC composites are one of the promising materials for turbine engine components of future turbo-fan aero engines. It is known that SiC/SiC composites exhibit considerable nonlinear stress-strain behavior due to matrix crack propagations, delamination, and fiber breakages. For the practical use of SiC/SiC matrix composites, it is necessary to predict the deformation of components. Various kinds of continuum damage mechanics (CDM) models have been proposed to estimate the nonlinear stress-strain behavior of SiC/SiC composites. The object of this study is to verify the validity of a CDM model for SiC/SiC composites experimentally using a digital image correlation (DIC) technique. On-axis, off-axis tensile tests, and Iosipescu shear tests were carried out to determine the parameters for the CDM model. Full-field strain distribution of open-hole tensile test specimen was determined using a digital image correlation (DIC) technique. As a result, the full-field strain distribution estimated by the present CDM model agreed well with the experimental result.proposed in this study showed almost good agreement with the experimental results.

(ICACC-S1-P014-2016) Degradation evaluation of Si_3N_4 ceramic surface in contact with molten aluminum by using microcantilever beam specimens

S. Fujita*[1]; J. Tatami[1]; M. Iijima[1]; 1. Yokohama National University, Japan

Although Si_3N_4 ceramics are utilized as structural components for Al-casting industry owing to excellent properties, their breakage failure occasionally resulted from thermal stress due to the difference in the thermal expansion coefficient between Si_3N_4 ceramics and Al-alloy. Such fracture should occur when the thermal stress is higher than the strength of the component. Although there is a possibility that the vicinity of the Si_3N_4 ceramics is degraded because of contact with molten Al, the strength of the Si_3N_4 ceramic surface after contact with molten metal has not been clarified yet. In this study, degradation of the Si_3N_4 ceramic surface after contact with molten Al was evaluated by using microcantilever beam specimens. Si_3N_4 ceramics were contacted with molten Al alloy at 750° for 6h in the atmosphere. Microcantilever beam specimens to measure the bending strength of the vicinity of the Si_3N_4 ceramic surface were fabricated by focused ion beam technique. The average bending strength of the specimens before and after contact with molten Al were 4.14 ± 0.65 and 2.40 ± 0.12 GPa, respectively. Namely, it was shown that the bending stress of the Si_3N_4 ceramic surface decreased about a half by contact with molten Al. Such strength degradation was explained by the corrosion of intergranular glassy phase in Si_3N_4 ceramics due to molten Al.

(ICACC-S1-P015-2016) Modified asymmetric four-point bend test method for in-plane shear properties of ceramic matrix composites at elevated temperatures

I. Hisato*[1]; M. Takanashi[1]; T. Nakamura[1]; T. Aoki[2]; T. Ogasawara[2]; 1. IHI Corporation, Japan; 2. Japan Aerospace Exploration Agency, Japan

In-plane shear properties of a 3D woven SiC fiber-reinforced SiC (SiC/SiC) composite were measured by the asymmetric four-point bend test method at room temperature and 1150°C. The contacts between the test specimen and loading pins were modified to expand the selection of specimen geometries. Finite element analysis was performed on the specimen. The results showed that the pure shear states were obtained in the center of specimen. To confirm the strain states, the strains in the discussion area were measured by digital image correlation method. The in-plane shear strength of the 3D woven SiC/SiC at 1150°C was lower than that at room temperature by about 20%.

(ICACC-S1-P016-2016) Fracture Analysis of the Encapsulation Layer for Flexible OLED by Using Electrical Method

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The generation and density of cracks in the silicon nitride (SiNx) encapsulation layer of flexible organic light emitting displays (OLEDs) were measured by an electrical method, such as a current density vs. electric field measurement. The metal-insulator-metal (MIM) specimens were prepared on polymer substrates. The 100-nm-thick SiNx encapsulation layer was deposited on a bottom electrode of ITO/Pt/ITO by PECVD. Pt top electrode was formed by E-beam evaporation using shadow mask. Bending test of an encapsulation layer was performed by a two-point bending method. As the number of bending times increased, both the crack density and the leakage current density of the SiNx layer were increased, indicating that the cracks, which were generated during the bending test, provided the current paths. The water vapor transmission rate (WVTR) was also increased as a function of the bending times, suggesting that the cracks in the encapsulation layer played main sources of the vapor transmission. Both leakage current density and WVTR showed a direct proportional relationship with a crack density. In conclusion, the generation and density of cracks in the SiNx encapsulation layer can be quantitatively evaluated by measuring electrical leakage current through the layer.

(ICACC-S1-P017-2016) Lithium disilicate glass-ceramics fabricated by heat treatment of lithium metasilicate glass-ceramics obtained by hot-pressing

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Lithium disilicate glass-ceramics are widely used as dental ceramics due to their machinability and translucency. In this paper, lithium disilicate glass-ceramic was fabricated through heat treatment of lithium metasilicate glass-ceramics obtained by hot-pressing of glass powder composed of SiO_2–Li_2O–P_2O_5–ZrO_2–Al_2O_3–K_2O–CeO_2 at low temperature. The crystalline phase, microstructure and mechanical properties were investigated. The results indicated that lithium metasilicate glass-ceramic with a relative density of higher than 99% was obtained after hot-pressing, and glass-ceramic with interlocked rod-like $Li_2Si_2O_5$ crystals and good flexural strength (338 ± 20 MPa) was successfully obtained through heat treatment. The two-step method was believed to be feasible in tailoring the microstructure and mechanical properties of lithium disilicate glass-ceramics.

(ICACC-S1-P018-2016) Infrared spectral emissivity of SiC fiber / SiC matrix composites at eleveted temperatures

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This paper presents infrared spectral emissivity data of SiC-fiber / SiC matrix composites such as Nicalon-fiber/ CVI-SiC, Tyranno Lox-M fiber/ PIP-SiC, Tyranno ZMI fiber/ CVI-SiC, SA-Tyrannohex. Spectral emissivity was measured using an FT-IR in accordance with a black body reference method up to 1027 K. Monolithic ceramics such as Al2O3, ZrO2 (PSZ), SiC, Si3N4, and glassy carbon, were also examined for direct comparison. The quasi-total emissivity of SiC fiber / SiC matrix composites were estimated to be 0.85-0.9 for the wavelength of 2.5 - 25 μm. The spectral emissivity of SiC fiber and SiC matrix derived from pyrolysis of polycarbosilane was almost independent of the wavelength, whereas considerable wavelength dependency was observed in monolithic ceramics and CVI-SiC matrix. The experimental results were discussed using a conventional dielectric dispersion theory, and rule of mixtures.

(ICACC-S1-P019-2016) Effect of BaO addition on the properties of glass-ceramic materials from the SiO_2-Al_2O_3-CaO-MgO-Na_2O-K_2O system

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An important group of glass-ceramic materials are composites from the oxide molar system. SiO_2-Al_2O_3-CaO-MgO-Na_2O-K_2O. In the present work barium oxide BaO was introduced in an amount of 4, 9 and 14 wt % to selected compositions of the glass-ceramic materials. These compositions differ in SiO_2/Al_2O_3 ratio. Presented results are focused on the impact of barium oxide on the phase composition, structure and major physicochemical properties.

(ICACC-S1-P020-2016) Effect of the M-A bonds on the Mechanical Properties in MAX phases

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In this work, we present a systematic investigation of the mechanical and structural properties of $Ti_3Si_xAl_{1-x}C_2$ (x= 0, 0.25, 0.5, 0.75, and 1) using the Density Functional Theory (DFT), which is implemented in the Vienna Ab initio Simulation Package (VASP). The ground state energy is calculated using the DFT with GGA coupled with Projected Augmented Wave (PAW) pseudopotentials. The structural properties (position of atoms and electron-density distributions) and mechanical properties (the elastic constants, bulk modulus, shear modulus, Young's modulus, and hardness) were calculated on the ground state energy. The structures were visualized using the VESTA, and the number of valence electrons is obtained using the bader code. The Hardness values are derived from the cleavage energy under loading mode I.

(ICACC-S1-P021-2016) Development of transthickness tension test method for ceramic matrix composites at elevated temperatures

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SiC fiber reinforced SiC (SiC/SiC) composites are attractive materials for thermostructural components. Although the low transthickness tensile strength of 2D woven SiC/SiC is a serious concern, no standard test method addresses the characterization of transthickness tensile strength at elevated temperatures. A new test method to evaluate the transthickness tensile strength at elevated temperatures was developed. At first, the tests for a 2D woven SiC/SiC composite were conducted at room temperature in accordance with the developed method. The test results were compared with those by a conventional adhesively bonding method. Then the test was carried out at 1150°C. The test results showed that the developed method was applicable to the test at elevated temperatures.

(ICACC-S1-P022-2016) Microstructure and mechanical properties of mullite–whiskers reinforced lithium disilicate glass-ceramic matrix composites for dental restoration

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Lithium disilicate (LD) glass–ceramic composites reinforced with different volume fractions (0, 5, 10, 15 wt.%) mullite whiskers were succesfully fabricated by a hot–pressing method. The microstructure, whisker/matrix interface structure, phase constitution and mechanical properties of the composites have been systematically studied by DSC, SEM, XRD techniques as well as three–points bending, unilateral gap method, luminousness test. It was demonstrated that the incorporation of mullite whiskers could disperse uniformly in the LD glass–ceramic matrix, and effectively promotes the LD–to–LAS transformation of $LiAlSi_3O_8$ at the intersurface. Although the bending strength of the matrix composite was decreased (from 330 to 310 MPa) at a high mullite whiskers content due to the low densification and crack of LD/mullite whiskers glass-ceramic composite, whiskers bridging and pullout during glass-ceramic fracture obviously increased the fracture toughness at a mullite whisker content of 10wt.% to 4.1 $MPa \bullet m^{1/2}$.The luminousness was slightly decreased with the increased content of mullite whiskers, which primely satisfied the application in dental restoration system.

(ICACC-S1-P023-2016) Effect of chemical diffusion between Si_3N_4 ceramics and Stainless Steel on cutting performances of the ceramics cutting tools

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Si_3N_4-based ceramics have been widely applied in high-speed cutting tools in machining cast iron and nickel-based alloys. However, their application for cutting steels was reportedly poor which could be attributed to interdiffusion between the workpiece and tool. Although some investigations concerning the interdiffusion between steel and Si_3N_4-based ceramics have been carried out, the detailed failure mechanism is still vague. A further experimental study is necessary for understanding the effect of elements interdiffusion on the cutting performances of Si_3N_4-based ceramic cutting tools for steel machining. In the present work, interdiffusion experiments between stainless steel 304 will be taken between 600°C and 900°C for 2h to study the temperature effects on interdiffusion processes and diffusion mechanism. Turning tests will be carried out on Si_3N_4-based ceramic cutting tools for cutting performance and wear behavior investigation by cutting 304 stainless steels under dry environment. The relationship between the metal/ceramic interdiffusion on cutting performances and failure mechanism will be studied. The results of the present work are supposed to provide effective guidance on modification and improvement of Si_3N_4-based ceramic cutting tools suitable for steel cutting.

(ICACC-S1-P024-2016) Fabrication and characterization of joined single-end type RBSC radiant tube

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The aim of this study is to develop fabrication method of single-end type RBSC tube which was focused on joining of tube and cap. Because it have many merits like high thermal efficiency and low pollutant emission, RBSC radiant tube will be used gradually for heat treat applications. SiC powders were mixed with thermo-set polymers in a chamber at low temperature. Pouring it into the casting mold, tube was formed by centrifugal casting and cap was formed by gel casting method. The formed bodies were heat treated in order to transform polymers to carbon in Ar purging atmosphere. The above tube and cap were connected with SiC based paste which were filling the gap. Joining were and infiltrated by molten Si at 1500°C in vacuum. The flexural strength was measured in order to investigate which joining was successful or not and the microstructure of joint layer were observed using microscopy as processing variables were controlled. The leak test to check sealing of joined layer was performed also.

(ICACC-S1-P025-2016) The Study on Variables of SiC Granule Prepared from Solar Cell Wafer Sludge

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This study is designed to investigate effects of granulation parameter on the size (distribution) of granules prepared from solar cell wafer sludge. The wafer sludge are composed of about 10um SiC and <1um Si powders. This sludges were heat treated with phenol resin in vacuum in order to transform Si to SiC. These powders were milled to sub-micrometer level using ball milling. Granules for sintering experiments were spray-dried with sintering aids of B4C and carbon resin by pilot scale spray dryer. Yield ratio and the size distribution of granules were studied as granulation variables such as RPM, solid loading were controlled. Granules are pressed with uniaxially pressed at 50MPa, followed by being pressed with CIP at 200MPa. The formed bodies were sintered at over 2130°C for 1hr in Ar purging atmosphere. The density, flexural strength, hardness and toughness were measured and SiC grain size of sintered specimen were investigated using SEM.

(ICACC-S1-P026-2016) Effects of plasma-treated glass fiber on mechanical properties of glass fiber-reinforced epoxy concrete

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Epoxy concrete is used as flexible joint of the road and bridge because of its good elasticity. However the joints are easily damaged by wear and tear because epoxy has low mechanical strength even though glass fibers reinforce the epoxy. The durability of the glass fiber-reinforced epoxy concrete mainly depends on adhesion strength among glass fibers, flakes of stone and epoxy. In this study, we activated the surface of glass fiber using atmospheric pressure plasma to get high adhesiveness of the fiber and epoxy. The glass fibers were treated by argon or helium with oxygen gas dielectric barrier discharge (DBD) generated at 4~8kV using 30kHz AC power. By only a few seconds DBD treatment the wettability of epoxy on the glass was enhanced, contact angle was decreased about 30 degree. The tensile strength of the epoxy composite using surface treated glass fiber was improved about 30 percent. We will investigate the mechanical properties of epoxy composited with glass fiber and flakes of stone. The effects of DBD treatment on the properties of the epoxy concrete will be discussed.

(ICACC-S1-P027-2016) Modeling of Crack Arrest Process of Discontinuous Carbon Fiber/SiC Matrix Composites: For Design of Optimum Microstructure

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Discontinuous carbon fiber-dispersed SiC matrix (DCF/SiC) composite exhibits "tough behavior." However, fracture toughness of the composite is quite low and close to monolithic engineering ceramics. The origin of tough behavior depends on heterogeneous microstructure of DCF/SiC composite. The present study has been focused on classification of local crack arrest mechanisms by carbon fiber bundle, SiC, Si, and C phases in the composite. Fracture tests of DCF/SiC composite are done under various stress/strain fields and damage evolution process is modeled. Semi quantitative analysis has been done on the individual crack arrest mechanism using the developed models. Optimum combination of the arrest mechanism, i.e., optimum microstructure, is discussed to achieve maximum damage tolerance of DCF/SiC composite.

(ICACC-S1-P028-2016) Effect of short artificial crack on deformation and fracture behavior of discontinuous carbon fiber-dispersed SiC matrix composite

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Discontinuous carbon fiber-dispersed SiC matrix (DCF/SiC) composite have been used as frictional components. Usually DCF/SiC composite has initial microcracks and new cracks are introduced during service. The scale of introduced crack is nearly the same order of initially existed cracks. However, the effect of artificially introduced short cracks on the strength is still unclear. In the present study, fracture behavior of a disk shape DCF/SiC specimen with artificially introduced short crack is evaluated using ring-on-ring test. Artificial short crack is introduced by Vickers indentation and/or scratching. The set of experimental results reveal that fracture behavior of DCF/SiC composite show no dependence of newly introduced artificial cracks. Deformation and fracture behavior of the composite seem the same as those of original one. The deformation and fracture behavior are discussed in terms of interaction between short crack and heterogeneous microstructure of DCF/SiC composite. Special attention has been focused on the "tough behavior" of low toughness DCF/SiC composite.

(ICACC-S1-P029-2016) International Standards for Properties and Performance of Advanced Ceramics – 30 years of Excellence

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Mechanical and physical properties/performance of brittle bodies (e.g., advanced ceramics and glasses) can be difficult to measure correctly unless the proper techniques are used. For three decades, ASTM Committee C28 on Advanced Ceramics, has developed numerous full-consensus standards (e.g., test methods, practices, guides, terminology) to measure various properties and performance of a monolithic and composite ceramics and coatings that, in some cases, may be applicable to glasses. These standards give the "what, how, how not, why, why not, etc." for many mechanical, physical, thermal, properties and performance of advanced ceramics. Use of these standards provides accurate, reliable, repeatable and complete data. Involvement in ASTM Committee C28 has included users, producers, researchers, designers, academicians, etc. who write, continually update, and validate through round robin test programmes, more than 45 standards in the 30 years since the Committee's inception in 1986. Included in this poster is a pictogram of the ASTM Committee C28 standards and how to obtain them either as i) individual copies with full details or ii) a complete collection in one volume. A listing of other ASTM committees of interest is included. In addition, some examples of the tangible benefits of standards for advanced ceramics are employed to demonstrate their practical application.

(ICACC-S1-P030-2016) Effect of Sintering Additive and Temperature on Densification and Physical Property of Sintered Silicon Carbides

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Silicon carbide(SiC) is well-known for extremely useful properties, such as hardness, mechanical strength, thermal conductivity, and oxidation resistance. It has broad industrial applications as a refractory, as an abrasive, and as a high-grade structural ceramic. Due to its high melting point and covalent bonding, manufacturing dense ceramic materials requires various densification processes, for example reaction bonding, oxide bonding, nitride bonding, and solid-state sintering. In this study, SiC materials are fabricated by a solid-state sintering with sintering additives. B_4C and C are used for sintering additives. Density, Microstructure, and physical are examined with the solid-state-sintered samples. The effect of different sintering additives on densificaiton is also discussed.

(ICACC-S1-P031-2016) Super-Low Friction Mechanism of Carbon Nitride Thin Films by Tight-Binding Quantum Chemical Molecular Dynamics Simulations

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Carbon nitride (CNx) thin films have gained much attention as solid lubricants for automotive engines, aerospace instruments, etc. Experiments showed that CNx gives lower friction coefficient than diamond like carbon (DLC) films. This mechanism has not been clarified, because it is very difficult to clarify the chemical reaction dynamics during friction process by experiments. Therefore we developed tribology process simulator based on our tight-binding quantum chemical molecular dynamics method [1,2]. We calculated friction coefficients of H-terminated CNx and H-terminated DLC under 1 GPa pressure. Both simulation results show low friction coefficient of 0.05. We also simulated friction coefficients of H-terminated CNx and H-terminated DLC under 5 GPa pressure. H-terminated CNx shows low friction coefficient of 0.07 and

H-terminated DLC shows high friction coefficient of 0.43 under 5 GPa. Here, C-C and C-N bonds are not generated at the interface of H-terminated CNx, however many C-C bonds are generated at the interface of H-terminated DLC. Thus, we proposed that H-terminated CNx shows low friction coefficient than H-terminated DLC under high pressure because H-terminated CNx prevents the generation of C-C bonds at the friction interface.

(ICACC-S1-P032-2016) Chemical Reaction Process of Si_3N_4 under Water Lubrication by Tight-Binding Quantum Chemical Molecular Dynamics Method

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Si_3N_4 is used as low friction material under water lubrication. An experiment suggests that the low friction is caused by chemical reaction between the Si_3N_4 substrates and water at the friction interface [M. Chen et al., Tribol. Lett. 11 (2001) 23]. The understanding of its mechanism is needed to improve the friction property. However, it is hard to directly observe the chemical reaction dynamics at atomic scale by experiments. Thus, we aimed to reveal the chemical reaction on the Si_3N_4 surface under water lubrication by our developed tight-binding quantum chemical molecule dynamics simulator. We perform the sliding simulation of Si_3N_4 under water lubrication. In the model, 50 H_2O molecules are located between two amorphous Si_3N_4 substrates. The top of the upper substrate is loaded by 1 GPa and slid by 100 m/s. Si atoms and N atoms of the surfaces are terminated by OH group and H atom, respectively. During friction, an H atom of Si-OH bond on the Si_3N_4 surface moves to a nearby N atom and the Si-OH bond is changed to Si-O bond. Moreover, the O atom of the Si-O bond approaches another Si atom of the surface, and a Si-O-Si bond is generated. This reaction continues at interface and then the number of Si-O-Si bond increases. We suggest that the generation of Si-O-Si bond is an initial reaction of the generation of SiO_2 gel, which is suggested by the experiment.

(ICACC-S1-P033-2016) Microstructure and Phase Relationship of Aluminum Boride/Carbide Composites

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Low density and high hardness aluminum boride phases were formed using crystalline boron powder containing compacts and infiltrating them with Aluminum and Al-Si alloys. The effects of varying the Si:Al ratio on several different ceramic compositions were investigated. The experiments were performed with alloys of 70% Si-30% Al, 50% Si-50% Al and 100% Al and preforms containing crystalline boron powder, a boron-boron carbide mixture, and a boron-diamond particle mixture. Aluminum dodecaboride (AlB_{12}) was formed in both the boron and boron-B_4C preforms infiltrated with an aluminum alloy. Several other Aluminum-Boron-Carbide phases were formed in the remaining preform compositions. All composites were characterized via microstructural imaging.

(ICACC-S1-P034-2016) Removal of methomyl insecticide from wastewater using new synthesized anodes

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The research of agricultural yields led to massive use of fertilizers and pesticides. Among these chemical products, the insecticides are commonly used in agriculture. Their massive use has resulted in their ubiquitous presence in the environment in form of sub-lethal pollution and led to their leaching into subsurface zones and subsequent contamination of surface and ground waters. Therefore, considerable research efforts have been undertaken to develop powerful methods for their monitoring and elimination, amongst which anodic oxidation process on different anodes. In order to contribute into the understanding of the interaction phenomenon, we have undertaken a study concerning the degradation of an insecticide by simple and easily synthesized materials; such as nanocomposite materials. In this work, we studied the electrochemical elaboration of our nanomaterials based on copper (I) oxide by electrodeposition, then, the following of this presentation will focus on the removal of the methomyl. Data on the influence of pH, supporting electrolyte, initial insecticide concentration, temperature of the electrolysis, are presented. The localization of the insecticide in the interlayer space and/or on external surfaces of the anodes was discussed from the measurement of chemical oxygen demand (COD), by SEM microscopy and by UV-Visible spectroscopy. The results will be presented and discussed.

(ICACC-S1-P035-2016) Dynamic Compressive Response of Boron Carbide With Carbon Additive Prepared By Spark Plasma Sintering

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The development of armor-grade boron carbide requires a variety of processing aids for better densification. These additives may form secondary phases or precipitates at the grain boundaries or within the grains. Such processing-induced carbon inclusions have been shown to be crucial contributors to the dynamic failure process. In this study, boron carbide materials with various free carbon contents are produced using a spark plasma sintering process. Before the tests, the samples are characterized using a resonant ultrasound spectroscopy technique. A combined SEM/EDS/EBSD analysis is used to determine the characteristic chemical composition and crystal structure. A quantitative analysis of the carbon inclusions is performed using a series of optical microscopy images treated with image processing tools. The mechanical properties are evaluated in the quasi-static and dynamic regimes, the latter using a modified Kolsky Bar technique at strain rates of $10^2 - 10^3\ s^{-1}$. The progression of damage in the specimens is visualized by using a high-speed video camera. Fragments collected from the dynamically deformed specimens are used to investigate the failure mechanisms by using the SEM and EDS techniques. Through these experiments we seek to understand the influence of free carbon inclusions on the dynamic response of these advanced ceramics.

(ICACC-S2-P036-2016) Effect of composition on microstructure development in $MgO–CaO–Al_2O_3–SiO_2–(K_2O, ZnO)$ glass-ceramic glazes

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Several glasses were studied with the aim of obtaining glass ceramic compositions suitable for application as tile glazes. Tested materials based on compositions located in the primary crystallization field of diopside and anorthite within the system $MgO\text{-}CaO\text{-}Al_2O_3\text{-}SiO_2$. The sintering and crystallisation behaviour and microstructure of the selected compositions were investigated. Well crystallised microstructures were observed showing diopside and anorthite as the main crystalline phases. It has been observed that the addition of K_2O promotes diopside crystallization while the addition of ZnO promotes anorthite crystallization. Glass-ceramics layers of the quaternary system $MgO–CaO–Al_2O_3–SiO_2–(K_2O, ZnO)$, were examined with use of DSC, XRD and SEM methods.

(ICACC-S2-P037-2016) Evaluation of invisible changes in BSAS/BSAS/Mullite Si/SiC/SiC) environmental barrier coating system

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Invisible changes of EBC system, which composed of BSAS, BSAS-mullite, Si and SiC/SiC substrate, are studied. Residual stress change in Si bond coat layer is one of important invisible changed under high temperature thermal fatigue condition. The EBC system is cyclic heat exposed above and below melting point of Si. Change of

microstructure and associated microfracture behavior are observed. Thermal stress in Si bond coat layer is measured by Raman spectroscopy. The changes of residual stress, both local and global, are discussed in terms of visible microstructural change. Discussions are made on the application of invisible information to degradation detection and life prediction of EBC system.

(ICACC-S2-P038-2016) Measurement of Delamination Toughness in Mullite/Si/(SiC/SiC) Model Environmental Barrier Coating System

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Delamination toughness of mullite/Si/(SiC/SiC) model composite system is measured using a couple of different methods. The change of delamination toughness as a function of cyclic heat exposure of the model EBC system is also measured. The change in the delamination toughness is compared with the change in microstructure of EBC system and microcracking behavior of constitute materials. It is found that the delamination toughness strongly depends on the microfracture behaviors of Si bond coat and interfaces between Si bond coat and mullite top coat, Si bond coat and SiC/SiC substrate. Discussions are made on the origin and degradation of delamination toughness, and application of the toughness for life prediction of EBC system.

(ICACC-S4-P039-2016) Characterization of Boron Carbide Fragments Subjected to Dynamic and Static Loading

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Boron carbide is an extremely hard ceramic and finds applications in the armor, abrasives and nuclear industries. Boron carbide has a wide homogeneity range, with single phase boron carbide extending from ~9 to 20 at% carbon. Mechanical properties and ballistic response varies with the change in the stoichiometry. This work focuses on understanding the effect of stress and strain rates experienced by boron carbide during static and dynamic loading and linking it to the deformation in the crystal structure of boron carbide. Investigations of the possible changes in the stoichiometry and phase transformations were conducted on the ballistic fragments which could provide an insight into the possible reasons for failure. Connecting some of these results to the failure mechanisms will help explain the factors that affect ballistic performance.

(ICACC-S4-P040-2016) Improved Method for Preparing TEM Specimens of the Deformation Zones Beneath Knoop Indents in Boron Carbide and Silicon Carbide

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Previously, a multi-step process involving mechanical grinding, Tripod polishing, FIB milling, epoxy impregnation, and more FIB milling was reported for making TEM specimens of the heavily cracked deformation zones beneath Knoop indents in a commercial silicon carbide. In this study, mechanical grinding and Tripod polishing steps were replaced with a single masked ion milling step to improve efficiency. Polished commercial boron carbide and silicon carbide variants were Knoop indented using a 1 kgf load. A line of equally-spaced indents were placed parallel to specimen edges with indent diagonals oriented perpendicular to these edges. Indent distances from both specimen edges and each other were sufficient to reduce interaction effects. A Leica TIC-3X was used to mill away the edge material revealing Knoop indent sub-surface cross-sections located near indent centers. Specimens were vacuum-infiltrated with epoxy to fill in open cracks, improving structural integrity and preventing re-deposition of FIB-milled material. After locating and uncovering epoxy-covered indents using the FIB, standard FIB techniques were used to make the TEM specimens. This new process improves upon the previous process for revealing the extent of the sub-surface deformation zones and deformation mechanisms associated with Knoop indents at relatively high indent loads.

(ICACC-S4-P041-2016) Low temperature fabrication of reaction bonded composites

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The fabrication of fully dense SiC/(Si-Al) and (SiC+B_4C)/(Si-Al) composites was performed at temperatures lower than 1000°C under Mg vapor atmosphere. Under this atmosphere an adequate wetting (contact angle of about 30°) between ceramics and liquid alloys for free infiltration process is achieved. The green density of SiC performs fabricated from powders with various particle sizes was about 75vol.% . Infiltration by Si-20%Al alloy was conducted at 950°C. A special set of experiments was performed with preforms containing 20vol. % of a fine boron carbide powder as a source of carbon. The green density of the SiC-B_4C preforms was about 73-75vol.%. In both cases successful infiltration was achieved and the composites were fully dense. The density of the composites was about 3g/cm^3. For the SiC based composites the hardness value was 750±50HV, Young modulus -280GPa and bending strength-240±30MPa. These values for (SiC-B_4C)/(Si-Al) composites (1460±200HV, 317GPa and 360±20MPa) were significantly higher due to the formation of novel ceramics phases. Microstructural characteristics of the composites and their phase composition will be discussed.

(ICACC-S4-P042-2016) SPS sintered silicon carbide-boron carbide composites

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SiC and B_4C have similar physical properties such as a high melting point, hardness, mechanical strength, Young's modulus, chemical stability, and a low thermal expansion. Those properties make both SiC and B_4C important materials for use in spray nozzles, turbine engines, heat conducting tubes, and the defense industry (armor plate). Alpha-SiC powder has been used as a starting material. Commercial silicon carbide has a grain size of half a micron, and it an oxygen level of 1.66%. In order to lower the oxygen level of SiC it is washed with a 50% HF solution for 1 hour. The composites are formed using mixtures of SiC and boron carbide. Silicon carbide and B_4C quantities ranging from 10-50% along with 1.5% C are added via ball mill mixing and sintered using spark plasma sintering under vacuum at 1950°C for 5 minutes. After sintering, density is measured by the Archimedes method, microstructure and mechanical properties will be characterized via FESEM, XRD, and hardness testing is performed.

(ICACC-S4-P043-2016) Simulation of Dwell-to-penetration Transition Velocity for SiC Ceramics

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For SiC ceramic armour impacted by long rod projectiles, increasing the dwell-to-penetration transition velocity significantly improves its ballistic performance, whereas it can be achieved by prestressing of SiC ceramics or placing a buffer over the impact surface. In this paper, numerical simulation is conducted to investigate how the transition velocity is affected by the prestress and the presence of a buffer. Hydrocode LS-DYNA using dynamic relaxation algorithm is applied to simulate the steady-state response of SiC ceramics when it is subjected to a surface pressure generated by long rod impact, where Johnson-Holmquist model (JH1) for SiC ceramics is applied. Two types of damages, i.e. cone cracking near to the edge of the projectile and yielding of SiC ceramics beneath the impact surface, are revealed from simulation. These damages inside the ceramics can be effectively suppressed by applying radial prestress or adding a buffer. Simulation indicates that yielding of SiC beneath the impact surface plays critical role in dwell-to-penetration transition for SiC ceramics under long rod impact. The simulation procedure when

compared against experimental data from literature predicts transition velocities which are consistent.

(ICACC-S4-P044-2016) Rate-dependent Hardness and Amorphization Response of Nano-grained Boron Carbide

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The strain-rate dependent hardness, compressive strength, and amorphization behavior of nano-grained boron carbide (B4C) are investigated. While micro-grained boron carbide is well-documented in literature, limited information is available regarding the behavior of nano-grained B4C. Quasi-static and dynamic compression techniques in addition to quasi-static and dynamic Vickers indentation techniques are utilized to determine mechanical properties and amorphization response of the nanomaterial. Micro-Raman spectroscopy is utilized to determine the intensity of amorphization induced during both quasi-static and dynamic indentation, and to spatially map the distribution of amorphized zone. Nano-grained B4C has shown increases in quasi-static hardness and compressive strength, in comparison to micro-grained B4C. Raman analysis has suggested that there is a decrease in amorphization intensity present in similar indents. Transmission electron microscopy (TEM) investigations revealed a large number of amorphized bands beneath the indentation in micro-grained B4C, whereas nano-grained B4C had significantly fewer amorphous bands.

(ICACC-S4-P045-2016) Chemical Interactions in B_4C/WC-Co and B_6O/WC-Co Powder Mixtures Heated Under Inert and Oxidizing Atmosphere

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Chemical interactions in B_4C/WC-Co and B_6O/WC-Co powder mixtures (50/50 by volume) heated under inert and oxidizing atmospheres was investigated. Baseline powders (B_4C, B_6O, WC, WC-CO) and powder mixtures (B_4C/WC, B_4C/WC-Co, B_6O/WC, and B_6O/WC-Co) were examined by DSC/TGA up to 1000ºC (10ºC/min) under flowing Ar (high-purity) and Ar/O_2 (20 vol.% O_2) atmospheres. Under flowing Ar, only the baseline WC-Co powder displayed appreciable thermal and mass change activity. This activity is attributed to the formation of CoO (due to low O_2 impurity concentration in the Ar bottle) at low temperatures and its subsequent reduction at high temperatures. Under flowing Ar/O_2, all baseline powders and powder mixtures displayed thermal and mass change activity believed to be associated with oxidation reactions. Guided by these results, controlled atmosphere tube furnace experiments were performed to produce sufficient powder for XRD and SEM/EDS analyses. These results, along with DSC/TGA results and experimental procedures, will be presented and discussed.

(ICACC-S10-P046-2016) Elastic constants of binary nitride epitaxial thin films MeN (Me= Ti, Zr, V, Nb AND Ta) grown by reactive magnetron sputter deposition

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Transition metal (TM) nitrides have been extensively studied owing to their excellent performance as hard, wear- and corrosion resistant coatings. For most of the applications, the thermal stability and the elastic properties are of great interest to deal with the durability of the material. Several coatings of multinary alloys have been proposed in order to design new properties. Assessing their elastic properties remains challenging as they relate on many attributes and defects. Strategies should be employed to tackle this challenge, studying systems of increasing degree of complexity. This is the aim of the present work dedicated to cubic single-crystal binary thin films: TiN, VN, ZrN, NbN and TaN epitaxially grown by reactive magnetron sputtering on a MgO(001), (110) and (111)-oriented substrate. Elastic constants of thin films can be accurately studied by photoacoustic measurements and can be compared to the few existing experimental results and to the ab initio calculations performed with the density functional theory.

(ICACC-S10-P047-2016) First Principles Study of Defect Formation in Bulk Boron Suboxide

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B_6O is a promising material for light-weight armor applications. It is chemically inert, has an ultra-high hardness (24 - 45 GPa), low density (~2.61 g/cc), high mechanical strength (26 - 30 GPa), and high oxidation resistance (below 1200ºC). However, it has yet to be fielded due to several processing and performance based challenges including: (1) trans-granular failure resulting in low fracture toughness (2) a reduction in shear strength under extreme environmental conditions such as high temperature / pressure and (3) manufacturing challenges. To maximize its performance, we must first understand the competing influences of crystal structure, defect populations (i.e. vacancies, twins, stacking faults), stoichiometry, and surface reconstructions on the nature of the atomic bonding within the bulk crystal and near interfaces (i.e. grain / phase boundaries, free surfaces). In this study, we calculate the vacancy formation energies and structural reconstructions for single atom and multi-atom vacancies at Bpolar, Bequatorial, and oxygen lattice sites as well as their vacancy-vacancy interactions for the first, second, third, and fourth nearest neighboring vacancies. Understanding the effect of vacancies on the electron distribution within the B_6O crystal structure may lead to a better understanding for how to dope boron suboxide in order to improve its mechanical performance.

(ICACC-S10-P048-2016) First principle calculation of crystal structure, electronic structure, and optical properties of rare earth element doped Ba(Zr,Mg,Ta)O3

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Perovskite structure ABO3 is a cube in which site A locates at corners of cube, site B locates at the center of octahedron formed by oxygen atoms which occupy face centers of the cube. This structure can be deformed into different structures. This work, for the first time, reports modeling and simulations of crystal structures, electronic structures, and optical properties of rare earth (RE) elements doped Ba(Zr,Mg,Ta)O3 (BZMT) using the DFT+U method. Due to absence of experimental refinement, modeling structures of BZMT and doped BZMT is developed from BaZrO3 (BZO3) refinement. This work demonstrates a most stable BZMT and its RE elements doped model, the structural distortion, the preferred location of RE elements in BZMT. Based on this model, electronic structures and optical properties are predicted. Furthermore, the work explores which element(s) is the best candidate for BZMT ceramic materials.

(ICACC-S10-P049-2016) Simulations of Anisotropic Texture Evolution on Paramagnetic and Diamagnetic Materials Subject to a Magnetic Field Using Q-State Monte Carlo

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The present work incorporates a modified Q-state Monte Carlo (Potts) model to evaluate two-dimensional annealing of representative paramagnetic and diamagnetic polycrystalline materials in the presence of a magnetic field. Anisotropies in grain boundary energy, caused by differences in grain orientation (texturing), and the presence of an external magnetic field are examined in detail. In the former case, the use of the Read-Shockley equations are used, in which grain boundary energies are computed using a low angle misorientation approximation. In the latter case, magnetic anisotropy is simulated based on the relative orientation between the principal grain axis and the external magnetic field vector. Among other findings, the results of texture development subject to a magnetic field showed an increasing ODF asymmetry over time, with higher intensities favoring the grains with principal axes most closely aligned with the magnetic field direction. The magnetic field

also tended to increase the average grain size, which was accompanied by a corresponding decrease in the total grain boundary energy.

(ICACC-S10-P050-2016) Crystal Growth Simulation of MgO Thin Film on SiO_2 Substrate by Molecular Dynamics Simulation

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MgO as an electrode protection film in a plasma display panel shows a large secondary electron emission coefficient, and contributes to lower electricity consumption. In past studies, it was found that secondary electron emission of MgO depends on crystal orientation, surface shape, and surface composition. Therefore, it is important to design the surface and interface of a MgO thin film at atomic scale. However, it is difficult to observe crystal growth process at atomic scale by experiments. In this study, to elucidate crystal growth process of MgO, we performed crystal growth simulation of MgO thin film on a SiO_2 substrate by our molecular dynamics simulator and analyzed the grain boundary and crystal plane of the generated MgO thin film. First, we performed crystal growth simulation of MgO on a SiO_2(111) substrate. We irradiated MgO molecule at a velocity of 1.5 km/s. The result shows that the rough MgO thin film surface was formed and grain boundaries were generated. Then, we analyzed the structure of the formed MgO thin film based on the coordination number of Mg and angle between the substrate and the generated MgO layer. We observed [111] and [001] directing growth in the MgO thin film. Moreover, we found that [111] directing growth was more than [001] directing growth. Thus, we suggest that the MgO thin film prefer [111] directing growth on the SiO_2 substrate.

(ICACC-S12-P051-2016) Effect of carbon fiber and boron carbide particle on the distribution and content of residual silicon of reaction bonded silicon carbide composites

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The aim of this study is to carry out analysis for controlling the distribution and content of residual silicon in the RBSC composite. Different volume fractions of chopped carbon fibers were introduced into C/SiC/B4C slurry to act as carbon source. The reaction between carbon fiber and molten silicon was complete. The phase compositions of the composites were α-SiC, β-SiC, B_4C, Si and $B_{12}(B,C,Si)_3$. Especially, when the volume fraction of the carbon fiber is 40%, some carbon fibers were found in the fracture surface. Furthermore, the microstructures show the presence of two types of core-rim structures and a bunchy dispersion silicon phase in the sintered body. The residual silicon content of the specimen reachs 1.62 Vol. % and the size of the silicon island is nanometer order of magnitude. The results indicate that the volume fraction of residual silicon decreases with the improvement of the volume fraction of carbon fibers. The addition of B_4C particles improve the mechanical properties and set up the silicon capillary vessel channel for the green body, which prompts a completed silicon infiltration. The flexural strength and fracture toughness of the composites were higher than the values reported for conventionally prepared RBSC composites, reaching peak values of 413MPa and 6.5MPa•$m^{1/2}$, respectively.

(ICACC-S12-P052-2016) TEM and XPS Investigations of Ordered MAX Phases: Mo_2TiAlC_2 and $Mo_2Ti_2AlC_3$

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A recent development in the MAX phase field is the existence of $(M',M'')_{n+1}AlC_n$ ordered phases, in which two M' layers sandwich one or two M" layers such as Cr_2TiAlC_2 and V_2CrAlC_2 phases. Herein we report on two newly discovered ordered, quaternary MAX phases - Mo_2TiAlC_2 and $Mo_2Ti2AlC_3$. The phases were synthesized by sintering the elemental mixtures of Mo, Ti, Al, and C at elevated temperatures around 1600 deg C in Ar flow. High Resolution Scanning Transmission Electron Microscopy (HR-STEM) accompanied with Energy-dispersive X-ray spectroscopy (EDX) mapping was used to show that the ordered stacking sequence is Mo-Ti-Mo-Al-Mo-Ti-Mo for Mo_2TiAlC_2 and Mo-Ti-Ti-Mo-Al-Mo for $Mo_2Ti_2AlC_3$. X-ray Photoelectron Spectroscopy (XPS) analysis confirms the ordered structure of both phases. Mo_2TiAlC_2 has only one C species in the 1s carbon region at a binding energy of 242.5 eV, while $Mo_2Ti_2AlC_3$ has two peaks, one which is the same as that for Mo_2TiAlC_2 and the second one at a lower binding energy of 242.1 eV corresponding to C bonded to Ti in the inner layers. Their ratio is 2 to 1 which corresponds to the ordered structure proposed. These results confirm that, in both phases the major M element in the outer layers is Mo and the major M element in the inner layers is Ti.

(ICACC-S13-P053-2016) Plasma Spray Coating on the Graphite between Ceramic and Uranium Alloy Compatibility

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Graphite is high heat conductivity and high-processed ceramic material. Therefore, it is substantially used to manufacture metal fuel reactor in vacuum or inert atmosphere at the metal dissolution and nuclear energy area. However, it is used by anti-oxidation, heat-resisting and anti-corrosion coating now that it's hard to use it in air or oxidizing atmosphere. Many researchers coated it in various terms and there was reaction of coating layer desquamation or molten metal treatment and coating layer when dissolving alloyed metal uranium in high temperature. This research practiced coating for blocking coating layer, molten metal treatment and reaction to increase adhesive strength on graphite. It observed reactivity and movement after practicing dipping alloyed metal uranium molten metal. By this experiment, it tried to find coating ceramic material and condition suitable for crucibles for melting alloyed metal uranium. As a result of experiment, the method to practice middle buffer layer firstly, and coat molten metal anti-erosion layer secondly resulted in a few high temperature desquamation phenomenon, and relatively superior corrosion resistance.

(ICACC-S13-P054-2016) Effect of Yttria-Scandia Addition on Thermal Properties of Particle Based Accident Tolerant Fuel

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The Particle-Based Accident Tolerant (PBAT) fuel consists of the nuclear fuel as tri-isotropic carbon (TRISO) particles embedded in a SiC matrix and formed into pellets. The PBAT fuel provides higher safety margins under beyond design-basis accidents. The PBAT fuel embedded in SiC matrix enables a nuclear reactor to reduce stored energy in the core and to produce more thermal energy. Thus, the development of SiC matrix with improved thermal conductivity is an important issue for the development of PBAT fuel. The effect of additive content on the thermal properties of hot-pressed liquid-phase sintered (LPS)-SiC ceramics with 0.5-3 vol% Y_2O_3-Sc_2O_3 additives were investigated. The SiC samples exhibited the thermal conductivity as high as 138-234 W/m•K, depending on the Y_2O_3-Sc_2O_3 content. An optimum Y_2O_3-Sc_2O_3 content exists for which (1) the absence of amorphous films at grain boundaries, (2) the confinement of poor-conducting RE-containing phases in the junction areas, (3) the reduction of oxygen concentration in lattice, and (4) suppression of β- to α-SiC phase transformation, resulting the maximum thermal conductivity. The thermal conductivity of SiC-TRISO composites will be discussed in relation with their microstructures and phonon mean free paths.

(ICACC-S13-P055-2016) Fabrication and corrosion behavior of graphite foil-bonded commercial graphite

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Despite its excellent chemical compatibility with molten fluoride salts, the inherently high porosity level of graphite is one major challenge to the material in contact with such salts for extended periods of time. To overcome the porosity-related molten salt permeation problem, a graphite foil has been successfully bonded to a commercial graphite substrate in the authors' laboratory. One purpose of the present study was to investigate the effect of process parameters on graphite foil-graphite substrate bonding behavior and other properties. One other purpose was to evaluate the effect of the graphite foil on corrosion behavior of the graphite foil-bonded graphite in molten fluoride salt. The experimental results indicate that the graphite foil has effectively sealed the graphite substrate against permeation of the high-temperature molten salts. The graphite foil remains tightly bonded to the graphite substrate during the entire fabrication process as well as after the corrosion test. The research is supported by MOST 102-2221-E-006-059 (Taiwan, Republic of China).

(ICACC-S13-P056-2016) Synthesis of Li_5AlO_4 powder by using Li_2CO_3 and Al_2O_3 and atmosphere controlled calcination method

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Ceramic breeders used in a fusion reactor blanket, which play a role in the production of tritium by the reaction with neutron, are required to have high lithium density in the pebble. Li_5AlO_4 contains lithium by high concentration and have a great ability of tritium breeder. However, in order to prepare the high purity powder of Li_5AlO_4, only a few methods with disadvantageous economically because of their requirement of a high-cost powder, Li_2O. In this study, Li_2CO_3 powder was used instead of Li_2O powder, which are not always commercially available, and a high-purity powder of Li_5AlO_4 was synthesized *via* an atmosphere controlled calcination method. Mixed powders of Li_2CO_3 and Al_2O_3 with a suitable initial Li/Al molar ratio were fired at around 640 °C in H_2 for several hours and several times. This low firing temperature inhibited the vaporization of lithium during the heating, so that the excess amount of lithium compounds is not necessary and the suitable Li/Al ratio in the starting material is 5/1-6/1. In this synthesis process, Li_2O is generated during the firing in H_2, reacts with Al_2O_3 to form $LiAlO_4$, and also reacts with the $LiAlO_4$ to be Li_5AlO_4.

(ICACC-S14-P057-2016) Spark-Plasma Sintered Translucent Mullite Ceramics with Anisotropic Grains

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The motivation behind this work was to fabricate a high-performance, translucent mullite ceramic with anisotropic grains by sintering a commercial powder that was co-doped with silica and yttria beforehand, simply by mixing the required powder-like ingredients. The sintering was conducted in an SPS furnace at a relatively low temperature (1370 °C), with only contact pressure. The compositions and microstructures of the sintered specimens were inspected with XRD and SEM, while the mechanical properties in terms of bi-axial flexural strength (~420 MPa), Vickers hardness (~15 GPa) and indentation toughness (~2.5 $MPa \bullet m^{1/2}$) were evaluated using the piston-on-three-balls test and a Vickers indenter, respectively. Lastly, the light-transmittance measurements were recorded (~50-80 % at 1-2.5 μm) on a UV-VIS spectrometer. It will be shown that the combination of suitable amounts of dopants and the use of SPS sintering yielded an enhanced densification of the samples, also provoking the anisotropic grain growth, presumably due to the lowered glass viscosity during the viscous-flow sintering. Thus, we were able to meet the conflicting demands of obtaining a highly dense mullite ceramic at low sintering temperatures, consisting of anisotropic grains and thereby having increased mechanical properties, while at the same time retaining an excellent Vis-NIR transmittance.

(ICACC-S14-P058-2016) Electrical and microstructural properties of $NiMn_2O_4$ NTC thermistors by doping 0.1 mol B_2O_3 without calcination

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The aim of this work is to investigate the effect of B_2O_3 addition as sintering aid to the electrical and microstructural properties of nickel manganite based NTC thermistors fabricated by the conventional solid-state reaction method without calcination. High purity NiO, Mn_2O_3 and H_3BO_3 (as a source of B_2O_3) powders were weighed and the powder mixtures were ball-milled using ZrO_2 balls as a grinding media with ethyl alcohol in a jar for 6 hrs. The obtained slurries were dried and only undoped $NiMn_2O_4$ powders were calcinated at 900°C for 2 hrs. The disc shaped samples were sintered at 1100°C for 5 hrs in air. The bulk density of the sintered samples were calculated from their weights and dimensions. The electrical resistance was measured in a temperature programmable furnace between 25°C and 85°C. The microstructure of samples was observed using scanning electron microscopy. The resistance of samples was logged every 0.1°C and the plots of log ρ versus 1000/T for the samples were generated. The material constant "B" and sensitivity coefficient "α" values were calculated for the NTC thermistors. *This study is supported by TÜBITAK (The Scientific and Technical Research Council of Turkey), Project number 3001-114M860. We would like to thank TÜBITAK for its financial support.*

(ICACC-S14-P059-2016) Investigation of microstructure properties in Al_2O_3 and Al_2O_3-B_2O_3 doped ZnO ceramics

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The effect of Al_2O_3 and Al_2O_3-B_2O_3 doping on the microstructural properties of ZnO ceramics was investigated. Three compositions were prepared, undoped ZnO (composition code: Z), 0.5 mol% Al_2O_3 doped ZnO (composition code: A) and 0.5 mol% Al_2O_3-0.5 mol% B_2O_3 doped ZnO (composition code: AB). These samples were sintered at 1100, 1200 and 1300 °C for 1 and 3 hours. The XRD analysis of A and AB samples revealed the $ZnAl_2O_4$ phase. The highest relative bulk density value of Z samples was found as 84 % when the sample was sintered at 1300 °C for 3 hours. The relative bulk density of A sample sintered at 1100 °C for 1 hour was 90% increasing to 97% with the addition of B_2O_3 (AB sample). The average grain size of Z, A and AB samples were found in the range of 4-10, 6-32 and 10-50 μm, respectively. The addition of B_2O_3 as a sintering aid increased the average grain size as well as the relative bulk density of samples by forming a liquid phase during sintering.

(ICACC-S14-P060-2016) Attempts to improve the optical transmission on spark plasma sintered YAG ceramics

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The transparency of ceramics is affected by scattering at the pores and at the grain boundaries. SPS allows high heating rates and lower sintering temperatures compared to conventional sintering. Densities close to the theoretical one can be reached within several minutes, while retaining a fine microstructure that avoids light scattering in the visible and IR range. SPS of YAG has been extensively studied but the influence of the different SPS parameters on the sintering behavior is still unclear. In this work 2 different YAG powders (one commercial and another coprecipitated) have been compared to assess the influence of SPS parameters: heating rate, pressure, temperature and dwelling time on density, microstructure and optical transmission. One of the most important parameters is the dwelling temperature: its increase between 1350°C and 1450°C

allows the achievement of fully dense materials, without any intergranular porosity and keeping the grain size around 200nm. In spite of high density values,no transparency in the visible range was observed in the YAG ceramics issued from the commercial powder. On the contrary,samples issued from our home-made powder showed better optical transmission, even at lower sintering temperatures. Several attempts focused on the increase in the optical transmission as dispersion of the powders and lithium fluoride addition were tested and are discussed

(ICACC-S14-P061-2016) The thermoelectric properties of STO crystals grown by the EFG technique using Mo crucibles

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The SrTiO3 (STO) single crystal is not only used as substrate materials such as an oxide semiconductor or the superconducting material but also attracted as a promising candidate for n-type thermoelectric material. It is known that the n-type carrier in STO single crystals is caused by the oxygen defect. In this study, we grew STO single crystals using the edge-defined film-fed growth (EFG) technique with Mo crucible under Ar atmosphere in order to introduce more oxygen defects and measured the thermoelectric properties of the STO crystals. These crystals have high Seebeck coefficient (-2×10^{-4}V/K) and low electrical resistivity(10^{-5} Ω)compared to the Nb doped STO single crystals grown by Verneuil technique.

(ICACC-S14-P062-2016) $NaNbO_3$/PVDF composite: a flexible functional material

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Sodium niobate can be used as precursor of flexible composites with great properties aiming the use in devices that combine properties like piezoelectricity and photoluminescence (PL). In this work, we obtained $NaNbO_3$ fiber-like particles and cubic-like particles by microwave hydrothermal synthesis. The composites were made matching different volume fraction of $NaNbO_3$ particles and PVDF polymer. The particles showed band gap around 3.2-3.3 eV and PL emission in blue region. The composites with less $NaNbO_3$ volume fraction showed better flexibility. The piezoelectric property of composite with fiber particles was 7.8 pC/N and to composite with cubic particles the value was 1.1 pC/N. The composites with anisotropic particles had higher remnant polarization measured at 20 Hz. The UV-visible spectra of composites provided band gap values similar to particles. PL emission of composites were in a lower energy region when compared to particles (600 nm to composite with fiber particles, and 550 nm to material with cubic like particles), indicating contribution of different structural defects to emission. According the results, the anisotropy of $NaNbO_3$ particles, improve the electrical and optical characteristics. Since the materials combine properties like piezoelectric and photoluminescence, they can have a potential application in flexible piezophotonic devices.

(ICACC-S14-P063-2016) Tunable Eu/Mn-Coactivated $Mg_2Al_4Si_5O_{18}$ phosphor prepared in air via valence state-controlled and energy transfer

J. Chen[1]; Y. Liu*[1]; Y. Xia[1]; B. Wang[1]; 1. China University of Geoscience Beijing, China

With the aid of valence state-controlled and energy transfer, a series of blue-to-orange emitting $Mg_2Al_4Si_5O_{18}$:Eu, Mn phosphors were synthesized via high-temperature solid state reaction in air atmosphere. The reduction of Eu^{3+} to Eu^{2+} and the stable Mn^{2+} photoluminescence in air atmosphere was observed in $Mg_2Al_4Si_5O_{18}$:Eu, Mn. Photoluminescence (PL), excitation (PLE) spectra, X-ray photoelectron spectroscopy (XPS), and the fluorescence decay curves were employed to detect the presence of Eu^{2+} and Mn^{2+} ions in the compound. Under near-ultraviolet (UV) light excitation of 365 nm, Eu^{2+}-doped $Mg_2Al_4Si_5O_{18}$ exhibits a broad blue emission band peaked at 469 nm, and Mn^{2+}-doped $Mg_2Al_4Si_5O_{18}$ shows a broad orange-red emission band near 600 nm. The energy transfer from Eu^{2+} to Mn^{2+} in $Mg_2Al_4Si_5O_{18}$ host matrix can be found, and the resonant type is demonstrated by a dipole–quadrupole mechanism. The emission hue can be tuned from blue to white and finally to orange by properly varying the ratio of Eu^{2+}/ Mn^{2+}.The mechanism of reduction from Eu^{3+} to Eu^{2+} and stable Mn^{2+} in this compound was discussed in detail and verified by first principles and photoluminescence properties.

(ICACC-S14-P064-2016) Enhanced Dielectric and Ferroelectric Characteristics in Ca-Modified $BaTiO_3$ Ceramics

X. Chen*[1]; X. Zhu[1]; W. Zhang[1]; 1. Zhejiang University, China

Synergic modification of $BaTiO_3$ ceramics was investigated by Ca-substitution, and the superior dielectric and ferroelectric properties were determined together with the structure evolution. X-ray diffraction (XRD) analysis demonstrated a large solubility limit above x=0.25 in $Ba_{1-x}Ca_xTiO_3$ solid solution where the fine grain structure was observed with increasing x. Room temperature dielectric constant as high as 1655 was achieved in the present ceramics together with the significantly reduced dielectric loss of 0.013 (x=0.20 at 100 kHz), where the Curie temperature kept almost a constant while other two transition temperatures decreased continuously with increasing x. More importantly, the remanent polarization P_r and dielectric strength E_b were significantly enhanced by Ca-substitution, and the best P_r (11.34 μC/cm^2) and the highest dielectric strength E_b (75 kV/cm) were acquired at x=0.25.

Wednesday, January 27, 2016

40th Jubilee Symposium: Engineered Ceramics: Current Status and Future Prospects

Engineered Ceramics IV

Room: Coquina Salon C

Session Chair: Andrew Wereszczak, The Pennsylvania State University

8:30 AM

(ICACC-JUB-020-2016) Oxide ceramics: the role of surface and grain boundary for reliable applications (Invited)

J. A. Varela*[1]; M. O. Orlandi[1]; 1. UNESP, Brazil

Oxide ceramics have applications in several segments of the human life, once they are used as the functional materials in several devices, such as sensors of chemical species for monitoring and/or controlling environment, surge protectors for electronic appliances and electrochemical transducers for sustainable alternative energy production. Other applications involve detectors in medical appliances, components of mobiles and computers, etc. One of the most important features deal with the electrical behavior of these oxides, which span from superconductors to insulators, including ionic/electronic/mixed conductors and semiconductors, and this is possible due to the capacity of producing pure and doped materials in a controlled way. For any desired application of these oxides, defects, such as the grain boundaries and the material surface, place an important role on the presented property. Based on it, this work presents a brief overview of ceramic oxide semiconductors and ionic conductors, taking into account the role of surfaces and interfaces on their performance as components in surge protectors - varistors, in chemical sensors and solid electrolytes in solid oxide fuel cells.

9:00 AM

(ICACC-JUB-021-2016) Engineering Diffraction: Multiscale Characterization of Electroceramics (Invited)

E. Ustundag*[1]; 1. Istanbul Technical University, Turkey

Engineering Diffraction employs advanced characterization techniques (e.g., X-ray and neutron diffraction), coupled with solid mechanics modeling, to study the mechanical behavior of materials. In essence, it is an inverse analysis since it attempts to deduce a material's constitutive behavior using diffraction data. This presentation will summarize recent developments in the field, concentrating on electroceramics, to illustrate its powerful capabilities, especially its unique ability to quantify *in-situ* multiscale material deformation (from sub-mm to cm) under a wide range of external stimuli. Examples will include: (i) The use of X-ray microdiffraction to study domain mechanics in ferroelectrics at the microscale, (ii) The application of high energy X-ray microscopy (also known as 3-D XRD) in the investigation of mesoscale (grain-level) constitutive behavior of electroceramics, (iii) Macroscale (bulk average) evolution of lattice strain and domain switching (texture) in polycrystalline $BaTiO_3$ under electric field and/or mechanical loading studied with high energy XRD and neutron diffraction.

9:30 AM

(ICACC-JUB-022-2016) Phonon Engineering in Advanced Ceramics: Challenges and Opportunities (Invited)

J. Wang*[1]; 1. Shenyang National Laboratory for Materials Science, Institute of Metal Research, China

Searching for ceramic with extremely low lattice thermal conductivity is the key concern to improve the performances of advanced thermal insulation materials. The well understood qualitative guidelines are described by complex crystal structure, significant bonding heterogeneity, and large average atomic weight. In addition, minimum lattice thermal conductivity at high temperature limit frequently serves as a good material selection criterion. Recently, temperature dependent lattice thermal conductivities of advanced ceramics, such as rare-earth containing silicate, phosphate, and zirconate, are precisely predicted based on reasonable theoretical models. These progresses provide us the opportunity to optimize specific material parameters that tailor phonon behaviors in complex ceramics. Future challenges and opportunities address to effective phonon engineering through crystal chemistry and defect configuration in light weight and/or rare-earth free ceramics in order to succeed extremely low thermal conductivity.

10:20 AM

(ICACC-JUB-023-2016) Fused Silica and Other Transparent Window Materials (Invited)

J. Salem*[1]; 1. NASA Glenn Research Center, USA

Several transparent ceramics, such as spinel and AlONs are now being produced in sufficiently large areas to be used in space craft window applications. The work horse transparent material for space missions from Apollo to the International Space Station has been fused silica due in part to its low coefficient of expansion and optical quality. Despite its successful use, fused silica exhibits anomalies in its crack growth behavior, depending on environmental preconditioning and surface damage. This presentation will compare recent optical ceramics to fused silica, and discuss sources of variation in slow crack growth behavior and areas for material improvements.

10:50 AM

(ICACC-JUB-024-2016) Graphite Foam/Phase Change Material Composite as a High-Efficiency Thermal Energy Storage System for Solar Applications (Invited)

D. Singh*[1]; 1. Argonne National Lab, USA

The focus of the presentation is on the development of a high efficiency latent heat based thermal energy storage (LHTES) system. Most of the current LHTES systems are limited by poor thermal performance. As part of this work, we have impregnated high thermal conductivity, low-density graphite foams with a phase change material (PCM) salt, thereby, offering a combined system with conductivities significantly greater than the salt alone. Further, this LHTES system provides high storage densities and high specific thermal conductivities, and allowing rapid charge/discharge cycles. Three-dimensional (3-D) heat transfer simulations were conducted for the storage system using commercial software COMSOL to demonstrate the performance of a full-scale system. The anisotropic thermal conductivity of graphite foam-PCM combination was considered in the simulations. The results show that the graphite foam can considerably enhance the heat transfer performance and exergetic efficiency of the LHTES system. As part of this presentation, experimental results on the fabricated graphite/PCM composite will be presented.

11:20 AM

(ICACC-JUB-025-2016) Processing and morphology control of porous ceramics for themal management (Invited)

M. Fukushima*[1]; T. Ohji[1]; N. Kondo[1]; Y. Yoshizawa[1]; 1. National Institute of Advanced Industrial Science and Technology (AIST), Japan

This presentation reviews various processing strategies in macroporous ceramic components for thermal management and different ways for achieving control of their pore morphology at different length scales. Two advanced processing methodologies to produce precisely controlled pore configurations have been discussed in terms of: 1) partial sintering of nanoparticles to enlarge the neck areas between grains, 2) elongated ice templating to create unidirectional pore channels or highly closed porosities via gelation of ceramic powder dispersed slurry with ice binding additives, and the freezing. These simple and versatile approaches proposed can be used to produce porous morphologies with engineered hierarchical porosity, and yield macroporous components with various distinct characteristics.

S1: Mechanical Behavior and Performance of Ceramics & Composites

Processing - Microstructure - Mechanical Properties Correlation II

Room: Coquina Salon D

Session Chairs: Kevin Plucknett, Dalhousie University

8:30 AM

(ICACC-S1-031-2016) Microstructure-Property-Performance Relationship to Develop Better Silicon Nitride Based Ceramics for Different Applications (Invited)

S. Turan*[1]; 1. Anadolu University, Turkey

Due to their high performance, Si_3N_4 and SiAlON ceramics found wide range of applications in different areas as light emitting diodes, cutting tools, ball bearings etc. The high cost of starting Si_3N_4 powders, sintering additives, production equipment and running cost prevents the wide spread use of these ceramics. Therefore, there is a need to understand the microstructure of these materials at atomic level and relate this with the properties and performance of the resulting material. In this study, microstructure-property-performance relationship will be shown for different compositions and processing routes with the aid of advanced characterisation techniques such as spherical aberration corrected scanning transmission electron microscopes. Hardness, toughness, luminescence, thermal, oxidation, creep and wear properties of various compositions were investigated and also tested at real applications. Whenever necessary, coating and joining were also applied to improve the properties or to understand the interaction between metal work pieces and ceramics. The atomic scale

observations of SiAlON will be presented for the understanding of the roles of starting powders, type of cations and the type of intergranular phase obtained through either sintering and/or sintering followed by heat treatment on the different properties of the Si_3N_4 based ceramics.

9:00 AM

(ICACC-S1-032-2016) Ceramic turbo charger of silicon nitride - material development and fabrication

H. Klemm*[1]; W. Kunz[1]; J. Abel[1]; E. Zschippang[1]; J. Stockmann[1]; 1. FhG IKTS Dresden, Germany

Even taking into account new technologies such as fuel cell technology or hybrid concepts, the internal combustion engine will continue to occupy a leading position as power unit in the medium term. New generations of combustion engines are measured mainly related to their efficiency, environmental impact and cost. In recent years, silicon nitride came back into focus as the material of engine parts, such as a ceramic turbocharger. Besides benefits as the consequence of the elevated-temperature potential of silicon nitride, the efficiency of these systems can be improved in particular by a shorter light-off performance due to their lower density as compared to metallic materials. In the present study, the fabrication of silicon nitride based turbo chargers will be presented. Based on comprehensive material development optimized silicon nitride with Y_2O_3 and Al_2O_3 as sintering additives was obtained. Ceramic prototypes were fabricated first by isostatic pressing, green machining and sintering. The up scaling to serial fabrication was achieved by the development of injection molding process. Based on the detailed understanding in properties and behavior of silicon nitride and ceramic processing and sintering, ceramic turbo chargers with superior properties were obtained finally.

9:20 AM

(ICACC-S1-033-2016) Composites in the aluminum oxynitride – MeN (Me=Ti, Ta, Cr) system prepared from SHS-derived powders

M. M. Bucko*[1]; 1. AGH University of Science and Technology, Poland

Aluminium oxynitride, γ-alon, is a spinel-type solid solution of Al_2O_3 and AlN. Due to its good mechanical and chemical properties γ-alon has a great potential application in high-performance structural ceramics. Additions of different types of hard and stiff inclusions such as Al_2O_3, AlN, SiC, ZrN, TiN and TiC enhanced mechanical properties of γ-alon. The aim of the work is to present a new idea of producing CMC composed of aluminium oxynitride matrix and some nitride particle inclusions. The precursor powders were formed in a single step process using the SHS synthesis. Starting powder mixtures were composed of aluminium oxide, aluminium and titanium, tantalum or chromiu, respectively. Alumina and Al powders remained a ratio of 4:1 when adding other metal powders. The powder mixtures were subjected to SHS reaction in nitrogen atmosphere under a pressure of 1 MPa. The powders were hot-pressed at 1750-1850°C for 1h under 25 MPa. The dense samples were composed of gamma-alon, small amount of aluminium nitride and respective nitrides: MeN and Me_2N. Increase of the nitrides content in the composites improved significantly their mechanical properties. The samples prepared from the powder containing formally 30 mol% of the metals show Vicker's hardness over 16 GPa, fracture toughness about 7 $MPam^{0.5}$ and wear resistance three order of magnitude better than dense corundum material.

9:40 AM

(ICACC-S1-034-2016) Thermal and Mechanical Properties of Silicon Carbide-Zirconium Nitride Composites

S. Jang*[1]; Y. Kim[1]; 1. University of Seoul, The Republic of Korea

On approach for tailoring properties is to combine the properties of different materials. SiC is known as important engineering ceramics for structural applications due to its good thermal conductivity, oxidation resistance, and high-temperature strength. In contrast, ZrN exhibits excellent properties including high melting temperature, high electrical conductivity, and gold color. In the present work, SiC-ZrN composites were fabricated from SiC and ZrN powders with 2 vol% Y_2O_3-Sc_2O_3 additives by conventional hot pressing in a nitrogen atmosphere. Thermal and mechanical properties of the SiC-ZrN composites were investigated as a function of initial ZrN content. Relative densities above 98% were obtained for all samples. The thermal conductivity decreased with increasing ZrN content. Typical thermal conductivity and flexural strength values of the SiC-10 vol% ZrN composites were 166 W/m K and ~640 MPa, respectively.

10:20 AM

(ICACC-S1-035-2016) Experimental investigation of refractory powders compaction and identification of the constitutive behavior

A. Kallel*[1]; S. Romero Baivier[1]; 1. Vesuvius, Belgium

An elasto-viscoplastic constitutive model for densification of composite refractory powders is proposed here. The studied material is a mixture of alumina particles and a viscous binder made of amorphous carbon. The powder is first uniaxially cold pressed with different velocities to investigate the strain rate sensitivity. Then cylindrical samples with relative density ranging from 60% to 95% are prepared at room temperature and at a strain rate of $10^{-5}s^{-1}$. The mechanical properties of obtained green bodies are determined from Brazilian tests and instrumented triaxial compression loading experiments performed at quasistatic conditions. Thus, the evolution of yield surfaces according to the relative density is modeled in the plane of hydrostatic and deviatoric stresses. Experimental data show that the behavior of the porous material is related to the mechanical properties of the mixture, to particles morphology (shape, size distribution, bonds) and to the loading path. In seek of simplicity, only the dependency to material properties is taken into account in the established constitutive equation. Reliability and robustness of the identified constitutive model are discussed. The model is under implementation in a commercial finite element method software. This approach is used to propose alternative route that limits the density gradient during manufacturing process.

10:40 AM

(ICACC-S1-036-2016) Exploring the morphological factors behind ferroelastic toughening

C. S. Smith[1]; J. A. Krogstad*[1]; 1. University of Illinois at Urbana-Champaign, USA

The contribution of ferroelastic switching to the toughness of ceramic coatings or devices is usually described in terms of transformation strain, cohesive stress and two process zone parameters. It is typically assumed that the microstructure is a randomly oriented single-phase polycrystal with little or no input of grain size or distribution. Examples from various applications that depend on the effective activation of this mechanism, ranging from thermal barrier coatings to piezoactuators, will be used to emphasize the morphological factors that must be better understood. These examples will include the influence of coherent boundaries between ferroelastically active/inactive domains, loss of this coherency, grain size, and phase fraction. Micromechanical methods under development to strategically probe specific microstructural configurations will also be described.

11:00 AM

(ICACC-S1-037-2016) Simulation and Experimental Validation of the Stress Evolution during Constrained Sintering of Ceramic Laminated Composites

S. E. van Kempen*[1]; U. A. Ozden[1]; A. Bezold[1]; C. Broeckmann[1]; 1. RWTH Aachen University, Germany

Co-sintering of heterogeneous multilayer ceramic laminates often leads to premature fracture and delamination. The failure is induced by stresses resulting from mismatches in thermal expansion and sinter shrinkage between layers, as they are mutually constrained after their initial bonding. In this work, the Skorohod-Olevsky model for viscous sintering was modified and implemented in an FE environment to predict and control the residual stresses, to simulate laminate deformation, and to determine processing conditions that reduce critical stresses for arbitrary laminate layups. Material and laminate data for simulation and validation included, among others, the shear viscosity and creep activation energy that have been determined using viscosimetry experiments, high temperature E-modulus measurements using impulse excitation, and dilatometry measurements to determine sinter shrinkage evolution and macroscopic curvature of single layers, bilayers, and 3-layer laminates. The simulated densification and deformation behavior of monolithic materials and multilayer laminates are in good agreement with the experimental data. Furthermore, the implementation of fracture criteria based on principal stresses allowed for an adequate prediction of laminate fracture during sintering. Future work will include the implementation of delamination criteria.

11:20 AM

(ICACC-S1-038-2016) AC field-induced metastable phase in $Na_{0.5}Bi_{0.5}TiO_3$-$KNbO_3$ piezoceramics detected by high-resolution synchrotron x-ray diffraction

G. Wang*[1]; D. Hall[1]; 1. University of Manchester, United Kingdom

The correlation between structure and electrical properties of lead-free $Na_{0.5}Bi_{0.5}TiO_3$-$xKNbO_3$ (x=0.01-0.09) polycrystalline piezoceramics was investigated systematically by in situ synchrotron diffraction technique, combined with electrical property characterization. It was found that as-sintered ceramics for all compositions appeared to be single phase pseudo-cubic. Furthermore, only application of a high AC field led to an irreversible structural phase transformation from pseudo-cubic to a rhombohedral ordered ferroelectric phase for compositions containing 1% and 3% KN. The underlying mechanism of phase switching behavior, NBT-xKN was evaluated by measuring polarization-field loops and low-field dielectric properties over a range of different temperatures. Increasingly constricted P-E loops were observed when increasing the KN content or increasing temperature, indicating the occurrence of a reversible field-induced weak-polar to ordered ferroelectric phase transition. In order to transform polar nanoregions (PNRs) into micro-domain structure in relaxor-FE materials, cycling AC high field is able to align PNRs and transform them into metastable rhombohedral domain structure. This AC field-induced phase transformation is associated with composition and temperature, which depends on the amount of PNRs exists at initial state.

11:40 AM

(ICACC-S1-039-2016) The fatigue behavior and failure mechanism of a needled C/SiC composite under tension-compression cyclic loading

G. Fang*[1]; X. Gao[1]; Y. Song[1]; 1. Nanjing University of Aeronautics and Astronautics, China

The tension-compression fatigue behavior for a needled C/SiC composite at room temperature was studied and compared with the properties under tension-tension fatigue loading. The microstructure of the composites and the morphology of the fractured surfaces of the failure specimens were observed by optical microscope and SEM. The results show that the needled C/SiC composites present an outstanding tension-compression fatigue resistance. The fatigue limit under tension-compression loading is found to be slight lower than that of tension-tension fatigue. In addition, the procedure of fatigue failure and the mechanism of enhancement were discussed after microstructure observation. Tension-compression fatigue resulted in more micro damages, and these damages, such as matrix cracks parallel to fibers and fiber break within needled fiber bundles, can accelerate the failure of needled C/SiC composites.

12:00 PM

(ICACC-S1-040-2016) Comprehensive investigations on the mechanical and thermal properties of X2-RE_2SiO_5 (RE = Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y) for ETBC materials

Z. Tian*[1]; L. Zheng[2]; J. Wang[1]; P. Wan[1]; J. Wang[1]; 1. Institute of Metal Research, Chinese Academy of Sciences, China; 2. Imperial College London, United Kingdom

Recent progresses showed that X2-RE_2SiO_5 were promising candidates of environmental/thermal barrier coating materials for silicon-based ceramics due to their excellent durability in harsh high-temperature environments and probable low thermal conductivities. However, due to the multiple polymorphs and species of rare earth silicates, it difficult to screen in optimal candidates through property evaluations of X2-RE_2SiO_5 coating materials. We herein study the intrinsic properties of X2-RE_2SiO_5 in experiments using bulk samples and a combination of DFT predictions. Comprehensive mechanical and thermal properties of X2-RE_2SiO_5 from room temperature to high temperature are evaluated for the first time. The mechanical and thermal properties are summarized into two groups: flexural strength, elastic modulus, and thermal shock resistance are more sensitive to the species of RE element; whilst thermal conductivity, thermal expansion coefficient, and brittle-to-ductile transition temperature (BDTT) are less dependent on RE elements. Specifically, these silicates show excellent elastic stiffness at high temperature, high BDTTs, very low experimental thermal conductivities, and compatible thermal expansion coefficients. The reported information provides important material selection and optimization guidelines for X2-RE_2SiO_5 as ETBC candidates.

S2: Advanced Ceramic Coatings for Structural, Environmental, and Functional Applications

Environmental Barrier Coatings

Room: Coquina Salon H

Session Chairs: Dongming Zhu, NASA Glenn Research Center; Bryan Harder, NASA Glenn Research Center

8:30 AM

(ICACC-S2-029-2016) High-Temperature Resistant SiC/HfC_xN_{1-x}/C Nanocomposites: Microstructure and Application (Invited)

Z. Yu*[1]; 1. Xiamen University, China

Amorphous SiHfC(N) ceramics have been prepared upon pyrolysis of single-source-precursors synthesized via reaction of allylhydridopolycarbosilane and tetrakis (dimethylamido) hafnium (IV). After subsequent annealing at 1300 to 1700°C, high-temperature resistant multiphase SiC/HfC_xN_{1-x}/C ceramic nanocomposites with in situ formed carbon ribbons and HfC_xN_{1-x}-Carbon core-shell nano particles embedded homogeneously within the β-SiC matrix were obtained. Their dielectric properties were determined on a N5222A PNA-X Microwave Network Analyzerin the X-band (8.2-12.4 GHz) at room temperature. The SiC/HfC_xN_{1-x}/C nanocomposites show significantly enhanced dielectric loss and microwave absorption capability compared with SiC. The highest reflection loss values (RL) of SiC/5HfC_xN_{1-x}/C-1700°C and SiC/15HfC_xN_{1-x}/C-1700°C are -46.8dB and -32.6dB, and the broadest effective absorption bandwidths are 3.1 and 3.6 GHz, respectively. The feature of segregated

carbon phase and the connection mechanisms between the carbon ribbons and HfC_xN_{1-x}-Carbon core-shell nano particles account for the unique dielectric behavior of the SiC/HfC_xN_{1-x}/C nanocomposites. Therefore, the obtained SiC/HfC_xN_{1-x}/C nanocomposites are promising EBC/TBC candidate materials with microwave absorption properties.

9:00 AM

(ICACC-S2-030-2016) Microstructural Stability of Aerosol Deposited Mullite Coating for EBCs under High Temperature Exposure

T. Mizuno*[1]; S. Sato[1]; A. Iuchi[1]; M. Hasegawa[1]; 1. Yokohama National University, Japan

Environmental barrier coatings (EBCs) for SiC fiber reinforced SiC ceramic matrix composites are the leading candidate coatings for high temperature structural components in next generation gas turbine engines. Due to the shrinkage of the coating by sintering at high temperature, vertical cracks initiate at EBCs. In order to prevent the vertical cracking of EBCs, dense ceramic coatings are required from the as-deposit state. Aerosol deposition (AD) method is known to fabricate a dense and uniform ceramic coating directly on a substrate without oxidation at room temperature. In this study, mullite which is one of the component materials for EBCs is deposited on several substrates such as alumina and silicon by AD method. Microstructure change of mullite coating under heat treatment in a vacuum and heat exposure in an air is investigated. The thickness of mullite coating increased with the increase in coating time. After heating the coatings at 1573 K for 10 hours, the thickness of the mullite coating is same as that of the as-deposited state. This indicates that mullite coating produced by AD method is fully dense from the as-deposited state.

9:20 AM

(ICACC-S2-031-2016) First-principles calculation of thermodynamic phase stability of rare earth disilicate $RE_2Si_2O_7$

T. Yokoi*[1]; A. Ioki[1]; M. Yoshiya[1]; 1. Osaka University, Japan

Rare-earth disilicate $RE_2Si_2O_7$, where RE is rare-earth element, is a potential structural high-temperature material since the material exhibits high melting point, oxidation resistance and low thermal conductivity. However, its thermodynamic stability, in particular the phase stability at a given high temperature, is still unclear because it is difficult to synthesize a single-phase sample; the six different polymorphs of $RE_2Si_2O_7$ have been reported and samples usually contain more than two different phases including SiO_2, RE_2O_3 and RE_2SiO_5. To understand the thermodynamic stability of the individual phases, we evaluate internal energy, free energy, and enthalpy of formation by using first-principles calculations and lattice dynamics methods. For systematic analyses, several types of rare earth element are studied. As a result, it is found that the two phases named beta and gamma phase are energetically more stable than the other phases for $Y_2Si_2O_7$. The results of phase stability are in satisfactory agreement with experimental results. In addition, results of various rare earth elements indicate that the most stable phase strongly depends on the type of rare earth element.

9:40 AM

(ICACC-S2-032-2016) Development Status and Performance Comparisons of Environmental Barrier Coating Systems for SiC/SiC Ceramic Matrix Composites

D. Zhu*[1]; B. J. Harder[1]; 1. NASA Glenn Research Center, USA

Environmental barrier coatings (EBC) and SiC/SiC ceramic matrix composites (CMCs) will play a crucial role in future aircraft turbine engine systems because of their ability to significantly increase engine operating temperatures, reduce engine weight and cooling requirements. This presentation will focus on current NASA EBC-CMC development emphases, including the coating composition and processing improvements, laser high heat flux thermomechanical fatigue - environmental testing methodology development, and property evaluations for next generation EBC-CMC systems. Environmental barrier coatings processed with various deposition techniques including Plasma Spray, Electron Beam - Physical Vapor Deposition, and Plasma Spray – Physical Vapor Deposition (PS-PVD) will be particularly discussed. Recent testing and demonstrations of advanced EBCs-CMCs in complex simulated engine thermal gradient cyclic fatigue, oxidizing-steam and CMAS environments will help provide insights into the coating development strategies to meet long-term engine component durability goals.

10:20 AM

(ICACC-S2-033-2016) Hot corrosion behaviors of BSAS Environmental Barrier Coatings (Invited)

Y. Wang*[1]; X. Huang[1]; 1. Northwestern Polytechical University, China

SiC/SiC composites are potential structural materials for high temperature applications. However, the poor water vapor corrosion resistance limits their application in combustion environments. Usually, the environmental barrier coatings (EBC) are applied to reduce such an effect. Barium-strontium aluminosilicate (BSAS) is one of the most used EBC in present. However, its hot corrosion behavior was seldom reported. In this presentation, we were trying to report the hot corrosion behaviors of BSAS in the environments of molten Na_2SO_4 and calcium-magnesium-aluminosilicate (CMAS) coupled with water vapor at different temperatures. It was found the diffusion out of Ba and Sr ions into the molten salts, resulting in the destruction of BSAS. The corrosion mechanism was proposed accordingly.

10:50 AM

(ICACC-S2-034-2016) Advanced Environmental Barrier Coating Systems Deposited via Plasma Spray- Physical Vapor Deposition

B. J. Harder*[1]; D. Zhu[1]; 1. NASA Glenn Research Center, USA

The incorporation of Si-based ceramic matrix composites (CMCs) into advanced turbine engines will provide increased combustion temperature capability while reducing weight and cooling requirements. However, the volatility of the protective SiO2 layer requires the use of an environmental barrier coating. Next generation turbine engine systems are expected to require hot section components to reach temperatures of 2700°F or greater, which will necessitate new environmental barriers and bond coats. Advanced EBC systems were processed using Plasma Spray- Physical Vapor Deposition (PS-PVD), which can tailor microstructures and compositions to optimize performance. Multilayer bond coat/top coat architectures were deposited and tested up to temperatures of 2700°F. Durability was tested in gradient heating using a high heat flux laser and cyclically with standard furnace cycling methods. Coating composition and crystal structure were tracked with X-ray diffraction and microstructure with electron microscopy.

11:10 AM

(ICACC-S2-035-2016) Microstructure Development of Dense Alumina Coating for Advanced EBCs under Heat Exposure

M. Hasegawa*[1]; S. Sato[1]; M. Komuro[1]; M. Tanaka[2]; S. Kitaoka[2]; Y. Kagawa[3]; 1. Yokohama National University, Japan; 2. Japan Fine Ceramics Center, Japan; 3. The University of Tokyo, Japan

An advanced environmental barrier coatings (EBCs) composed of a multilayer of alumina and $Y_2Ti_2O_7$ reflect thermal energy from radiation and prevent oxidation of the substrate of SiC fiber reinforced SiC ceramic matrix composites. During the high temperature service, structure and microstructure of EBCs are required to be stable. Thus, EBCs are necessary to have a dense ceramic coating from the as-deposit state. Aerosol deposition (AD) method is known to fabricate a dense ceramic coating without oxidation of substrate at room temperature by impacting fine ceramics particles on the substrate. In this study, microstructural stability and texture

development of alumina coating by AD method at high temperature heat exposure are researched. Alumina particles are deposited on the mullite and Mo substrate. After the coating, the materials are heated from 1173 K to 1673 K up to 100 hours. The thickness of alumina coating seems to be increase with the increase in gas flow rate. Weak fiber texture where the (0001) plane of alumina is tilting approximately 15 degree from the coating plane is observed in as-deposited state. With the increase in heating temperature and time, texture changed to (0001) fiber texture. Heating of the alumina coating for 10 hours at 1673 K may stabilize the microstructure of the coating for further heating.

11:30 AM

(ICACC-S2-036-2016) Control of Structural Stability of Mullite Layer under Oxygen Potential Gradients at High Temperatures

S. Kitaoka*[1]; T. Matsudaira[1]; M. Takata[1]; 1. Japan Fine Ceramics Center, Japan

Environmental barrier coatings (EBCs) can play a key role in allowing SiC fiber reinforced SiC ceramic matrix composites (SiC_f/SiC_m) to be applied to hot-section components in advanced airplane engines for better environmental stability and durability. Because mullite ($Al_{4+2x}Si_{2-2x}O_{10-x}$) has excellent heat resistance and its thermal expansion coefficient is close to that of SiC_f/SiC_m, it is a candidate for use in EBCs, which are exposed to a steep oxygen potential gradient ($\triangle\mu_O$) at high temperatures. However, the mass transfer mechanism in mullite layers in such environments is not well understood. In this study, the oxygen permeability of polycrystalline mullite wafers, which served as a model EBC layer, was evaluated at high temperatures above 1673 K. The $\triangle\mu_O$ was produced by exposing the upper and lower surfaces of the wafer to atmospheres with a different oxygen partial pressure (P_{O2}). Oxygen permeation occurred via grain boundary (GB) diffusion of oxygen from the high-P_{O2} surface to the low-P_{O2} surface, and simultaneous GB diffusion of aluminum in the opposite direction, resulting in decomposition of the mullite near the low-P_{O2} surface. The situations where a mullite layer would be used as an EBC were predicted to maintain the soundness of the layer.

S3: 13th International Symposium on Solid Oxide Fuel Cells (SOFC): Materials, Science and Technology

Electrode Materials / Transport and Reaction Mechanisms

Room: Crystal

Session Chairs: Nguyen Minh, University of California, San Diego; Enrico Traversa, King Abdullah University of Science and Technology

8:30 AM

(ICACC-S3-026-2016) Ce(Mn,Fe)O_2 dense anode for tubular type Solid Oxide Fuel Cells using $LaGaO_3$ electrolyte film (Invited)

T. Ishihara*[1]; K. Hosoi[1]; S. Ida[1]; 1. Kyushu University, Japan

Effects of $Ce_{0.6}Mn_{0.3}Fe_{0.1}O_{2-d}$ (CMF) interlayer on power generation properties of microtubular SOFC using doped $LaGaO_3$ (LSGM) electrolyte were investigated. Two types of microtubular cells (10mm in diameter) were prepared with (type A) or without (type B) CMF interlayer by dip-coating method. The power generation properties of A and B type cell sintered at 1350 °C were measured. It was revealed that A type cell showed much higher performance (0.7W/cm^2 at 700 °C than that of B type cell at temperature from 500 to 700 °C because of decreased electrode polarization by introducing CMF anodic interlayer. The amount of Ni diffused in LSGM electrolyte of A- and B-cell was analyzed with EDX analysis. It was found that the diffusion of Ni into LSGM/LDC interlayer was much suppressed by CMF interlayer and dense anode (A-cell). This is because Ni was trapped in the CMF interlayer and they formed Ni-CMF composite layer. Decrease in the polarization resistance might be assigned to the formation of Ni-CMF composite layer. Thus, CMF is promising for increasing the power generation property of microtubular SOFC using LSGM electrolyte prepared by dip coating method.

9:00 AM

(ICACC-S3-027-2016) Strontium and vanadium co-doped NaNbO3 as Ceramic Anode Material for LT-SOFC

K. Pan*[1]; A. Hussain[1]; E. D. Wachsman[1]; 1. University of Maryland, USA

Traditional nickel based solid oxide fuel cell anodes such as Ni-YSZ and Ni-GDC cermets are known to be promising materials for high and low operating temperature SOFCs, respectively. Nevertheless, intrinsic problems such as redox instability and carbon coking in hydrocarbon fuels present challenges. Compared to cermets, ceramic oxides are relatively stable in both reducing and oxidizing atmospheres and have a lower tendency for carbon deposition in hydrocarbon fuels. However, ceramic anodes have less catalytic activity and much lower conductivity than that of cermet anodes, and most of them should be fired in H_2 or reduced at high temperature to show good properties. In this work, we have reported the possibility of using strontium and vanadium doped sodium niobates as potential anode materials for LT-SOFCs operating below 600ºC. Three types of compositions based on vanadium doping level, $Sr_{0.2}Na_{0.8}Nb_{0.9}V_{0.1}O_3$ (SNNV10), $Sr_{0.2}Na_{0.8}Nb_{0.8}V_{0.2}O_3$ (SNNV20) and $Sr_{0.2}Na_{0.8}Nb_{0.7}V_{0.3}O_3$ (SNNV30) were synthesized via wet chemical method. After sintering at 1300ºC, SNNV10, SNNV20 and SNNV30 showed single perovskite phase. They exhibited conductivities up to 300S/cm at 650ºC (10% H_2 / 90% N_2) and the conductivities increase as temperature decreases. The ceramic oxides reported exhibit high conductivity and studies are underway to explore the possibility of making a LT-SOFC operated in hydrocarbon based fuels.

9:20 AM

(ICACC-S3-028-2016) Direct utilization of ethanol as fuel in a solid oxide fuel cell: Ceramic synthesis, anode fabrication and performance (Invited)

P. Miranda*[1]; S. Venancio[1]; 1. Coppe-Federal University of Rio de Janeiro, Brazil

An innovative anode based on the solid solution phase $Zr_xCe_{1-x}O_2$ and Al_2O_3 was engineered into an SOFC anode component with copper dispersed by impregnation to allow the direct utilization of ethanol as fuel. The CeO_2–Al_2O_3 ceramic powder was synthesized by the amorphous citrate method and calcined at 900 °C. Two layers composed the SOFC anode. Anode layer 1 contained YSZ to facilitate adhesion to the electrolyte. Anode layer 2 was richer on the active electrocatalyst. Successive impregnations of a copper nitrate solution, ($Cu(NO_3)_2.3H_2O$), were performed. The techniques of Raman spectroscopy, X-ray Diffraction and of scanning electron microscopy were used to identify the phases present in the anode functional layers and their morphology after ceramic processing and sintering. This enabled the inference that strong interaction occurred between YSZ and ceria with Zr^{4+} ions substituting Ce^{3+} ions upon forming the Cu–($Zr_{1-x}Ce_xO_2$-Al_2O_3) anode. Electrochemical performance of 16 cm^2 single SOFCs operating at 850ºC or 950ºC with the direct utilization of hydrogen or ethanol as fuels were presented and discussed. Thus, the need for previous fuel reforming and purification was abolished, in the absence of the occurrence of carbon coking and clogging within the SOFC anode.

9:50 AM

(ICACC-S3-029-2016) Understanding the Impacts of H_2S and CO_2 as Fuel Contaminants on the Performance of Proton Conducting SOFCs

S. Sun*[1]; Z. Cheng[1]; 1. Florida International University, USA

Proton conducting solid oxide fuel cells (SOFCs) can operate at significantly reduced temperatures such as 700 deg C and below when properly chosen electrolytes such as $BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$ (BZCYYb) are used. Here we present the results of our study aimed at understanding the fundamentals for the impacts of H_2S and CO_2 as fuel contaminants on the performance of proton conducting SOFCs. Anode-supported cells consisted of BZCYYb proton conducting electrolyte with Ni-BZCYYb anode and $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ cathode are subjected to hydrogen (H_2) fuel mixtures with and without H_2S and CO_2 contaminants. Preliminary study showed for such proton conducting SOFCs, cell performance remained unchanged when 5 ppmv of H_2S was introduced into the H_2 fuel (humidified or not). On the other hand, for CO_2, cell performance dropped instantaneously and reached a steady state when 5 vol.% of CO_2 was introduced into humidified H_2 fuel, and it recovered later after CO_2 was removed from the fuel. Detailed studies will be carried out to understand the fundamentals for such electrochemical behaviors of apparent "sulfur tolerance" and "CO_2 poisoning" for proton conducting SOFCs, which seem contrary to oxide-ion conducting SOFCs. The implications of such interesting electrochemical behaviors on the roles of proton conducting oxides play in the electrochemical oxidation of H_2 will be discussed.

10:30 AM

(ICACC-S3-030-2016) Evaluating Thin Film Defect Equilibria and Kinetics by *In Situ* Optical Transmission: Application to $Sr(Ti,Fe)O_{3-\alpha}$ Electrodes (Invited)

N. H. Perry*[1]; J. Kim[2]; H. L. Tuller[2]; 1. Kyushu University, Japan; 2. Massachusetts Institute of Technology, USA

Thin films serve both as model systems with well-defined geometries, e.g., for fundamental studies of surface exchange kinetics, and as functional layers in devices such as solid oxide fuel/electrolysis cells. In the latter case, performance is often dependent on the defect equilibria in the film, which may differ from its bulk counterpart. This presentation will describe the recently introduced "optical transmission relaxation" technique as a means of in situ/operando, continuous, contact-less interrogation of both thin film defect equilibria and surface exchange kinetics. Thin films of the mixed conducting electrode, $SrTi_{1-x}Fe_xO_{3-\alpha}$ ($0.05 \le x \le 0.5$), were deposited by pulsed laser deposition. Optical absorption corresponding to the concentration of Fe^{4+} was monitored over time in different oxygen activities and temperatures. Rapid, precise, and reversible electrochemical control of oxygen activity in the films over a wide range was demonstrated. Defect concentrations were in reasonable agreement with the bulk model, and surface exchange coefficients differed only slightly from those measured by concurrent impedance spectroscopy; the difference in the latter case is attributed to the absence of metal current collectors in the optical measurements. Possibilities for broader application of the technique will be discussed.

11:00 AM

(ICACC-S3-031-2016) The electrode reaction mechanism analysis and electrode design on SOFC cathode (Invited)

S. Hashimoto*[1]; R. Budiman[1]; Y. Uzumaki[1]; H. Kudo[1]; I. Susuta[1]; S. Noda[1]; T. Hoshi[1]; K. Yashiro[1]; T. Kawada[1]; 1. Tohoku University, Japan

Lower operation temperature of solid oxide fuel cells (SOFCs) is one of the important issues for widespread diffusion because low cost Fe-Cr based alloy can be used as the support and/or interconnector. Especially, improvement of cathodic reaction below 600°C is important for improvement of the efficiency, and new design of high performance cathode is desired. Since SOFC cathodes react with oxygen at two or triple phase boundary, basic properties such as oxygen non-stoichiometry, surface exchange reaction coefficient, activity on hetero junction activity and so on, are very important for understanding of the reaction process and mechanism. In this study, our established electrode reaction mechanism analysis techniques using basic property measurements are presented, and the case studies for new design of cathode based on the techniques, including Proton conducting Ceramic Fuels Cells (PCFCs) are also introduced. It was found out that interface controlling such as presence of abnormal valence elements, catalysis effect of CeO_2 based oxides, 113-214 hetero junction effects and so on, is very important to improve the interfacial conductivity. The parts of this work were made as a part of JST CREST research project and JSPS Kakenhi project, project No. 25289246.

11:30 AM

(ICACC-S3-032-2016) Anion and Cation Diffusion Properties of Grain Boundary Engineered Sr-doped $LaMnO_3$

T. M. Huber[1]; E. Navickas*[3]; G. Harrington[1]; D. Mendler[3]; H. Tellez[4]; J. Druce[4]; K. Sasaki[1]; J. Fleig[3]; B. Yildiz[2]; H. L. Tuller[2]; 1. Kyushu University, Japan; 2. Massachusetts Institute of Technology, USA; 3. Vienna University of Technology, Austria; 4. I2CNER, Japan

Sr-doped lanthanum manganite is the most commonly used cathode material in SOFCs. Nevertheless, many aspects of oxygen reduction at LSM electrodes are not yet fully understood. Particularly important in this respect is the long time stability and degradation effects upon the oxygen reduction kinetics. By understanding the mechanism and determining factors related to the diffusive properties, faster oxygen transporting and more stable thin films can be designed, respectively. Much attention has recently been focused on the oxygen reduction via LSM grain boundaries since their oxygen transport is 1000x faster and their surface incorporation is also nearly 1000x higher than the LSM bulk. In this work, LSM thin films were deposited by pulsed laser deposition and analyzed by ToF-SIMS, Van der Pauw and impedance spectroscopy. Cation diffusion was investigated by heterogeneous doping. ^{18}O tracer exchange experiments were performed in a novel operando experimental design to study the influence of cathodic bias upon surface exchange and transport properties of both LSM grains and grain boundaries. This facilitates the ability to investigate several voltage changes in every required voltage region under SOFC operation conditions within one thin film. Polarized films showed an apparent uphill diffusion that could be fitted by a 3D finite element model with two parallel and interacting diffusion pathways.

11:50 AM

(ICACC-S3-033-2016) Visualizing Oxygen Defect Equilibria and Transport Kinetics in Oxide Thin Films

J. Kim[1]; S. Bishop[1]; S. N. Cook[1]; D. Chen[1]; H. L. Tuller*[1]; 1. Massachusetts Institute of Technology, USA

An improved fundamental understanding of oxygen defect equilibria and transport kinetics in oxide thin films is essential for engineering enhanced performance in many miniaturized oxide-based device applications including μ-solid oxide fuel cells. In this work we are able to access the behavior of oxide thin films by monitoring changes in color intensity. Here we present experimental results obtained by our novel experimental apparatus, capable of simultaneously performing in situ optical absorption and impedance measurements at elevated temperatures and controlled atmospheres. This technique, when applied to model material systems such as $Pr_xCe_{1-x}O_{2-\delta}$ (PCO), allows the direct investigation of nonstoichiometry via absorption change and chemical capacitance and oxygen surface exchange kinetics via absorption relaxation and electrode reaction resistance. We also demonstrate how color front migration in PCO films can be used to extract oxygen diffusivity. The non-contact optical absorption technique provides an additional, quantitative insight into the defect equilibria of oxide thin films. Time dependent and spatial changes in optical absorption can be used to study oxygen transport kinetics in thin film structures. This

technique is especially beneficial when examining the impact of surface chemistry on these kinetics without complicating contributions from catalytically active metal electrodes.

S4: Armor Ceramics

Developments in Materials Characterization, Properties, and Response II

Room: Coquina Salon E
Session Chair: Jerry LaSalvia, Army Research Laboratory

8:00 AM

(ICACC-S4-033-2016) Update: Robust Nondestructive Testing Tools for Ceramic Armor

K. Schmidt*[1]; J. Little[1]; R. Goitia[1]; W. Ellingson[2]; W. Green[3]; L. Prokurat Franks[4]; 1. Evisive, Inc., USA; 2. ERC Company, USA; 3. US Army Research Laboratory, USA; 4. US Army, USA

A Portable Automated Microwave Scanning System (PAMSS) and companion Hand-Held Microwave Inspection Tool (HMIT) were developed for on-vehicle damage assessment of ceramic armor. The PAMSS equipment has been delivered to US Army users. Damage assessment is by operator differentiation of volume images. Operator training uses a library of validated examination examples, created using the PAMSS. Operators will be able to independently study examples from the library. Training for the HMIT, will be based on a novel program of on-board training and testing which requires no formal instruction. Operator training and determination of performance metrics are simultaneously implemented by the self-study course and tests on the operator interface computer. Using analysis of variance gauge repeatability and reproducibility techniques, the overall performance and performance of individual operators can be characterized by use of Cohen's kappa coefficient. The technique has been implemented on Stryker armor and has been demonstrated to be effective on other composite ceramic armor systems and dielectric parts, including those with complex structure and complex materials. This work is supported by the US Army Tank-Automotive Research, Development and Engineering Center (TARDEC), the US Army Research Laboratory and by Evisive, Inc. internal research and development.

Developments in Ballistic Behavior I

Room: Coquina Salon E
Session Chair: Tyrone Jones, US Army Research Laboratory

8:20 AM

(ICACC-S4-035-2016) Effects of layered plate materials on the ballistic performance of alumina armor plate

J. Lo*[1]; R. Santos[1]; R. Zhang[1]; D. Walsh[1]; R. Bowes[1]; C. Craciun[1]; H. Jin[1]; J. Saragosa[1]; F. Fazeli[1]; C. Scott[1]; 1. CanmetMATERIALS, Canada

Layered armour plates have been developed for the purpose of improving the ballistic performance of monolithic ceramics. Generally, the first layer consists of a hard ceramic which serves to deform and fracture incoming projectiles, while the backing layers are meant to direct, reduce and absorb shock waves, as well as to confine fracture debris. In this work, the effects of ballistic performance of alumina with different backing plate materials (steels, aluminum, and aluminum composite) were investigated. All backing materials investigated in this work were fabricated at CanmetMATERIALS with the intention of improving the ballistic resistance of alumina plate. The mechanical properties and microstructural information of each of the backing materials made were measured and acquired respectively. Depth of Penetration (DOP) test was used as an initial comparison for the alumina front plate variations, followed by ballistic testing of stand-alone full armour solutions (front plates and various backings), against 7.62-mm AP projectiles. The ballistic testing protocol was based on NATO AEP-55 Volume 1 publication. Correlation was made between the test data and the property of the backing materials. Finally, failure analyses were conducted on the tested plates to elucidate the penetration mechanisms and the effects of the backing plate materials on the ballistic behaviour of alumina plate.

8:40 AM

(ICACC-S4-036-2016) Microstructure-Based Design of Advanced Ceramics for Light-Weight Protection Systems

J. D. Hogan*[2]; L. Farbaniec[4]; D. Mallick[3]; B. Schuster[3]; T. Sano[3]; J. W. McCauley[1]; K. Ramesh[5]; 1. Army Research Laboratory/Johns Hopkins University, USA; 2. University of Alberta, Edmonton, Canada; 3. US Army Research Laboratory, USA; 4. Johns Hopkins University, USA; 5. Hopkins Extreme Materials Institute, USA

Understanding brittle fragmentation is important in the design of the next generation of light-weight ceramic protection systems, where desired fragmentation outcomes may lead to increased performance through enhanced projectile erosion. In this study, we investigate the impact fragmentation of a commercially available hot-pressed boron carbide, focusing on the relationships between the microstructure, and the failure mechanisms governing its impact behavior. We couple experimental insights with a newly developed compressive brittle fragmentation model and explore its applicability to the design of new light-weight protection materials.

9:00 AM

(ICACC-S4-037-2016) Performance of Nano Zirconia Toughened Alumina Ceramics under Dynamic Impact Conditions

Y. Zhu*[1]; H. Shuo[1]; H. Wu[1]; J. Binner[2]; B. Vaidhyanathan[1]; 1. Loughborough University, United Kingdom; 2. University of Birmingham, United Kingdom

This work focuses on investigating the high strain rate impact performance and the potential of ballistic damage resistance of nano zirconia toughened alumina (nZTA) ceramics. The nZTA samples comprised of 15 and 20 wt% nano yttria stabilised zirconia (nano YSZ) in a submicron alumina matrix and the baseline submicron alumina samples were prepared through pressureless sintering. Both nZTA and alumina samples were tested for dynamic performance using split Hopkinson pressure bar (SHPB) test, gas gun test and ballistic test. Dynamic impact induced phase transformation and plastic deformation in post-testing nZTA remnants were quantitatively studied with micro-Raman and Cr^{3+} fluorescence spectroscopy respectively. The variation of transformed zirconia, dislocation density in alumina, and surface residual stress were measured under different impact conditions. Transmission electron microscopy (TEM) was used to validate the phase transformation/mechanic deformation inside the materials. FEGSEM was also used to analyse the development of micro-cracks on the damaged surface and identify the variation of fracture mode of the fragments. The results demonstrated that the transformation of zirconia phase in nZTA can provide improved damage resistance even at the very high strain rate generated by ballistic test. The possible damage mechanisms will be discussed based on the experimental observations.

9:20 AM

(ICACC-S4-038-2016) Ballistic testing of small 3D printed Alumina disks with the energy method

E. Carton*[1]; J. Weerheijm[1]; 1. TNO, Netherlands

Proper confinement allows ballistic testing of small sized samples. The sample and a circular hole in a confining steel plate both had 15° slanted edges (chamfer). This enables both to have a close fit and avoids the more often used crimp fitting of a disked shaped sample in a cylindrical hole. The slanted edges allow the ceramic sample to be easily adhesively bonded into the steel plate. Alumina samples have been manufactured at TNO Industry by 3D printing greens of Alumina starting powder. This allows manufacturing of specially shaped disks without machining of hard ceramic samples.

After burning away of the binder, the samples have been sintered. This resulted in samples with a diameter of 30 mm and a thickness of 5 mm. In order to test the efficiency of the confinement technique small confined samples, as well as large tiles of a commercially available armor grade Alumina have been used. This 5 mm thick material has been machined into samples with the same shape and dimension as the 3D-printed samples. All samples have been ballistically tested using the energy method. The testing of the confined Alumina samples and the full scale tiles showed the same energy loss and mass loss of the AP core, demonstrating the effectiveness of the confinement technique. Subsequently, the 3D-printed Alumina samples were tested in confined condition and compared with the results of the armor grade Alumina.

Developments in Ballistic Behavior II

Room: Coquina Salon E
Session Chair: Sikhanda Satapathy, Army Research Laboratory

10:20 AM

(ICACC-S4-040-2016) A Comparison of Damage in Glass and Ceramic Targets

B. Aydelotte*[1]; P. Jannotti[1]; M. Andrews[1]; B. Schuster[1]; 1. US Army Research Laboratory, USA

Ballistic impacts on oxide glasses and ceramics result in a complex failure process that includes varying levels of comminution, cone cracking, and radial cracking. Sphere impacts are a useful tool to study the response of brittle materials to ballistic impact because they are amenable to comparison with analytical solutions as well as 2D and 3D simulations. Sphere impacts result in limited penetration and comminution relative to cylindrical projectiles, yet significant cone cracking and radial cracking is produced. Sphere impacts were conducted on glass and ceramic targets at various obliquities and velocities. X-ray computed tomography data generated from recovered glass and ceramic targets are contrasted and compared. The results of the impacts are discussed with an emphasis on the effects of obliquity and the similarities and differences between glass and ceramic target responses.

10:40 AM

(ICACC-S4-041-2016) Effect of surface layer on elastic waves and cracking in brittle materials

J. R. McDonald*[1]; 1. US Army Research Laboratory, USA

Surface defects and flaws play an important role in the impact response of brittle materials by interacting with elastic waves to inititiate cracking and failure. The goal of this study is to investigate wave-flaw interactions at the surface of brittle materials and explore possible mitigation strategies. Prior experimental studies have shown substantial benefit of surface treatment on the ballistic performance of ceramics. The exact mechanisms involved and the correlation between material properties and degree of ballistic improvement, however, is not well understood. One of the difficulties of the numerical study of thin coatings, subjected to high-rate loading, is the spatial resolution required to capture short-wavelength stress fields. Both finite element and finite difference methods tend to filter high frequency content depending on the spatial resolution employed, and very fine spatial discretizations often lead to exceedingly small time steps and large accumulated round off errors in explicit schemes. To this end, we implemented a computational scheme based on Laplace transforms to study surface wave effects. The method was applied to the problem of cone crack extension from an existing flaw under dynamic loading and then extended to treat the surface coating problem. The paper will discuss computational results with limited comparison with available experimental data.

11:00 AM

(ICACC-S4-042-2016) Phenomenological Mechanochemistry of Fracture of Polarizable Solids

M. Greenfield*[1]; 1. The US Army Research Laboratory, USA

Integrity of solids is supported by the bonds of different origin. Fracture and fragmentation are the final stages of mechanical and chemical processes which cause breaking of these bonds. The integral energy of those bonds is huge and can trigger the explosion-like phenomena, and the shear stresses are able to accelerate the rate of the chemical bonds breaking by several orders of magnitude. Fracture and fragmentation phenomena are of particular importance in the processes accompanying impact and penetration of glass and ceramic. In the paper we discuss how phenomenological mechanochemistry of damage addresses some of those phenomena. In the paper we put emphasis on the further developments of the original theory required for a consistent accounting of electromagnetic effects.

11:20 AM

(ICACC-S4-043-2016) The First Static And Dynamic Analysis of 3-D Printed Sintered Ceramics for Body Armor Applications

T. Jones*[1]; 1. US Army Research Laboratory, USA

As the landscape of warfare changes, the strategy of the US Army must adapt to maintain its warfare dominance. New technological advances in manufacturing enable the dismounted Soldier to tailor their body armor material needs to the demand of the environment. Traditional manufacturing of ceramics present limitations of long lead times, fabrication of complex geometries, and cost expensive components. Ceramic 3-D printing offers engineering-grade ceramic components in approximately 90% less time than traditional ceramics. Typical turn around can be in as little as five days depending on complexity of the part. This not only allows for faster time to market, but also allows for more iterations during the design process resulting in a better end product. The US Army Research Laboratory invested in a research partnership with HotEnd Works to create the world's first sintered Alumina tiles using a novel 3-D printing methodology. This research will examine the static and quasi-static parameters including density, hardness, and fracture toughness, dynamic parameters such as Hugoniot limit, spall strength, and semi-infinite analysis, of sintered alumina. These results will be parametrically compared to SAPI grade, traditionally sintered alumina.

S5: Next Generation Bioceramics and Biocomposites

Bioceramics I

Room: Coquina Salon F
Session Chairs: Akiyoshi Osaka, Okayama University; Jacqueline Johnson, UTSI

8:30 AM

(ICACC-S5-001-2016) Nanohybrids formed with photon upconverting nanoparticles for photodynamic therapy by near infrared irradiation (Invited)

K. Katagiri*[1]; 1. Hiroshima University, Japan

Photodynamic therapy (PDT) is a medical treatment for cancers using photosensitizers. Fullerenes are expected as one of possible candidates for photosensitizer of PDT. However, fullerenes are excited by visible light, which has limited penetration depth due to the light absorption and scattering by biological tissues. Development of photosensitizers which can generate singlet oxygen by near infrared (NIR) irradiation is one of the important targets of researches of PDT since biological tissues have the minimal light absorption in the NIR region. In this study, nanohybrids formed

with lipid-coated photon upconverting nanoparticles (UCNPs) incorporating C_{70} fullerene have been developed. UCNPs have the ability to convert NIR light to visible photons, which can activate C_{70} via resonance energy transfer. Oleate-coated $NaYF_4$:Er/Yb NPs were prepared by the solution process. Water-dispersable nanohybrids were obtained by lipid-coating of clusters of these NPs. The energy transfer from UCNPs to C_{70} is confirmed from upconversion luminescence spectra. The singlet oxygen production was determined by a dye-bleaching test. The amount of dyes decreases exponentially with NIR irradiation time when incubated with nanohybrids. This observation illustrates that singlet oxygen could be generated only from the cooperation of UCNPs and C_{70} via an efficient energy transfer process.

8:50 AM

(ICACC-S5-002-2016) γ-ray and neutron imaging enhancement using nanoscience (Invited)

J. A. Johnson*[1]; R. Leonard[1]; 1. UTSI, USA

The purpose of this work is to develop a γ-ray glass-ceramic and/or neutron scintillator to enhance imaging capabilities in computed tomography, positron emission spectroscopy and single photon emission computed tomography. Glass ceramics can be made in any shape or size and at a low cost. Samples have been synthesized based on a ZBLAN (zirconium, barium, lanthanum, aluminum and sodium fluoride) formulation additionally doped with chlorine and one or two rare-earth halides. The glasses are prepared in an inert atmosphere and later heat-treated in order to develop $BaCl_2$ nanocrystals within the glass matrix. Depending on size and number of the embedded nanocrystals they are optically transparent in the visible spectral range and offer the potential of high spatial resolution. Characterization methods include differential scanning calorimetry (DSC), photoluminescence (PL), x-ray diffraction (XRD), and Mössbauer spectroscopy. Results will be presented assessing the suitability of such a material for γ-ray and/or neutron scintillation.

9:10 AM

(ICACC-S5-003-2016) Healing of Bone Defects in a Rat Calvarial Defect Model Using Strong Porous Silicate 13-93 Bioactive Glass Scaffolds Doped with Copper or Loaded with Bone Morphogenetic Protein-2 (Invited)

M. N. Rahaman*[1]; 1. Missouri University of Science & Technology, USA

There is a clinical need for synthetic implants that can reliably repair large bone defects, particularly segmental defects in load-bearing bones. However, synthetic biomaterials typically function mainly as osteoconductive implants and commonly fail to produce clinically significant bone formation in a clinically relevant time. The capacity of osteogenic growth factors such as bone morphogenetic protein-2 (BMP2) and angiogenic factors such as copper (Cu) ions to improve healing of rat calvarial defects by strong porous silicate 13-93 bioactive glass scaffolds will be described. The amount of new bone and blood vessels that infiltrated the scaffolds at 6 weeks post-implantation was not affected by CuO dopant concentrations below approximately 1.0 wt. % in the glass whereas scaffolds doped with 2.0 wt. % CuO significantly inhibited bone regeneration. Loading the scaffolds with BMP2 (1 microgram per defect) was considerably more effective in stimulating osteogenesis and angiogenesis. The BMP2-loaded scaffolds significantly enhanced bone regeneration and angiogenesis at 6 weeks and they were almost completely infiltrated with new bone within 12 weeks.

9:40 AM

(ICACC-S5-004-2016) The Use of Bioceramic Dental Cements - an Overview (Invited)

L. Hermansson*[1]; J. Loof[1]; 1. Doxa Dental AB, Sweden

Bioceramic dental cements belong to the main system CaO- Al_2O_3-SiO_2- P2O5-H_2O (CASPH), with basically three sub-systems, i.e CaO- Al_2O_3-H_2O (CAH), CaO-SiO_2- H_2O (CSH), and CaO-P_2O_5-H_2O (CPH). The microstructures were studied with HRTEM with samples prepared using focused ion beam microscopy (FIB). The surface and bulk composition was analysed using thin-film XRD and SEM with EDAX. *In vitro* bioactivity testing was performed using the ISO standard 23317, and the toxicological endpoints using ISO 10993:2003. Antibacterial evaluation was performed using leakage test. These biomaterials seem all to exhibit nanostructures, both nanocrystals and nanoporosity. The potential use of the biomaterials for dental applications are based on the following features; 1) Nanostructural integration with reduced risk of secondary caries, 2) Reduced post-operative sensitivity, 3) Environmentally friendliness, 4) No allergy, 5) Hydrophilic acid-base systems with no extra bonding, 6) No dry field precaution, and 7) Excellent retentive and mechanical properties. The use so far is mainly restricted to Dental luting cements. These biomaterials have great opportunities based on experimental material data, pre-clinical studies, pilot studies and on-going clinical studies as general dental cements, endodontic products, bases, restoratives, and pastes for augmentation and dental implant coatings.

10:20 AM

(ICACC-S5-005-2016) Nanoscale structure and modification of Biomaterials (Invited)

F. Rosei*[1]; 1. INRS, Canada

Modifying the nanostructure/chemistry of materials allows to optimize their properties. Our strategy rests on creating nanopatterns that act as surface cues, affecting cell behavior. Chemical oxidation creates unique topographies, becoming a general strategy to improve biocompatibility. Our treatment selectively inhibits fibroblast growth while promoting osteogenic cell activity in vitro. Enhancement of mechano-biocompatibility may occur by coating with spider silk. Improvement of antibacterial properties using laser and plasma strategies will also be discussed.

10:40 AM

(ICACC-S5-006-2016) Delivery of CpG-ODN with Chitosan-derived Nanoparticles (Invited)

S. Chen[3]; A. Osaka*[1]; N. Hanagata[2]; 1. Okayama University, Japan; 2. National Institute for Materials Science (NIMS), Japan; 3. Taiyuang University of Technology, China

Cytosine-phosphodiester-guanine oligodeoxynucleotide (CpG ODN) is one type of potential immunoadjuvants. However, it has a main drawback of low immunostimulatory response. Nanoparticles are easily taken up by the cells due to small size and can efficiently deliver CpG-ODN into immune cells to enhance its immunostimulatory response. Chitosan/DNA nanocomplexes have been considered as one of typical gene delivery systems due to ease of fabrication via an electric force, strong resistance against DNase I degradation, and strong affinity to cell membrane. In this study, we reported two methods to fabricate the chitosan/CpG-ODN nanocomplex with enhanced immunostimulatory response. In the first method, chitosan-silicate hybrids were synthesized by introducing negative silicate component into the chitosan chain and then condensed CpG-ODN to yield chitosan-silicate/CpG-ODN nanocomplexes. The presence of silicate component effectively enhanced the release of CpG-ODN from nanocomplexes. In the second method, chitosan/CpG-ODN nanocomplexes were synthesized by condensing CpG-ODN with chitosan in a microfluidic device. Size and morphology of the resultant nanocomplexes were well adjusted by tuning the flow ratio of chitosan and CpG-ODN in the microfluidic device.

11:00 AM

(ICACC-S5-007-2016) Ion release kinetics from melt-derived bioactive silicate glasses (Invited)

L. Hupa*[1]; 1. Åbo Akademi University, Finland

Ion release kinetics controls the tissue regenerative capability of bioactive glasses. The release rate must be high enough to activate the biological processes over a critical period of time while not too high to give toxic effects. In addition, the ion release needs to be compatible with the tissue healing or remodelling rate. The in vitro reactions of bioactive glasses are usually studied in static solutions. However, the static environments fail to give detailed information of the leaching of the glasses in the dynamic body environment. Recently, dynamic systems in which the fluid continuously flows at a controlled rate through a sample of glass particles or spheres have been developed. The concentrations of the ions leaching from the glasses are measured either continuously on-line or for solutions collected during a certain time period. The initial ion release rate from highly bioactive to slowly resorbing melt-derived silicate glasses into continuously flowing buffered solutions will be discussed. The normalized ion concentrations are used to compare the dissolution mechanisms of the glasses. In addition, the ion release rate will be used to estimate the ability of the glasses to activate and stimulate genes and cells involved in tissue regeneration.

11:20 AM

(ICACC-S5-008-2016) Tantalum and Tantalum-Based Ceramic Coatings for Increasing the Biocompatibility of Conventional Metal Implant Alloys (Invited)

J. Stiglich*[1]; B. Williams[1]; 1. Ultramet, USA

Tantalum has long been used as an implant material in bone and soft tissue, and Ultramet developed and licensed a process for fabricating open-cell tantalum metal foam bone implants that are approved by the Food and Drug Administration. Under NASA funding Ultramet developed a process to diffuse highly corrosion-resistant tantalum metal into the surface of conventional stainless steels and superalloys to improve acid corrosion resistance of precision valve components. A thin, metallurgically bonded surface layer was established that graded from pure tantalum to a mixture of tantalum and the substrate elements. The tantalum surface layer precisely replicates intricate substrate features and does not require machining. This diffusion coating can increase the biocompatibility of conventional metal implant alloys, and the ability to harden the surface via partial or full conversion to tantalum nitride has been demonstrated. Additional surface treatments to alter texture may be used to improve biological functionality (e.g. enhance bone formation) of dental and orthopedic implants.

S6: Advanced Materials and Technologies for Direct Thermal Energy Conversion and Rechargeable Energy Storage

Supercapacitors

Room: Tomoka A

Session Chairs: Daniel Belanger, Université du Québec à Montréal; Yury Gogotsi, Drexel University

8:30 AM

(ICACC-S6-024-2016) Energy Storage Properties of Two-Dimensional Materials (Invited)

B. Dunn*[1]; 1. UCLA, USA

The intense interest in graphene for electrochemical energy storage has encouraged research groups to re-examine two-dimensional (2D) layered materials for both fundamental studies and energy applications. Although a number of different layered materials that support rapid Li and Na-ion transport are known, there are very few instances where the electrochemical properties for single to few-layered nanosheets of such 2D layered materials have been reported. This presentation will review our recent work on the synthesis and electrochemical properties of single to few-layered nanosheets prepared by either direct synthesis in solution or bulk-exfoliation. Among the materials we have investigated are those with well-established Van der Waals gaps (TiS_2,MoS_2) as well as 2D layered oxides such as $Na_2Ti_3O_7$. In most cases, the electrochemical properties of 2D nanosheets differ significantly from their bulk counterpart. Some of the more interesting properties observed for 2D nanosheets include higher capacity for ion storage, enhanced electrochemical reversibility, and electrochemical properties which exhibit both battery-like and capacitor-like behaviors. Our results suggest that 2D nanosheets have considerable promise for electrochemical energy storage applications.

9:00 AM

(ICACC-S6-025-2016) Two-Dimensional Materials and Electrode Architectures for Capacitive and Pseudocapacitive Energy Storage (Invited)

Y. Gogotsi*[1]; 1. Drexel University, USA

2D materials, including graphene, layered transition metal oxides (e.g., MoO_3) and carbides (MXenes) offer a unique opportunity to produce thin or thick films with high volumetric capacitance and energy density, because they can be packed denser than activated carbon or oxide particles, still providing accessibility for electrolyte. 2D particles can also be printed onto a variety of surfaces and assembled into flexible films without a polymer binder. However, when the lateral dimensions of particles become large and the electrode thickness increases, diffusion may limit the energy storage. To overcome this issue, 2D particles can be separated by one- or zero-dimensional particles (e.g., carbon nanotubes or onion-like carbon). By combining double-layer and pseudocapacitive (surface and fast intercalation redox processes) energy storage, it is possible to increase the capacitance well beyond conventional double-layer capacitors. Planar architectures that increase the volumetric energy density of electrodes also allow the use of very thin separators or replacing separators by a film of gel electrolyte, as no piercing by large particles or sharp tubes/rods is possible. MXenes films having metallic conductivity or graphene paper can be used to build current-collector free devices, further increasing the storage per unit of volume or weight.

9:30 AM

(ICACC-S6-026-2016) Manganese dioxide electrode: attempts to increase the electrochemical utilization (Invited)

D. Belanger*[1]; 1. Université du Québec à Montréal, Canada

Manganese dioxide has been the subject of intense research in recent years since it has been demonstrated that they are characterized by pseudocapacitor properties. Furthermore, hybrid electrochemical capacitor using a negative carbon electrode and positive manganese dioxide electrode together with an aqueous electrolyte allows to prepare a device with a higher cell voltage than either carbon/carbon or manganese dioxide/manganese dioxide symetrical electrochemical capacitor. Unfortunately, the high theoretical specific capacity of a manganese electrode cannot be obtained when thick and industrially relevant electrodes are investigated. In fact, no more than 20% of the manganese dioxide-based electrode material is electrochemically addressable. In this talk, attempts to increase the electrochemical utilization of manganese dioxide will be presented. The effect of carbon additives, shape of manganese dioxide particles and electrode formulation on the performance of manganese dioxide electrode tested in the three-electrode configuration (single electrode characterization) will be investigated.

10:20 AM

(ICACC-S6-027-2016) A biopolymer gel decorated cobalt molybdate nanowafer with improved energy storage: In-situ cross-linked electrode from Chitosan (Invited)

M. Minakshi*[1]; R. Ramkumar[1]; M. Ionescu[2]; 1. Murdoch University, Australia; 2. ANSTO, Australia

Mapping new materials for renewable energy storage is critical to our planet's future. It is well recognised that globally the dependence on fossil fuels (oil, gas and coal) and biomass (organic matter) for energy must be re-evaluated, as these sources are not sustainable. A global solution to this serious and significant threat to the environment and the world's energy needs must involve a radical shift to renewable, low-emission energies. The growing importance of environmental and non-renewable supply issues is such that energy storage will be a major driving force for the development of new materials technology. Nanoflake-like α-cobalt molybdate ($CoMoO_4$) was prepared with the aid of cationic surfactant as electrode material for supercapacitor by solution combustion synthesis. To achieve better energy storage, modification was done on $CoMoO_4$ by grafting chitosan in the presence of a weak, acetic acid (AA) or citric acid (CA) as a crosslinking agent. A biopolymer, chitosan is cross-linked using CA a cross-linking agent while in the case of acetic acid, grafting of chitosan/AA does not occur. The polymer modified composite exhibited the maximum specific capacitance of 71 F/g at 2 mA cm^{-2} with capacity retention of 81% after 2000 cycles. Influence of surfactant and chitosan concentration on the specific capacitance is also established.

10:50 AM

(ICACC-S6-028-2016) Pseudocapacitive transition metal oxides for energy storage and conversion (Invited)

V. Augustyn*[1]; 1. North Carolina State University, USA

Transition metal oxides are often the materials of choice for energy storage and conversion applications due to their numerous oxidation states, mixed electronic/ionic conductivity, and structural variability. A long-standing challenge for electrochemical energy storage involving transition metal oxides is to achieve both high energy and high power densities in the same device. This inability arises from the fundamental differences between storing energy within the solid state as opposed to the surface. Bridging the gap between energy and power is the motivation for the development of new high-energy and high-power energy storage materials. I will describe how such materials are possible with pseudocapacitance in transition metal oxides, whereby charge storage occurs via rapid redox reactions. Second, the search for highly active, non-precious metal electrocatalysts for efficient hydrogen production relies on correlating material properties with catalytic activity. I will describe the need to understand the material surface formed during electrocatalysis by discussing the behavior of a new class of oxygen evolution reaction catalyst materials, layered lithium transition metal oxides. In these materials, pseudocapacitive features before the onset of the oxygen evolution reaction give clues to the chemical and structural transformations occurring before and during the electrocatalytic reaction.

S7: 10th International Symposium on Nanostructured Materials: Functional Nanomaterials and Thin Films for Sustainable Energy Harvesting, Environmental and Health Applications

Synthesis, Functionalization & Assembly of Nanostructures I

Room: Coquina Salon A

Session Chairs: An Hardy, Hasselt University; Bart Michielsen, Flemish Institute for Technological Research

8:30 AM

(ICACC-S7-032-2016) Growing Integration Layer [GIL] Strategy: Fabrication of Compositionally, Structurally and Functionally Graded Nanostructured Oxide Coatings and/or Films on Metallic Materials in Solution (Invited)

M. Yoshimura*[1]; 1. National Cheng Kung University, Taiwan

We have proposed a novel concept and technology of the formation "Growing Integration Layer" [GIL] method,where GIL(s) can be prepared via integration of oxide film formation from a component of the metallic materials by chemical and /or electrochemical reactions in a solution at low temperature of RT-200. They have particular features:1)Widely diffused interface(s),2) Continuously graded layers grown from the bulk(substrate),3)Low temperature process,etc. They are quite different from so-called Layer-by-Layer[LBL] strategy, where every layer is deposited from the Top. $BaTiO_3$ or $SrTiO_3/TiO_x$ GIL films on Ti plates formed by hydrothermal-electrochemical method showed good adhesion. $CaTiO_3/Al_2O_3/Ti_2Al$ GIL films on TiAl exhibited excellent adhesion and anti-oxidation performances. On a Ti-base Bulk Metallic Glass, we could succeed to prepare bioactive titanate nano-mesh layer by hydrothermal-electrochemical techniques at 90-120· Since [GIL] have particular features described above the GIL method can be applicable for wide variety of applications like t environmental and/ or chemical coating, conducting and or insulating films, biological and/or medical coating, hermal barrier, mechanical parts,etc.

9:00 AM

(ICACC-S7-033-2016) Synthesis and Functionalization of Metal Oxide and Graphene Nanomaterials and Their Applications for Solar Cells (Invited)

Y. Hahn*[1]; 1. Chonbuk National University, The Republic of Korea

Metal oxide such as TiO_2 and ZnO and graphene based nanomaterials have been synthesized and functionalized for solar cells application. A simple reduction method without the need for high-temperature annealing is also proposed for highly conductive and dispersible graphene sheets, which consists of the grafting of graphene oxide (GO) with 1-pyrenecarboxylic acid (PCA) and the exothermic reduction of the PCA-grafted GO, followed by an endothermic decarboxylation with refluxing hot water. The PCA-grafted reduced grapheme oxide (PCA-rGO) has a high conductivity of ~$1.52x10^5$ S/m. By incorporating the rGO-PCA in active and electron transport layers of hybrid solar cells, a 16-fold increase in the power conversion efficiency is obtained, attributed to a substantial increase in short-circuit current density. We also have investigated the effect of composites of TiO_2 nanotubes-Ag nanoparticles (TiO_2 NTs-Ag NPs) on the performance of dye-sensitized solar cells (DSSCs). Compared to the DSSCs with TiO_2 NPs film only, the TiO_2 NPs/NTs-Ag NPs composites result in significant increase in phtocurrent density from 12.46 to 16.46 mA/cm^2 and power conversion efficiency from 8.05 to 10.53 %.

9:30 AM

(ICACC-S7-034-2016) Solid State 3D Li-ion Batteries (Invited)

M. Mees*[1]; 1. IMEC, Belgium

Emerging applications such as the Internet of Things (IoT) and Body Area Networks (BAN) typically require thin-film energy storage devices that possess a high energy and power output per unit area. All-solid-state 3D Li-ion batteries have the potential of meeting these requirements. In this approach, the functional battery materials (i.e. two Li-ion electrodes and a solid-state electrolyte of a few 100 nm thin) are deposited on a microstructured high-aspect ratio (HAR) current collector. The HAR current collector can take a variety of forms, where we currently focus on 60 µm high pillars with a 2 µm pitch. By scaling towards higher aspect ratios of these pillars, the energy and power output per unit area of the battery increases. Indeed, by increasing the height of the pillars, more active material per unit area can be deposited, resulting in a higher capacity. Simultaneously, the power output of the battery improves due to the increased internal surface of the 3D battery. Notice that a similar approach is not possible with conventional thin-film batteries. Increasing the active film thickness in these batteries results in more capacity, but this goes at the cost of power output due to the increased resistance of the thicker active layers. Because solid-state 3D batteries do not contain any flammable and corrosive liquid electrolytes, they are considered as intrinsically safe.

9:50 AM

(ICACC-S7-035-2016) From nano to macro: Assembly and processing of nanoparticles into 2D and 3D geometries over several length scales (Invited)

M. Niederberger*[1]; 1. ETH Zurich, Switzerland

Nanostructures including nanoparticles, nanowires and nanosheets are the ideal building blocks for the bottom-up fabrication of multi-component materials with tailored functionalities. They offer an immense variety of interesting properties, which not only depend on the composition, but also on the crystal structure, the particle size and shape and on the surface chemistry. However, for most applications the powdery building blocks have to be assembled and processed into useful geometries, architectures and bodies of macroscopic size, but without losing the nanoscale-specific properties. The talk will cover the synthesis and assembly of nanoscale building blocks, mainly metal oxides, in 2 and 3 dimensions and over several length scales. We will introduce the synthesis of a great variety of metal oxide nanocrystals by nonaqueous sol-gel chemistry, followed by discussing various strategies to fine-tune the surface chemistry, which is essential for the assembly of the nanoparticles into macroscopic aerogel monoliths and for their processing into films. Selected applications in the field of photoelectrochemical water splitting, gas sensing and lithium ion batteries will briefly be addressed.

Synthesis, Functionalization & Assembly of Nanostructures II

Room: Coquina Salon A

Session Chairs: Markus Niederberger, ETH Zurich; Masahiro Yoshimura, National Cheng Kung Univ.

10:30 AM

(ICACC-S7-036-2016) Characteristics of SnO_2:Ga powder prepared continuously in a micro drop fluidized reactor for chemical sensing (Invited)

D. Lim[1]; D. Yoo[1]; C. Lee[2]; G. Kang[3]; Y. Kang*[1]; 1. Chungnam National University, The Republic of Korea; 2. Institute for Advanced Engineering, The Republic of Korea; 3. Gentec Co., The Republic of Korea

Nano-structured SnO_2:Ga powders were prepared in a micro drop fluidized reactor continuously without calcinations, for application in the fields of chemical sensing. The powders were single crystal structures with the size was in the range of 50 ~ 300 nm. The main peaks of XRD shifted slightly, the band edge was extended, and the crystallite size decreased, with increasing doped Ga^{3+} contents. The surface area of spherical powders increased with increasing bubble flow rate. The PL spectra showed broad visible emission centered at 530-600 nm, indicating the charge transfer at the surface of the powder. The powder responded to the UV-Visible absorption spectra at room temperature in the atmosphere of methanol, ethanol, iso-propanol, ammonium hydroxide and AgNO3. The response was effective when the Ga content was 2at%. The sensitivities were also tested by means of voltage-current test.

11:00 AM

(ICACC-S7-037-2016) Towards a solution deposited 3D thin-film Li-ion battery

A. Hardy*[1]; 1. Hasselt University, Belgium

Lithium ion batteries (LIB) have important applications for mobile electronics, electric vehicles or storage of renewable energy. Conventional LIB are using powder based electrodes and a liquid electrolyte, and provide high capacity. Alternatively, thin film LIB provide higher power and employs solid electrolytes, which guarantees safety. To combine the advantages of both, 3D thin film batteries have been proposed, and devices up to half cells have been deposited using vacuum based methods because conformality is of the utmost importance. Here, we demonstrate a solution based deposition process for 3D thin film battery components, including anode, cathode and solid electrolytes as well as half cells. The methodology is based on an optimized ultrasonic spraydeposition process and a water based precursor solution containing citrate complexes, with finetuned surface tension and gelation upon contact with the substrate. In this way complete coating of the structures was achieved with a high degree of conformality. In conclusion, 3D structures were coated by ultrasonically spray depositing an aqueous solution-gel precursor, yielding electrochemically active electrodes, as well as half cell stacks. The method is promising to other application areas such as photocatalysis or capacitors as well. We acknowledge the IWT project SBOSOSLION and UHasselt (BOF-IOF) for financial support.

11:20 AM

(ICACC-S7-038-2016) Healthy indoor environment control utilizing novel photocatalytic materials (Invited)

G. Kiriakidis*[1]; 1. Univ. of Crete and IESL/FORTH, Greece

In the construction industry, buildings are major capital investments and the prospect of the occupants experiencing the adverse health effects of air quality and/or poor thermal comfort conditions strongly contradict a basic building's function: to provide protection to the occupants from atmospheric conditions and support their daily activities under a comfortable and safe umbrella. Especially in the case of large scale structures which host large number of occupants like office buildings or schools, several studies link indoor environmental quality not only to human health problems, but also to decreasing productivity. This highlights indoor climate (air quality and comfort temperature) as essential qualities these buildings must feature. In the past decades a large number of studies have identified the presence of many polluting chemical substances in indoor environments (buildings, homes).The solution to this problem is expected by a systematic and effective way to improved indoor environment quality utilizing heterogeneous catalysis and in particular photo-catalytic (PC) oxidation, a technique generally accepted as an effective way to tackle the pollutant emission problem and comfort levels for safe indoor applications.

11:50 AM

(ICACC-S7-039-2016) Development of Oxygen-Separation Perovskite Membranes for High-Temperature Applications (Invited)

B. Michielsen*[1]; 1. Flemish Institute for Technological Research, Belgium

When perovskites with mixed ionic-electronic conducting properties are exposed to an oxygen chemical potential gradient at temperatures typically higher than 700°C, they selectively transport oxygen in the form of oxygen ions from the high partial pressure side to the low partial pressure side of the membrane, without the need for electrodes and external electrical loadings. Both oxygen production and partial oxidation are two of the emerging applications of oxygen-permeable ceramic membranes. Nano-sized perovskites powders such as Ba0.5Sr0.5Co0.8Fe0.2O3−δ La0,6Sr0,4Co0,2Fe0,8O3-δ and CaTi0.9Fe0.1O3−δ are shaped into capillary or tubular membranes high membrane surface/volume ratios using phase-inversion spinning or extrusion. Afterwards they are thermally treated to obtain dense membranes. The oxygen permeation flux through these membranes is limited by surface-oxygen exchange kinetics. To improve this oxygen exchange, the membranes are coated with an activation layer, which can be either a porous layer of the membrane material itself to increase the surface area or a material layer with superior oxygen exchange properties. The flux of oxygen through these membranes depends on the operating temperatures and can reach values as high as 4 ml min-1 cm-2.

12:10 PM

(ICACC-S7-040-2016) Solution carbothermal nitridation of nano phase ZrN powder

S. Naim Katea*[1]; 1. Uppsala University, Sweden

ZrN is of great interest due to its high melting point, hardness, durability, thermal and electric conductivity. Lately the need for a nano-phase powder has emerged as ZrN is chosen as the matrix for U, Pu and Am in the Pb and Pb-Bi cooled Gen IV reactor fuels. The present micron sized and impure ZrN produced through carbothermal nitridation require very high sintering temperatures, even with SPS which is not suitable for production. The poor powder quality probably stems from the uneven mixing of the ZrO2 and carbon black. In this work, a new solution based process to nano-phase ZrN based on sucrose-Zr-alkoxide precursors was developed and investigated in detail with TG-DTA, XRD, IR and Raman spectroscopy SEM-EDS and TEM-EDS. It was found that an extremely intimate mixing of ca 4 nm sized ZrOx(OH)y particles and carbon as a graphene type coating surrounding the particles was obtained at 200C, and that the Zr-particles were converted to ZrO2 at 600C with retained structure at 600C. The carbothermal nitridation reactions started at 1200C and were finished at 1500C, resulting in a phase pure ZrN according to XRD, but TEM showed that the ca 20-30 nm sized particles had a 4-5nm thick amorphous or fine-crystalline shell and there might be some carbon in the structure.

S8: 10th International Symposium on Advanced Processing and Manufacturing Technologies for Structural and Multifunctional Materials and Systems (APMT10)

Novel Ceramic Processing II

Room: Coquina Salon B

Session Chairs: Junichi Tatami, Yokohama National University; Csaba Balazsi, Bay Zoltan Nonprofit Ltd. for Applied Research

8:30 AM

(ICACC-S8-029-2016) Fundamental aspects of the steric stabilization of aqueous dispersions by anion and cation type comb copolymers (Invited)

T. Graule*[1]; 1. Empa, Switzerland

The efficient stabilisation of ceramic based nanopowders is a prerequisite for the achievement of highly reliable ceramic materials. Agglomeration or re-agglomeration due to Van der Waals forces can be avoided using different concepts to increase the separation barrier by electrostatic or steric means. Recently we performed detailed studies applying anion and cation type copolymers for the surface modification and stabilisation of alumina and zirconia submicron and nanoparticles. The studies were performed in order to develop a basic understanding of the mechanism of steric stabilisation in aqueous media. We present here additionally new concepts to apply cationic comb copolymers as a promising alternative in case of the stabilisation of titania and silica. The effectiveness of the anionic and cationic dispersants is evaluated on the basis of adsorption, zeta potential measurements, rheology and particle size measurements.

9:00 AM

(ICACC-S8-030-2016) Characterization of Anisotropic Properties of Textured Lanthanum Silicate Oxyapatite Ceramics Fabricated by Magnetic Field-Assisted Colloidal Processing (Invited)

T. Uchikoshi*[1]; T. S. Suzuki[1]; K. Kobayashi[1]; 1. National Institute for Materials Science (NIMS), Japan

Lanthanum silicate oxyapatite $La_{9.33+2x}(SiO_4)_6O_{2+3x}$ is a lately-found oxide ion conductor. The oxide ion conduction mainly occurs along the *c*-axis; therefore, the *c*-axis orientation in dense polycrystals is preferable for its potential applications such as gas-sensing devices and solid oxide fuel cells at moderate temperatures. The lanthanum silicate oxyapatite is a diamagnetic material and it has anisotropic magnetic susceptibility depending on the *a*, *b*- and *c*-axes of the hexagonal crystalline structure. Therefore, when the lanthanum silicate oxyapatite particles suspended in a liquid medium are placed in a strong magnetic field, they will rotate in order to align their hard magnetization axis perpendicular to the applied magnetic field. We demonstrate in this presentation that the *c*-axis oriented ceramics can be fabricated using a magnetic field-assisted colloidal processing technique. The crystalline orientation was characterized by XRD, EBSD and SEM. The electric conductivity of the bulk compacts was evaluated by the complex impedance method.

9:30 AM

(ICACC-S8-031-2016) Fabrication of textured ceramics using magnetic field assisted forming and subsequet sintering

S. Tanaka*[1]; 1. Nagaoka University of Technology, Japan

Fabrication of crystal oriented ceramics have been examined using a colloidal processing in magnetic field and subsequent sintering. The subjects of this processing were to use strong magnetic flux density. Here, in order to use low magnetic flux density, the influence of sintering was examined on development of oriented structures. Several materials as alumina and alkali niobate with the tungsten bronze-type structure were used. Those slurries were prepare by ball

milling and casted in a mold. The powder compact was formed by drying slurry in a super conducting magnet. Magnetic flux density was changed in the range of 0-10 T. The influence of oriented structure in the powder compact was examined on development behavior of microstructure during sintering. As a result, for both materials, the oriented structure was well developed by grain growth during sintering even in the powder compact prepared in magnetic flux density less than 5T. Grain growth of oriented large grains contributed to development of textured structures. However, the powder compact with high orientation degree could be rarely densified by sintering.

10:10 AM

(ICACC-S8-032-2016) Anisotropic properties of c-axis oriented SiC prepared by slip casting in strong magnetic field and SPS

T. S. Suzuki*[1]; K. Kobayashi[1]; T. Uchikoshi[1]; T. Nishimura[1]; Y. Sakka[1]; 1. National Institute for Materials Science, Japan

Physical properties of materials depend on the direction of the crystal axis. Tailoring the crystallographic texture in ceramics is one effective way to improve their properties, such as electrical property, thermal conductivity and mechanical properties. We already reported that development of texture can be controlled by consolidation in a strong magnetic field followed by heating even for diamagnetic ceramics. In this study, we applied this processing to SiC(6H) for producing the textured SiC and investigate some properties. Aqueous suspensions of pH 10 were prepared that contained 30 vol% solids. The suspensions were then consolidated by slip casting in a strong magnetic field of 12 T at room temperature. The *c*-axis of the SiC was parallel to the direction of the applied magnetic field. The green SiC compacts were densified by hot pressing at 2000°C for 2 h at a pressure of 40 MPa and SPS at 1900°C for 10min at a pressure of 80 MPa. The preparation of the dense and textured SiC polycrystal was achieved. The 3-point bending strengths were 907 and 799 MPa for the crack-growth directions parallel and perpendicular to the *c*-axis in the c-axis oriented SiC, respectively, and for the random SiC, the strength was 724 MPa. The thermal conductivity and the electrical conductivity perpendicular to the c-axis was higher than that parallel to the c-axis in the textured SiC.

10:30 AM

(ICACC-S8-033-2016) High temperature interaction of MgO single crystalline substrates with liquid Ni alloys

J. J. Sobczak*[1]; N. Sobczak[1]; R. Purgert[2]; R. Asthana[3]; R. Nowak[1]; M. Homa[1]; J. Morgiel[4]; 1. Foundry Research Institute, Poland; 2. Energy Industries of Ohio, USA; 3. University of Wisconsin, USA; 4. Polish Academy of Sciences, Poland

The paper is focused on scientific and practical aspects of application of MgO as a base materials or sintering aid for refractory ceramics used in liquid-assisted processes of Ni-based superalloys (e.g. for such foundry appliances as crucibles, molds, filters). High temperature interaction of single crystalline MgO substrates with Ni-based binary alloys and commercial superalloys has been investigated at a temperature of 1500°C using a sessile drop method coupled with either contact or non-contact heating procedure followed by drop pushing or drop sucking for in situ opening the interfaces. Real time melting, wetting, spreading and solidification behavior of the alloy on a ceramic substrate were recorded by high-resolution high-speed CCD camera. The structure and chemistry of interfaces, both in situ opened and formed in the solidified sessile drop samples, were examined using optical, scanning and transmission electron microscopy in order to determine the stability and reactivity of selected oxide-based ceramics. The effects of contact time and type of Ni-alloy have been investigated. The results obtained are discussed from point of view of thermodynamic and kinetic factors affecting reactivity in MgO/Ni-alloy systems.

10:50 AM

(ICACC-S8-034-2016) Preparation of Passivated Magnesium Submicron Powders by Pulsed Wire Discharge

H. Suematsu*[1]; K. Tanaka[1]; K. Sugashima[1]; K. Suzuki[1]; T. Suzuki[1]; T. Nakayama[1]; K. Niihara[1]; 1. Nagaoka University of Technology, Japan

Magnesium (Mg) has been used in laptop PC, automobile and other parts utilizing its high specific strength. Powders of Mg should be useful in powder metallurgy, however, the production was difficult because of its high oxidation free energy and speed. Thus, for preparation of Mg powders, pulverization and passivation have to be carried out almost simultaneously. Pulsed wire discharge (PWD) has been known as an energy efficient and organic matter coating method to prepare various metal nanosized powders including Ti and Zr. In the present study, preparation of Mg powders was attempted in hydrocarbon fume/vapor, whose oxygen content was far less than that for Ti and Zr. A Mg wire with size of 0.3mm in diameter and 32mm in length was connected to a capacitor of 10μF charged at 5kV in Ar gas with hydrocarbon fume/vapor at 100kPa. After the TEM and XRD analysis of the prepared powder, Mg particles with size of 50-20nm were seen. The Mg particles did not oxidized in air at room temperature for one month. From these results, it was concluded that passivated Mg particles were prepared by PWD. As far as the author's knowledge, they are the first Mg submicron particles which can be stored in air in the dry form.

11:10 AM

(ICACC-S8-035-2016) Polymer-Derived (Carbo)Nitride Nanocomposites with multifunctionality

S. Bernard*[1]; 1. European Membrane Institute, France

There is a trend toward more flexibility and an increased interest in "smart" and "adaptive" materials with the objective to meet most industrial specifications. Nitrides can be considered as such strategic materials. They attract increasing interest due to their properties targeted for future materials and technologies, especially their relatively high thermal robustness and chemical inertness, while bearing intrinsic multi-functionality. Inherent difficulties to the traditional techniques for manufacturing shaped ceramics (with a controlled porosity for example) can be overcome by the development of synthetic paths where chemistry of materials and ceramic science are combined rationally to process multi-scale complex solid state architectures. The *Polymer-Derived Ceramics* (PDCs) route offers new preparation opportunities in chemistry and ceramic sciences. The molecular origin of preceramic polymers and the possibility to shape then pyrolyze them into "near net shape" advanced ceramics play a major role in the preparation of nitrides endowed with properties that reach far beyond those of existing materials. Here, we report the preparation of (carbo)nitride nanocomposite powders in which topologies, shapes and morphologies are tuned through the molecular design of preceramic polymers combined with shaping and pyrolysis processes.

11:30 AM

(ICACC-S8-036-2016) Low Temperature Densification of Ceramics and Cermets by the Intermediary Stage Activated Sintering Method

T. A. Restivo*[1]; S. R. Mello-Castanho[2]; J. A. Tenorio[3]; 1. UNISO, Brazil; 2. IPEN, Brazil; 3. Escola Politecnica USP, Brazil

The article explores new concepts in order to promote ceramic and cermet materials sintering at lower temperatures down to 1200°C. The principle of the new process method called Intermediary Stage Activated Sintering (ISAS) involves the preparation of the ceramic powder with dispersed doping agents, such as nanotubes and fibers, which shape the pore structure found at pressed pellets with stable interconnected thin cylinders between the grains. This feature resembles and extends the condition found during the intermediary stage sintering, which enhances the ions diffusion rate along tubular pores to increase shrinkage. Carbon nanotubes and fibers are

homogenized into cubic zirconia and alumina in amounts ranging from 1 to 10 vol.% at high energy milling devices and ultrasound disruptor under ethanol media. Mo/MoO3 can be also added to provide tubular channel filling. Sintering of uniaxially pressed pellets is carried out in a dilatometer and tubular furnaces at 1200°C under air, argon and controlled oxygen partial pressure atmospheres. The results demonstrate the ISAS process concept is valid since it further increases the ceramics final density by 10% of the theoretical density at 1200°C. The microstructures of pellets show a tendency to close the pores in the periphery while the core retains some residual porosity.

11:50 AM

(ICACC-S8-037-2016) Size and Temperature Dependent Single Photon Properties of Nitrogen Vacancy Embedded Diamond Nanopillars

W. Li*[1]; C. Gu[1]; Q. Jiang[1]; Z. Liu[1]; H. Ye[2]; J. Li[1]; 1. Beijing National Lab for Condensed Matter Physics, China; 2. Aston University, United Kingdom

Color centers in diamond are prominent candidates to generate and manipulate quantum states of light, even at room temperature. For improved single photon flux collection efficiency, which in bulk diamond, is greatly reduced by refraction at the diamond/air interface, various methods have been tried for diamond structuring. However, the size effect and the related temperature dependent properties of the nanostructured diamond single photon source has yet to be reported. In this work, we explored a combined technique of electron beam lithography nanopatterning and reacted ion etching to fabricate periodically-positioned nanoscale nitrogen vacancy color center embedded diamond nanopillars from bulk diamond structure and investigated the corresponding optical properties. We found that compared with the film counterpart, an enhancement of about ten folds in single photon collection efficiency was achieved with greatly improved signal to noise ratio. However, we observed that the coherence time for the NV color centers in the bulk material is only weakly affected for temperature up to 423K, while that for the nanopillar decreases significantly with the operating temperature. The mechanism behind this observation will be discussed in details along with the size effect.

S10: Virtual Materials (Computational) Design and Ceramic Genome

Modeling of Point Defects, Grain Boundaries and Interfaces I

Room: Ponce DeLeon
Session Chair: Haixuan Xu, Oak Ridge National Lab

8:30 AM

(ICACC-S10-024-2016) Challenges of Atomistic Manipulation at Grain Boundaries Based on Detailed Mechanisms of Grain Boundary Segregation of Point Defect Species (Invited)

M. Yoshiya*[1]; T. Yokoi[1]; 1. Osaka University, Japan

Lattice discontinuity at grain boundaries (GBs) brings about change in chemical potential of atoms in the vicinity of GBs. This results in deviation in chemistry of matrix phases found in phase diagram, not only confined to intrinsic or extrinsic point defect species including foreign element species but also for constituent atomic species of the matrix phase, which is referred to as GB segregation (GBS). Even with the latest scanning transmission electron microscopy with sub-Angstrom resolution, it is still challenging to fully characterize GBS as translational symmetry in marix phase is lost near GB. Grand canonical-like atomistic simulations with aids of energy minimization technique and Monte Carlo algorithm for site-interchange have revealed not only three dimensional configuration of segregants but also the mechanism behind GBS, enabling us to fully utilize the GBS for better properties originated from GB or GBS. We will present our recent findings of GBS in trivalent oxides-doped ZrO_2 at various symmetric tilt grain boundaries, attempting to classify what has been observed just enrichment or depletion of segregants. Remarkable in O^{2-} Ionic conduction near GBs governed by GBS is also discussed based on careful molecular dynamics simulations using the GBS configuration obtained in our studies.

9:00 AM

(ICACC-S10-025-2016) Predicting Grain Boundary Structures and Transitions (Invited)

S. Yang[1]; N. Zhou[1]; J. Luo*[1]; 1. UCSD, USA

Phase transitions are one of the most important physical phenomena in materials science. Recent experimental studies show that grain boundaries can often exhibit phase-like (complexion) transitions that will affect microstructural evolution and a broad range of materials properties. Significant recent efforts have been made to develop and test simplified (highly idealized) statistical interfacial thermodynamic models to forecast some useful trends in grain boundary structural and adsorption transitions, with some successes. More recently, atomistic simulation using generic algorithms was adopted and modified to predict grain boundary structures and transitions in multicomponent systems at finite temperatures. Our recent examples of Mo-Ni and Ni-S systems will be discussed. The results of statistical interfacial thermodynamic models and atomistic simulation are compared with experiments. A long-range scientific goal is to develop grain boundary "phase" (complexion) diagrams as a new materials science tool and a useful component for the Materials Genome Initiative.

Modeling of Point Defects, Grain Boundaries and Interfaces II

Room: Ponce DeLeon
Session Chair: William Weber, University of Tennessee

10:20 AM

(ICACC-S10-027-2016) Ionization Effects in Silicon Carbide (Invited)

Y. Zhang*[1]; R. Sachan[1]; O. Pakarinen[1]; M. Chisholm[1]; P. Liu[3]; H. Xue[3]; W. J. Weber[2]; 1. Oak Ridge National Laboratory, USA; 2. University of Tennessee, USA; 3. The University of Tennessee, USA

SiC is a wide band-gap material, capable of operating at extreme conditions. In an integrated computational and experimental approach, we show that the energy transferred to the electrons in SiC by MeV ions via inelastic ionization processes can effectively anneal pre-existing defects and restore the structural order. This self-healing process is activated at an unexpectedly low threshold value under MeV ions, much lower than a few tens of keV/nm reported for swift heavy ions with energy from a few hundreds of MeV to GeV. Our findings are validated by a substantial reduction in dechanneling yield due to the effective annihilation of a high concentration of interstitials and small defect clusters over a sub-micrometer depth, by evidence of a repaired crystalline structure with much less observed displacement at the atomic level, and by insights into corresponding defect dynamic processes revealed by MD simulations. This ionization effect can have a considerable impact not only on functionalizing SiC-based devices by providing a room-temperature approach to anneal defects and repair damaged crystalline structure, but also for predicting material performance in nuclear environment and space applications. Understanding ionization effects mechanism in SiC has significant implications for the study of irradiation effects in other ceramics for applications in extreme radiation environments. This work was support by U.S. DOE, BES, MSED.

10:50 AM

(ICACC-S10-028-2016) Defect Transport in Perovskite Oxide Superlattice from Density Functional TheoryDefect Transport in Perovskite Oxide Superlattice from Density Functional Theory (Invited)

H. Xu*[1]; 1. The University of Tennessee, USA

Oxide superlattices have attracted broad attentions because of their novel physical properties, e.g., the two-dimensional electron gas in the SrTiO3/LaAlO3 superlattices. In addition, the inevitable defects play a critical role in influencing superlattice properties. In this study, oxygen vacancy diffusion in perovskite oxide superlattices (SrTiO3/XTiO3, X=Pb, Ba, Ca) is investigated using density functional theory (DFT). The oxygen octahedral rotation patters in these superlattices are determined. Combining the effect of octahedral rotation and superlattice structure, different oxygen vacancy diffusion paths are identified and the vacancy diffusion energy barrier of each path is determined. It is found the oxygen diffusion is highly anisotropic and migration barriers differ significantly among layers in these superlattices, which could lead to defect accumulation and changes in physical properties. In addition, the effects of number of layers in the superlattice, (e.g. 1/1, 2/2, and 3/3) on the migration energy barriers are elucidated. This study provides detailed analysis of oxygen vacancy diffusion in oxide superlattices and fundamental insights of how to turn the defect transport to achieve desired properties. The work is supported by the UT-JDRD and ORNL-LDRD.

11:20 AM

(ICACC-S10-029-2016) On the competition between bulk fracture and interface debonding along wavy interfaces

S. Sehr*[1]; W. Pro[1]; M. Begley[1]; 1. University of California, Santa Barbara, USA

Non-planar interfaces can be an effective means to improve adherence, in that the far-field energy release rate needed to drive interface debonding can be higher than those associated with flat interfaces. In this work, the impact of wavy interfaces was analyzed under mixed-mode loading conditions using a discrete element method, which allowed for arbitrary crack growth directions (e.g. either through the bulk or along the interface). The results were used to generate regime maps that indicate the expected failure mode as a function of waveform parameters, interface-to-bulk toughness ratio and far-field loading conditions. These maps provide significant insight regarding material systems and loading-scenarios for which interface topology can be exploited to improve reliability.

11:40 AM

(ICACC-S10-030-2016) Computational Design of Nanograin Engineered SiC-Diamond Multiphase Ceramics for Improved Toughness

A. Adnan*[1]; J. Bhatia[1]; 1. University of Texas, USA

Silicon Carbide (SiC) is a strong and hard engineering material frequently considered for abrasives, rotating disks, bearing, high temperature coatings etc. Poor fracture toughness is one of the limitations that keeps SiC from widespread structural applications. In this study mechanical properties of a new type SiC-Diamond based multiphase ceramics where certain SiC and Diamond nanograins are "atomistically" blended to form a phase-separated multiphase ceramics structures are studied using MD simulation. Five different systems with different nominal grain sizes, namely 1 nm, 2 nm, 3nm, 4 nm and 5 have been investigated. The SiC-Diamond ratio was also varied between 25%, 50% and 75% and compared against pure SiC and pure Diamond polycrystals.. We explore the microstructures, specially near the SiC-diamond interfaces by measuring the average coordination numbers, which suggests that the newly designed materials have local microstructural change. We then evaluated tensile and shear response of these newly developed materials and found the mechanical properties depend on amount of SiC/diamond ratio as well as grain sizes.

S12: Materials for Extreme Environments: Ultrahigh Temperature Ceramics (UHTCs) and Nano-laminated Ternary Carbides and Nitrides (MAX Phases)

Novel Characterization Methods and Lifetime Assessment

Room: Tomoka B

Session Chair: Diletta Sciti, ISTEC-CNR

8:30 AM

(ICACC-S12-027-2016) TEM study on UHTCs and composites (Invited)

L. Silvestroni*[1]; D. Sciti[1]; S. Lauterbach[2]; H. Kleebe[2]; 1. CNR, Italy; 2. Technical University Darmstadt, Germany

Research on UHTCs has generally involved two major fields: the improvement of mechanical properties and the oxidation resistance. High performances are achieved upon careful tailoring of the microstructure, obtained through an aware control of the sintering additives, secondary phases and densification process. Recent advancements in high temperature strength have been achieved through addition of W-based compounds, thanks to the formation of highly refractory secondary phases. Another vivid issue related to UHTCs concerns strategies to improve their low fracture toughness. In order to increase their intrinsic brittleness, long and short fibers are added to ZrB_2. However, cautious choice of the sintering parameters must be paid, owing to the tendency of the fibers to react with the matrix at increasing temperatures, change their characteristic structure and thus lose their properties. The addition of fibers or sintering additive notably alters the oxidation behavior of monolithic ZrB_2, through the formation of new crystalline phases and change of the viscosity of the outermost silico-boride glass. In this work, a series of UHTCs possessing outstanding high temperature mechanical strength, or improved fracture toughness, or exceptional oxidation resistance will be reviewed. In particular, the microstructure evolution upon sintering or oxidation will be studied by SEM and TEM and correlated to the specific thermo-mechanical performances.

9:00 AM

(ICACC-S12-028-2016) Oxygen Diffusion Pathways During High Temperature Oxidation of ZrB_2-SiC

K. Shugart*[1]; E. Opila[2]; 1. UES, Inc., USA; 2. University of Virginia, USA

Oxygen diffusion mechanisms during oxidation of ZrB_2-30 vol% SiC were explored at temperatures of 1500°C and 1650°C using an $^{18}O_2$ tracer technique. Double oxidation experiments in $^{16}O_2$ and $^{18}O_2$ were performed using a modified resistive heating technique. A combination of scanning electron microscopy, energy dispersive spectroscopy, and time of flight secondary ion mass spectrometry was used to characterize the oxidation products. At short times oxygen was shown to permeate through the borosilicate scale. Oxygen exchange within the borosilicate glass was not uniform, attributed to possible compositional variation throughout the glass. At longer times, the oxygen exchanged with both the borosilicate glass and the ZrO_2 grains, though at a slightly slower rate in the ZrO_2.

9:20 AM

(ICACC-S12-029-2016) Analysis of dynamic Young's modulus and damping behavior of ZrB_2-SiC composites by the impulse excitation technique

A. K. Swarnakar*[1]; S. Ran[2]; J. Vleugels[1]; 1. KU Leuven, Belgium; 2. Anhui University of Technology, China

The high melting temperature of ultra-high temperature ZrB_2-based composites (UHTCs) makes them potential candidates for aerospace

applications. However, the high densification temperature of pure ZrB_2 powder requires sintering additives such as SiC, $MoSi_2$, etc. to achieve full densification at reasonable temperatures. Moreover, a precise knowledge of the high temperature behavior is necessary in order to fully exploit the potential of ZrB_2-SiC composites. In the present work, ZrB_2-composites with 20 vol% SiC were sintered by pulsed electric current sintering (PECS) from commercial and self-synthesized ZrB_2 powders mixed with nano-sized SiC powders to near full density (> 99%). The dynamic Young's modulus and damping analysis were performed up to 1400°C in vacuum using the Impulse Excitation Technique (IET). The E-modulus decreased up to 12% from room temperature to 1400°C. The nature of the starting powders clearly influenced the damping spectra and the observed damping peaks were associated with the presence of B_2O_3 and an amorphous grain boundary phase.

Materials Design, New Composition and Composites II

Room: Tomoka B
Session Chair: Laura Silvestroni, CNR

10:20 AM

(ICACC-S12-030-2016) Fabrication and high temperature characterization of UHTC-CMCs with SiC or C fibers (Invited)

D. Sciti*[2]; L. Zoli[1]; 1. CNR ISTEC, Italy; 2. ISTEC-CNR, Italy

Ultra-high temperature ceramics (UHTCs) have been identified as potential candidates for operating in harsh conditions owing to their melting point exceeding 3000°C and their resistance to ablation, but are severely plagued by poor fracture toughness and thermal shock resistance. UHTCMCs represent a novel class of materials, which can potentially couple the high oxidation resistance of UHTCs to the damage tolerance of CMCs, provided that a suitable matrix/fiber interface is tailored. In this talk, fabrication and characterization of SiC of C fibers - UHTCMCs are shown, considering different kinds of commercial products/preforms and different processing techniques. One of the processes used for impregnation of SiC preforms is vacuum-bag infiltration, whilst consolidation of the UHTC phase is obtained through hot pressing as typical of ceramic bulk materials. The densification process is affected by the type and content of fiber used (SiC or C). The overall fiber content varies from 40 to 70 vol %, and the final porosity of the composites is in the range 5-25vol%. The microstructure is examined in details to track the development of a matrix/fiber interphase. Fracture behavior and high temperature behavior (including arc-jet, HVOF) of selected compositions are discussed.

10:50 AM

(ICACC-S12-031-2016) Synthesis and Performance Optimization of ZrB_2-$MoSi_2$ Dual-Scale Composite Architectures for High Temperature Structural Applications

R. J. Grohsmeyer*[1]; G. Hilmas[1]; W. Fahrenholtz[1]; S. Faille[2]; F. Monteverde[2]; L. Pienti[2]; D. Sciti[2]; 1. Missouri University of Science and Technology, USA; 2. National Research Council of Italy - Institute of Science and Technology for Ceramics, Italy

Dual composite (DC) architectures have been shown to increase wear resistance while maintaining or increasing fracture toughness in WC-Co composites for room-temperature applications by containing multiple discretely segregated engineered microstructures. Composites of zirconium diboride (ZrB_2) and molybdenum disilicide ($MoSi_2$) are candidates for similar dual composite architectures for high-temperature structural use in corrosive environments, due to high-temperature ductility, strength and oxidation resistance of $MoSi_2$. After systematically measuring the mechanical properties of individual ZrB_2-$MoSi_2$ subcomposites at both room temperature and 1500°C in air, multiple DC architectures were prepared by synthesizing discrete granules of a subcomposite composition and dispersing them in a continuous matrix of another subcomposite composition with different properties. This research investigates the simultaneous co-densification of multiple microstructures, the effects of differing properties of granule and matrix subcomposites, differing oxidation resistance of the two compositions, as well as size and volume fraction of granules. Mechanical properties including flexure strength and fracture toughness at room temperature and at 1500°C in air of various DC architectures will be reported and compared to corresponding traditional particulate composites

11:10 AM

(ICACC-S12-032-2016) Synthesis of Nanocrystalline Ultrahigh Temperature Tantalum Hafnium Complex Carbide ($Ta_xHf_{1-x}C_y$) Powders

P. Foroughi*[1]; Z. Cheng[1]; 1. Florida International University, USA

Carbides of transition metals such as tantalum carbide (TaC) and hafnium carbide (HfC) are considered as ultrahigh temperature ceramics. TaC and HfC form a continuous solid solution at higher temperatures (>1000°C) but has a miscibility gap below 887°C. In this study nanocrystalline powders of ultrahigh temperature tantalum hafnium complex carbide ($Ta_xHf_{1-x}C_y$) are synthesized by solution processing of tantalum chloride ($TaCl_5$), hafnium tetrachloride ($HfCl_4$) and sucrose followed by pyrolysis and carbothermal reduction (CTR) reaction of the yielded molecular-scale mixed tantalum-hafnium oxide(s) and carbon. The phase and composition analysis of the powders are performed using X-ray diffraction (XRD) and energy dispersive spectroscopy (EDS). Morphology and grain size of the products are studied using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The effects of CTR and pyrolysis conditions such as temperature, dwell time, heating rate and gas flow rate/vacuum level and also solution processing conditions such as starting materials and solution homogeneity on product morphology and crystallite size are studied. In addition, special attention is given to investigate the effects of all the aforementioned factors on phase separation i.e., from uniform carbide solid solution to two distinctive carbide phases of HfC and TaC and its prevention.

11:30 AM

(ICACC-S12-033-2016) Thermal shock of refractories undergoing severe temperature changes

F. Dal Corso*[1]; T. Papathanasiou[1]; 1. University of Trento, Italy

Refractory ceramics constitute a class of high temperature resistant materials. Their thermal properties, in particular their very high melting and transformation temperatures as well as their low conductivity to specific heat capacity ratio, make them ideal for many advanced engineering applications (e.g. liquid steel industry, thermal barrier coatings etc.). With reference to severe thermal shock conditions, the thermo-mechanical response of a refractory specimen is simulated through a custom-made Finite Element code. All material properties are allowed to vary with temperature due to the considered severe thermal loading conditions. Two distinct phases to describe the loading cycle are considered, namely, a fast heating stage followed by a much slower cooling down period. Both convection and radiation heat transfer modes are present and their relative magnitude, during the different stages of the loading cycle, is evaluated. Thermal stresses generated inside the bulk of the material due to temperature transients are estimated with an incremental constitutive approach, where the possibility of plastic deformation is taken into account. The obtained results highlight the importance of considering nonlinear phenomena (e.g. radiation heat transfer and the temperature dependence of material properties) to properly describe the thermo-mechanical response of ceramics subject to severe temperature variations.

S13: Advanced Materials for Sustainable Nuclear Fission and Fusion Energy

Standard, Testing, and Joining

Room: St. John
Session Chairs: Chuck Henager, Pacific Northwest National Lab; Monica Ferraris, Politecnico di Torino

8:30 AM

(ICACC-S13-026-2016) Composition, Structure, Manufacture, and Properties of SiC-SiC CMCs for Nuclear Applications: Informational Chapters in the ASME BPV Code Section III (Invited)

M. G. Jenkins*[1]; S. Gonczy[3]; Y. Katoh[2]; 1. Bothell Engineering and Science Technologies, USA; 2. Oak Ridge National Laboratory, USA; 3. Gateway Materials Technology, USA

Future nuclear reactors planned by US DOE will use SiC/SiC CMCs to enhance fuel performance and improve accident tolerance. SiC/SiC CMCs are tolerant to the irradiation and chemical environments of current and future nuclear reactors. Because SiC/SiC CMCs are nonconventional materials, a concern with these plans involves the mission of the US Nuclear Regulatory Commission (NRC) which is to license and regulate the nation's civilian use of byproduct, sources and special nuclear materials. Note that the NRC regulates nuclear reactors and new reactor design as well as the reactor materials. The NRC not only imploys, but is legally required to use, consensus codes and standards as an integral part of the regulatory process. In particular, the ASME Boiler and Pressure Vessel Code (BPVC) Section III "Rules for Construction of Nuclear Components" (which codifies and standardizes acceptable materials for nuclear applications) is included in the NRC regulations. Therefore, for SiC/SiC CMCs to be incorporated into current and future nuclear reactors, they must be included in ASME BPVC as acceptable materials. This presentation provides an overview of two informational chapters regarding the composition, structure, manufacture, and properties of SiC/SiC CMCs for nuclear applications as currently being developed in ASME BPVC Section III.

9:00 AM

(ICACC-S13-027-2016) An ASTM C28 Standard Guide for the High Temperature Oxidation Exposure Testing of Advanced Ceramics at Atmospheric Pressures and Low Gas Velocities

S. T. Gonczy*[1]; Y. Katoh[2]; 1. Gateway Materials Technology, USA; 2. Oak Ridge National Laboratory, USA

Advanced ceramics, both monolithic and composites, are being developed and used for high temperature structural components in aerospace, nuclear power, and environmental systems. These ceramics (oxide and non-oxide compositions) are generally much more stable and oxidation resistant than the metals they are replacing. But they are seldom 100% inert at very high oxidation temperatures (>1000°C), especially in the presence of water vapor. Oxidation exposure testing is done to assess the oxidation reactivity and oxidation effects on the properties and life of the ceramic component. Defined test specimens (with and without coatings) are exposed to controlled atmospheres at defined temperatures for measured time periods. Changes in specimen mass and dimensions are measured and the exposed specimens are tested for retained functional properties. The ASTM C28 committee has developed a new guide for the high temperature oxidation exposure testing of advanced ceramics at atmospheric pressures and low gas velocities. Guidance is provided on oxidation reaction chemistry, test planning, test equipment, specimen geometry and preparation, critical test parameter control and measurement, reaction product/scale/substrate analysis, data analysis, and reporting requirements.

9:20 AM

(ICACC-S13-028-2016) Hoop Tensile Strength of Composite Tubes for LWRS Applications Using Internal Pressurization: Two ASTM Test Methods

M. G. Jenkins*[1]; J. Salem[2]; J. E. Gallego[1]; 1. Bothell Engineering and Science Technologies, USA; 2. NASA Glenn Research Center, USA

Conventional zirconium-alloy fuel rod tubes in light water reactors (LWR) will be replaced by US DOE with those consisting of SiC/SiC CMCs to enhance fuel performance and accident tolerance. SiC/SiC CMCs are tolerant to irradiation and chemical environments of LWRs. Failure modes in LWR fuel cladding include loss of gas tightness and reduced mechanical integrity due to the build-up of internal gas pressure and the swelling of fuel pellets. Therefore, determination of the hoop tensile strength is critically important for evaluation of SiC/SiC CMC fuel claddings. Two full-consensus ASTM test methods have been developed that use internal pressurization: [(i) one using expansion of an axially-loaded elastomer insert and (ii) one using pressurized fluid] to introduce hoop stresses in composite tubular test specimens. Both test methods are based on sound, theoretical analysis of the stresses developed in tubes subjected to internal pressure over a finite length inside a semi-infinitely long tube. These ASTM test methods contain test specimen dimensions, testing geometries, test conditions and results interpretation based on this theory and subsequent empirical tests applied to various materials and geometries. These test methods are intended for material development, material characterization, material screening, model validation, and quality assurance.

9:40 AM

(ICACC-S13-029-2016) Failure of SiC Composite-Based Fuel Cladding: Definition and Approach to Probabilistic Assessment

Y. Katoh*[1]; L. L. Snead[2]; K. Terrani[1]; 1. Oak Ridge National Laboratory, USA; 2. Independent, USA

Continues fiber-reinforced silicon carbide composites-based ceramic cladding is among the leading technologies that constitute highly accident-tolerant fuels for light water reactors. In these damage-tolerant composite clads, structural damages of different levels occur depending on the magnitude of excessive stresses resulting in a range of immediate and time-dependent consequences. In this paper, multiple levels of failure are defined for the silicon carbide composite-based fuel claddings for light water reactors. Based on the proposed failure definitions, the approach to estimate probability of failure is discussed. Research sponsored by Advanced Fuels Campaign, Office of Nuclear Energy, U.S. Department of Energy under contract DE-AC05-00OR22725 with UT-Battelle, LLC.

10:20 AM

(ICACC-S13-030-2016) Joining SiC for Nuclear Applications: Dual Phase and Single Phase Joint

C. Henager*[1]; B. Nguyen[1]; 1. Pacific Northwest National Lab, USA

The use of SiC and SiC-composites in fission or fusion environments requires joining methods for assembling larger components and systems. In this study, SiC joints were fabricated at 1425C (1698K) using displacement reactions between tape cast Si and TiC sheets to produce Ti_3SiC_2/SiC joints with CVD-SiC or Hexoloy-SiC as the base material. These dual-phase joints are compared to single-phase SiC joints fabricated using tape cast powders produced using SiC-filled polycarbosilane that was pre-cured in several stages up to 800C in inert environments and then joined at 1400C to 1600C (1673K to 1873K). The single-phase joints are expected to behave more uniformly in radiation damage environments. Substantial characterization of the joint materials is performed using optical and scanning electron microscopy. A finite element damage model is used to study simulated thermal and volumetric swelling fields on the physical and mechanical properties of the dual-phase and single-phase joints.

10:50 AM

(ICACC-S13-031-2016) Improving the damage-tolerance of Zircaloy cladding materials by MAX phase coatings

J. Zhang*[1]; Z. Tian[1]; J. Wang[1]; 1. Institute of Metal Research, China

The development of accident-tolerant fuel/clad system during Loss-of-coolant accident (LOCA) has been considered as a challenges of light water reactors (LWR) after the Fukushima Dai-ichi accident. During LOCA scenario, the insufficient coolant flow results in rise of surface temperature and internal overpressure of the clad tube. The sudden heat-up causes severe oxidation and degradation of mechanical properties of Zircaloy cladding and finally the clad tube will undergo ballooning and subsequent bursting. MAX phases display a high resistance to oxidation and ion irradiation from which a promising coating materials with application in enhancing the accident-tolerance of Zircaloy cladding. By applying Cr2AlC onto Zircaloy cladding the accident-tolerance of the nuclear system could be effectively improved. High quality Cr2AlC film was synthesized on Zr-4 alloy substrates, which is widely applied in current LWR. The mechanical and chemical compatibility between Cr2AlC coating and Zr-4 substrate in the as-deposited state as well as under LOCA scenario were investigated, aiming at evaluating the feasibility to apply Cr2AlC as protective layer on Zircaloy claddings under accident conditions.

11:10 AM

(ICACC-S13-032-2016) Low Temperature Air Braze Process for Joining Silicon Carbide Components Used in Heat Exchangers, Fusion and Fission Reactors, and other Energy Production and Chemical Synthesis Systems

J. Fellows*[1]; C. Lewinsohn[1]; Y. Katoh[2]; T. Koyanagi[2]; 1. Ceramatec, Inc., USA; 2. Oak Ridge National Laboratory, USA

Fabrication of large, or complex, components from silicon carbide, or other technical ceramics, used in heat exchanger devices, energy production and chemical synthesis systems, and for components within fusion and fission reactors require robust joining processes. Ceramatec has developed a novel method for achieving bonds using an air brazing process. For silicon carbide joining, the braze acts under certain conditions to promote diffusion bonding. The resulting joined regions are thought to form by rapid interdiffusion of the diffusion-enhancing braze material and silicon and carbon species, resulting in a microstructure more similar to one formed by diffusion bonding than brazing. Processing of these joints is accomplished at relatively low temperatures, i.e. 1000°C-1200°C in air, with minimal applied load. The resulting bond has mechanical properties that are similar to those of the substrates joined. Torsion tests on irradiated joined samples show that the joint's mechanical integrity is highly resistant to radiation degradation. This work is partially supported by the U.S. Department of Energy, Office of Nuclear Energy, for the Fuel Cycle Research & Development program under contact DE-AC05-00OR22725 with Oak Ridge National Laboratories managed by UT-Battelle, LLC.

11:30 AM

(ICACC-S13-033-2016) Joining of Silicon Carbide Composite Tubes for Nuclear Fuel Applications using Selective Area Laser Deposition

R. Neall*[1]; T. Abram[1]; 1. University of Manchester, United Kingdom

In light of the accident at Fukushima Daiichi the performance of zirconium alloys in nuclear recaotrs is being questioned and alternative materials may be better suited to improve safety. One material proposed is silicon carbide, which has superior mechanical and nuclear properties however it suffers from low strength thus requiring a pre-stressed composite. Several limitations exist when applying current SiC-SiC composite manufacturing techniques to the scale required for the current generation of pressurised water reactor fuel. In particular, Chemical Vapour Deposition is an expensive method of bonding the fibres to the tube's circumference, as it requires vacuum and temperature to be maintained across the entire substrate. This has led to the development of the Selective Area Laser Deposition technique which generates the same reaction without the need for a large vacuum chamber. This project aims to develop the initial work on the SALD technique to assess its application as a bonding technique between the SiC tubes and fibres. Having completed work on recreating the technique in a laboratory, initial deposits of SiC have been made and XRD results conclude the presence of β-SiC (the ideal crystal type for nuclear grade SiC). Further experimentation will aim to improve the stoichiometry of the deposit before moving on to apply the method to SiC fibres.

S14: Crystalline Materials for Electrical, Optical and Medical Applications

New Direction III

Room: Tomoka C

Session Chair: Frederic Mercier, CNRS-SIMAP

8:30 AM

(ICACC-S14-022-2016) Preparation of compositionally graded hollow spherical particles by spray drying (Invited)

T. Toyama*[1]; 1. Nihon University, Japan

In the spray-drying method, an aqueous solution containing dissolved materials is sprayed inside a furnace so that materials undergo instant drying to form a powder. This powder consists of hollow spherical particles. When the sprayed droplets of the aqueous solution desiccate, the dissolved materials form a particle wall. If two materials with different solubilities exist in the solution, the particle wall is formed by depositing the low-solubility material followed by the high solubility material on the inner side continuously. As an example, hollow spherical particles were obtained when the $Ca(HCO_3)_2$/potassium silicate mixture solution was spray-dried at drying temperatures of 100–200°C. Further, the obtained particles were 2–5 μm in size, and the wall thickness was in the range of 200–300 nm. The cross-sectional EPMA image of the particles indicated that Ca from $CaCO_3$ was distributed on the outer surface, and Si from potassium silicate was distributed on the inner side of the particle wall. Namely, these compositions are graded; they are not a simple double-layered structure. The compressive strength was estimated by measuring the microcompressive strength of only one particle. The compressive strength of the $CaCO_3$/potassium silicate hollow spherical particles was improved by ~15% to 14 MPa.

9:00 AM

(ICACC-S14-023-2016) Synthesis of spinon thermal conductivity materials by ordering process in Sr–Cu–O inhomogeneous system for thermal management materials (Invited)

N. Terakado*[1]; Y. Takahashi[1]; T. Fujiwara[1]; 1. Tohoku University, Japan

In order to prevent heat to be accumulated in integrating electronic devices and systems, various thermal management materials are strongly required. In these materials, *spinon thermal conductivity materials,* which show thermal conductivity due to *spinons*, i.e., magnetic excitation of spin chains, are especially attracting our interest because of three advantages for the thermal management materials: high, anisotropic thermal conductivity, its controllability, and high electric insulation. Nevertheless, it seems that research on the materials has been limited to that using large single crystals. For practical use of those materials, we propose a new synthesis way: we prepare vapor- and melt-quenching oxides including Sr and Cu as base materials and subsequently synthesize spatial-selectively the spinon thermal conductivity materials by excitation such as heating and light irradiation. This method enables ones to make active control devices for thermal energy, e.g., heat circuit and heat fiber. In this talk, I will report the synthesis of the spinon thermal conductivity materials from melt-quenched oxides, forming plates

and fibers, and sputtered films, and those thermal and structural properties.

9:30 AM

(ICACC-S14-024-2016) Novel single crystals for electro-optical applications (Invited)

K. Shimamura*[1]; V. Garcia[1]; N. Ohashi[2]; 1. National Institute for Materials Science (NIMS), Japan; 2. Tokyo Institute of Technology, Japan

A new concept of high-brightness white LEDs based on Ce:$(Y_{1-x}Lu_x)_3Al_5O_{12}$ single crystal phosphor plates (SCPPs), which can overcome the conventional temperature- and photo-degradation problems, is proposed. SCPPs demonstrated excellent thermal stability with no temperature quenching, high values of luminous efficacy and increased quantum efficiency. $Tb_3(Sc_{1-x}Lu_x)_2Al_3O_{12}$ (TSLAG), CeF_3 and PrF_3 single crystals have been designed and grown for high-power laser machinery. They showed a higher visible-UV transparency and a larger Faraday rotation than $Tb_3Ga_5O_{12}$. They are therefore very promising material in particular for new magneto-optical isolator applications in the UV-VIS-NIR wavelength. High quality $Ca_3TaAl_3Si_2O_{14}$ (CTAS) single crystals, which are compounds of Langasite ($A_3BC_3D_2O_{14}$) family, have been grown for high temperature sensor applications. CTAS single crystals grown under less oxygen atmosphere achieved the resistivity as high as 6 x 10^{10} Ω cm at 400C, suitable for combustion pressure sensor in vehicles. This work has been partially supported by JSPS KAKENHI Grant Number 25420308, also by the Ministry of Education, Culture, Sports, Science and Technology (MEXT) Elements Strategy Initiative to Form Core Center of Japan. Authors would like to thank to Tamura Corp., Koha Co., Ltd., Shinko Manufacturing Co., Ltd. and Fujikura Ltd., for the collaboration.

Semiconductor II

Room: Tomoka C

Session Chair: Nobuhito Imanaka, Osaka University

10:20 AM

(ICACC-S14-025-2016) Control of extended defects in diamond single crystals grown by PACVD (Invited)

A. Tallaire*[1]; 1. LSPM-CNRS, France

In addition to being a gemstone, diamond is a wide band-gap semiconductor exhibiting an exceptional thermal conductivity, high carrier mobilities and chemical stability making it a potential alternative to other materials in high power electronic devices operating under harsh environments. The synthesis of bulk high quality diamond single crystals by the plasma assisted chemical vapor deposition technique (PACVD) has witnessed tremendous progresses over the last decade. Growth rates can now reach several tens of micrometers per hour while millimeter-thick films have been demonstrated. The past few years have thus seen the introduction of thick CVD diamond plates into the market. Nevertheless the use of diamond films for active electronic applications has been seriously hampered by several issues. Doping impurities suffer from low doping efficiency and high activation energy, especially for the n-type. The area is at most a few mm^2 which complicates processing. Finally CVD diamond crystals exhibit a high density of threading dislocations (typically 10^4-10^6 cm^{-2}). Those are responsible for leakage current, low breakdown voltage and unreliable characteristics of the devices. In this presentation, the growth of bulk single crystal diamond by PACVD will be introduced. In particular the efforts that have been devoted in reducing dislocations in the synthetic material will be described.

10:50 AM

(ICACC-S14-026-2016) Impurity control in high pressure synthesis / Realization of promising potentials of boron nitride crystals as a wide bandgap material (Invited)

T. Taniguchi*[1]; 1. National Institute for Materials Science (NIMS), Japan

Hexagonal BN (hBN) and cubic boron nitride (cBN) are known as the representative crystal structures of BN. The former is chemically and thermally stable, and has been widely used as an electrical insulator and heat-resistant materials. The latter, which is a high-density phase, is an ultra-hard material second only to diamond. Some progresses in the synthesis of high purity BN crystals were achieved by using Ba-BN as a growth solvent material at high pressure (HP) of 5.5GPa. Band-edge natures (cBN Eg=6.2eV and hBN Eg=6.4eV) were characterized by their optical properties. The key issue to obtain high purity crystals is to reduce oxygen and carbon contamination in the HP growth circumstances. It should be emphasized that hBN exhibits attractive potential for deep ultraviolet (DUV) light emitter and also superior properties as substrate of graphene devices. As the lattice misfit between diamond and cBN is small, hetero-epitaxial growth can be carried out with exhibiting p-n light emitting features. Although the wavelength obtained by the electro luminescence is affected by some unknown deep levels, shallow donor level of cBN crystals may attract an attention as their unique wide bandgap natures. Recent plan-view STEM characterization for hetero-interfaces of the diamond and cBN single crystals will also be introduced. .

11:20 AM

(ICACC-S14-027-2016) Ultra-high pressure synthesis, stability, crystal chemistry and properties of metal nitrides (Invited)

M. Hasegawa*[1]; 1. Nagoya University, Japan

Metal nitrides have attractive chemical and physical properties, such as eminent hardness, distinguished catalytic capability, unique superconductivity, peculiar magnetism and so on. Therefore, they, particularly, nitrogen-rich metal nitrides are paid the most attention to now. High pressure synthesis technique recently provides us a lot of novel ones. A diamond anvil cell, DAC, is a well-used small ultra-high pressure generation apparatus in the range above 10 GPa. It can be easily combined with a laser heating system: LH-DAC. It is a powerful tool to synthesize various kinds of nitrogen-rich metal nitrides because one can utilize a direct nitriding chemical reaction between metal and nitrogen supercritical fluid in a closed sample space in DAC. We have reported systematic syntheses of various metal nitrides by using the original LH-DAC system. In this talk, a summary of our recent studies related to the metal nitrides synthesized in ultra-high pressures will be presented, such as synthesis technique, stability, crystal chemistry and properties investigated by the LH-DAC, the high-pressure in-situ synchrotron and lab-based X-ray diffraction and Raman scattering measurements, the TEM-EELS, the synchrotron XPS and the first principle calculations.

11:50 AM

(ICACC-S14-028-2016) Solution processed zinc-tin oxide (ZTO) charge-trapping memory

J. Li[1]; L. Liu[1]; J. Jeng[2]; J. Chen*[1]; 1. National Cheng Kung University, Taiwan; 2. National Tainan University, Taiwan

Zinc-tin oxide (ZTO) is a transparent semiconductor containing earth-abundant elements. While, most oxide semiconductors were previously fabricated by vacuum-based deposition techniques, solution processes are increasingly popular due the lower cost and feasibility for large area deposition. In this work, ZTO films prepared by a solution route have been applied as the active semiconductor layer in a thin film transistor (TFT) with SiO_2 dielectrics. With thickness less than 10 nm, the ZTO film exhibits a good field-effect mobility of ~10 cm^2/Vs, small subthreshold slope of ~0.5 V/decade and high on/off current ratio of ~10^7. Based on the ZTO TFT, a charge-trapping memory has been fabricated by introducing

a Ni charge trapping layer and an AlO_x tunneling layer in the gate dielectrics. With this configuration, the ZTO TFT I_D-V_G transfer characteristics can be horizontally shifted by ~7 V when applying a positive gate bias. Moreover, the shift of I_D-V_G transfer curve can be erased by applying a negative bias in conjunction with visible light illumination. The charge transport between ZTO TFT channel region and Ni trapping layer will be discussed based on the electron tunneling as well as migration of photo-ionized oxygen vacancies, under the influence of gate bias and visible light illumination.

FS2: Advanced Ceramic Materials and Processing for Photonics and Energy

Photonics, Electronics, Sensing

Room: Coquina Salon G
Session Chair: Farid Akhtar, Stockholm University

8:30 AM

(ICACC-FS2-025-2016) Bottom-up approach for the synthesis of graphene-oxide nanosheet interfaces (Invited)

A. Baraldi*[1]; 1. University of Trieste, Italy

The coupling of graphene with 2D nanosheet dielectrics is an important topic in contemporary materials science, due to its potential impact on a number of high-performance nanoelectronic applications. In this respect, Al_2O_3 films play a key role because of their employment as high-κ oxides in transistors and low-power chips, where the use of a high dielectric constant increases the gate capacitance. However, the conventional methods so far used for producing graphene-alumina interfaces, such as cehmical vapour or atomic layer deposition, inevitably lead to a degradation of the electronic properties of graphene. It is therefore desirable to develop simple, scalable, and economically affordable methods for the transfer-free production of graphene-dielectric interfaces. In this talk I will describe a novel approach for the direct synthesis of graphene-alumina interfaces, based on the CVD growth of graphene on a bimetallic surface alloy (Ni_3Al) and subsequent oxididation of the metallic surface, in such a way as to induce the formation of an alumina nanosheet. This method, based on the use of low cost raw materials, could be readily extended also to other alloys to produce high-κ dielectrics.

9:00 AM

(ICACC-FS2-026-2016) Electrolyte gating of metal oxides: materials, interfaces and devices (Invited)

C. Santato*[1]; 1. Ecole Polytechnque de Montreal, Canada

Electrolyte-gated (EG) thin film transistors make use of electrolytes, such as ionic liquids and ion gels, to replace conventional dielectrics, such as SiO_2. The low driving voltage (< 2 V) and printable nature of EG-transistors render them interesting for low power, large-area applications . The working principle of EG transistors can be explained by, at least, two mechanisms: (i) field-effect, where the channel conductivity is controlled by the electrostatic doping of the channel material and (ii) electrochemical, where the channel conductivity is modulated by ion insertion/removal in the film. Despite the advancements achieved in the past few years, the fundamental chemicophysical processes governing the doping of metal oxides of primary importance for energy conversion/saving and displays (e.g. electrochromic displays) are yet to be understood. Here, using a combination of cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and transistor measurements we studied doping/dedoping processes in EG transistors based on sol-gel synthesized WO_3 and TiO_2 thin films and ionic liquid or ion gel as the electrolytes.

9:30 AM

(ICACC-FS2-027-2016) Integration of III-V Semiconductors on Graphene (Invited)

O. Moutanabbir*[1]; 1. Ecole Polytechnque de Montreal, Canada

Heteroepitaxial growth of III-V on graphene is an attractive paradigm to implement hybrid systems with novel or enhanced functionalities combining the advantages of these two families of materials within the same platform. Herein, we exploit van der Waals epitaxy to implement these hybrid materials. We demonstrate the low-pressure metal-organic chemical vapor deposition of InAs, GaAs, InP, and GaP growth on single layer graphene sheets transferred on SiO2/Si(100) or grown on Ge (100), (110), and (111) substrates. The structural properties of the grown layers has been thouroughly investigated using a variety of techniques including x-ray micro-diffraction, coherent x-ray imaging, transmission electron microscopy, and scanning probe microscopy. Our analysis revealed the formation of flat and faceted crystals on all samples in addition to nanowires. We will also describe strategies to tune the morpholgy of the grown III-V-on-Graphene structures. For instance, we will show how the dimensions of the grown structures can be controlled from a few nanometers to tens of microns with a smooth surface (RMS roughness < 1nm). The ability to grow these crystalline structures with variable morphologies provides valuable opportunities to expand the fundamental understanding of the basic properties of III-V/Graphene/IV heterostructures and explore their use in innovative devices.

Bioimaging and Thermal Sensing

Room: Coquina Salon G
Session Chair: TOBE ANNOUNCED, NONE

10:20 AM

(ICACC-FS2-028-2016) Nanoparticles Emitting in the NIR: The Next Frontier for Bioimaging? (Invited)

F. Vetrone*[1]; 1. INRS, Canada

Nanoparticles excited in the near-infrared (NIR) are quickly emerging as useful tools in diagnostic and therapeutic medicine. In particular, the usefulness of these nanomaterials for applications in biology stems primarily from the fact that NIR light is silent to tissues thus minimizing autofluorescence, possesses greater tissue penetration capabilities, reduced scattering, and does not cause photodamage to the specimen under investigation. Moreover, tailoring of the nanoparticles' absorption and emission wavelengths allow them to operate within the so-called "biological windows", regions of the spectrum in which tissues are partly transparent. In this regard, rare earth (RE^{3+})-doped nanoparticles are at the vanguard since they posses multiple absorption and emissions in these "biological windows" (approximately 750-1000, 1100-1450, and 1500- 1700 nm). Here, we present the synthesis and surface functionalization of various NIR excited nanoparticles and demonstrate how they can be used for biological applications including nanothermometry. Furthermore, we show how they can be used as the cornerstone in the development of a multifunctional hybrid nanoplatform for the potential diagnostics and therapeutics of disease.

10:50 AM

(ICACC-FS2-029-2016) Heating, Thermal Mapping and Temperature-Sensing in the Terahertz Regime (Invited)

R. Naccache*[2]; A. Mazhorova[1]; M. Clerici[3]; L. Razzari[1]; F. Vetrone[1]; R. Morandotti[1]; 1. INRS, Canada; 2. Institut National de la Recherche Scientifique, Canada; 3. Heriot-Watt University, United Kingdom

In recent years, nanomaterials have garnered significant attention for the development of novel applications and technologies. Of particular interest are metallic nanoparticles, which show a surface plasmon resonance effect. A by-product of this effect is a transfer

of energy to the surrounding environment in the form of heat. The resultant rise in temperature finds applications particularly in cancer hyperthermia. We have used gold nanoparticles as "contrast agents" in combination with terahertz radiation to develop a contact-free approach for heating, temperature sensing and imaging. Specifically, we exploit the change in the refractive index of water, induced by localized NIR heating of gold nanoparticles. Gold nanorods were prepared using a conventional bottom up seed-mediated technique. Following NIR heating of the nanorods, we observe a linear relationship correlating the change in the reflected terahertz amplitude (and area under the curve) to the rise in temperature. This resulted in a thermometric relationship for temperature sensing following an induced heat stimulus. Our results were extended to the porcine skin model to mimic hyperthermia and demonstrated the capacity to sense temperature and map its distribution in a localized injection site, following controlled NIR plasmonic heating of our gold nanorods. As a result, we have developed a terahertz biological thermometer, or a "teramometer".

11:20 AM

(ICACC-FS2-030-2016) From Bioprobes to Potential Players in Energy Conversion Technologies - Multifunctional Lanthanide-Nanophosphors (Invited)

E. Hemmer*[1]; F. Legaré[1]; F. Vetrone[1]; 1. INRS, Canada

Lanthanide(Ln)-based materials are known for their optical properties such as the upconversion (UC) process (conversion of near-infrared (NIR) into UV/visible light) and the emission of NIR light under NIR excitation. This opens up the possibility for applications reaching from NIR bioimaging to nanothermometry and eventually energy conversion technologies. Here, Ln^{3+}:Gd_2O_3 has been shown as promising NIR bioprobe. Yet, surface modification is crucial to provide biocompatibility prior to in-vivo imaging. Beyond, Ln^{3+}-doped nanoparticles exhibit temperature (T)-dependent luminescence, which makes them promising candidates for the temperature monitoring of a biosystem. As thermal singularities are often one of the first indicators of a disease, cellular nanothermometry is a prospective nanoscopic diagnostic tool. Thus, the potential of Ln^{3+}:$NaGdF_4$ as nanothermometers will be discussed. Recently, upconverting nanoparticles (UCNPs) gained interest regarding applications in the energy sector. Yet, a major drawback is the limited efficiency of the UC process (typical quantum yields (QY) <1%). Understanding the physicochemical phenomena that influence the UC process is a vital step towards more efficient UCNPs. Novel insights in the QY on Er^{3+}/Yb^{3+} co-doped UCNPs will be presented mediating the UCNPs' potential and limitations with regard to energy conversion technologies.

11:50 AM

(ICACC-FS2-031-2016) Synthesis and spectroscopic behavior of RE:Y_2O_3 & MgO nanocomposites for mid-infrared solid-state lasers

V. L. Blair*[1]; N. Ku[1]; Z. D. Fleischman[1]; L. D. Merkle[1]; 1. US Army Research Laboratory, USA

Several challenges exist in developing mid-infrared laser materials, including 1) the need to dissipate heat generated during lasing; 2) the onset of luminescence quenching by multi-phonon relaxation and 3) the trade-off between high thermal conductivity and small maximum phonon energy. These challenges are being addressed by synthesizing ceramic nanocomposites in which multiple phases are incorporated into the same structure. In this process, the undoped majority species functions as the main carrier of high thermal conductivity, while the minority species possesses low maximum phonon energy. Two methods were explored, including a sol-gel method in which the components were synthesized separately and integrated during wet-mixing, and a co-precipitation method in which the components were synthesized together for intimate mixing on the smallest scale. Data on the selected synthesis technique, the calcination and characterization of the base powders, and the sintering behavior, as evaluated by spectroscopic analysis, will be presented.

S1: Mechanical Behavior and Performance of Ceramics & Composites

Processing - Microstructure - Mechanical Properties Correlation III

Room: Coquina Salon D
Session Chair: Hagen Klemm, FhG IKTS Dresden

1:30 PM

(ICACC-S1-041-2016) Understanding the Toughening Mechanisms in Ceramic/Carbon Nanotubes Nanocomposites

Y. Liu*[1]; L. Zhang[1]; W. Wu[1]; N. P. Padture[1]; 1. Brown University, USA

Carbon nanotubes (CNTs) possess excellent mechanical properties, which has motivated the use of CNTs as reinforcements in brittle ceramics to create new high-toughness nanocomposites. However, conflicting toughening results and diverse reinforcing mechanism are reported among recent published studies. In this work, a systematic study has been carried out to achieve improved mechanical properties and gain new understanding of the operative toughening mechanisms in ceramic/CNTs nanocomposites. Different types of multi-wall carbon nanotubes (MWCNTs) are either covalently or non-covalently functionalized, and they are colloidally mixed with alumina nanopowders. The resulting intimately mixed powders are densified using spark plasma sintering. Actual toughness values and rising toughness curves are calculated for all the nanocomposites based on single-edge "V" notch (SEVNB) tests. In particular, *in situ* observations of propagation of cracks in the MWCNTs/alumina nanocomposites have been performed in the scanning electron microscope (SEM) to elucidate possible toughening mechanisms. These results are presented, together with a discussion of the effects of functionalization, size, distribution, and morphology of the MWCNTs on the possible toughening mechanisms in these nanocomposites.

1:50 PM

(ICACC-S1-042-2016) Fabrication and characterization of alumina nanofibers with ultra-high strength

W. Sun*[1]; H. Yan[1]; A. Barber[2]; 1. Queen Mary, University of London, United Kingdom; 2. University of Portsmouth, United Kingdom

Fibers with ultra-high tensile strength have attracted unprecedented attention due to the rapidly increasing demand for strong fiber reinforced composites. The high theoretical strength (46 GPa) but relative low cost of alumina (Al_2O_3) make it a promising reinforcement material. However, Al_2O_3 fiber strength rarely reach 1 GPa for the influence of defects between the grains. Processing fiber with nano-scale diameters is expected to decrease the defect size for effective improvement of strength. Electrospinning is a particularly appropriate method for fabricating nanofibers with flexibly controlled diameters, thus supporting a systematic study on the relationship between fiber diameter and tensile strength. In this work, Al_2O_3 nanofibers were fabricated through electrospinning following calcination. Individual fiber tensile testing was carried out using an atomic force microscope within a scanning electron microscope. Resultant fiber strength was correlated to the crystal structures through a transmission electron microscope. The strength of single crystal α-Al_2O_3 nanofibers were found to have an average value of 11.4±1.1 GPa with little dependence on diameter variations. However, polycrystalline γ-Al_2O_3 fibers demonstrated a diameter dependent strength of less than 2 GPa to more than 6 GPa for fiber diameters decreasing from 135 nm to 75 nm, suggesting a defect controlled strength mechanism.

2:10 PM

(ICACC-S1-043-2016) Functional Properties of MWCNT-Alumina Composites Prepared by Novel Approach

O. Hanzel*[1]; J. Sedláček[1]; P. Šajgalík[1]; 1. Institute of Inorganic Chemistry, Slovak Academy of Sciences, Slovakia

Alumina – multi-wall carbon nanotube (MWCNT) composites were prepared by new approach. This process comprises the functionalization of MWCNTs by acid treatment, stabilization of alumina-MWCNT dispersion and freeze granulation. This freeze granulation process makes possible to retain the homogeneous distribution of MWCNTs achieved in the suspension also in the granulated powders. The preparation of green bodies was easier from granules compared to directly mixed powders. The composite granulated powders were sintered by two methods: hot pressing and rapid hot pressing at 1550°C applying 30 MPa load in argon atmosphere. Disaggregation and uniform dispersion of carbon nanotubes in alumina matrix are crucial requirements for the improvement of electrical conductivity and modification of thermal conductivity of alumina-MWCNT composites. With this new approach it was possible to tailor the thermal and electrical conductivity of composites by the addition of different amount of homogeneously distributed MWCNTs. The electrical conductivity of prepared composites increased significantly (up to 1400 S/m). On the other hand, the thermal conductivity of alumina-MWCNTs composites decrease with increasing content of MWCNTs in ceramic matrix.

2:30 PM

(ICACC-S1-044-2016) Multifunctional SiC ceramics by adding graphene-based fillers

B. Román-Manso[1]; J. Llorente[1]; A. Nistal[1]; M. I. Osendi[1]; P. Miranzo[1]; M. Belmonte*[1]; 1. Institute of Ceramics and Glass (ICV-CSIC), Spain

Nowadays, advanced technological applications require the development of new multifunctional materials able to work under highly demanding conditions. In this way, the purpose of this work is to manufacture light silicon carbide (SiC) ceramics with multifunctional properties, in particular, with enhanced mechanical and tribological performances, jointly with electrical conductivity. To achieve this goal, different type and content of graphene fillers were added to the ceramic matrix. Graphene nanoplatelets -GNPs- and reduced graphene oxide –rGO- were selected as fillers. Dense and homogenous SiC/graphene composites were fabricated by spark plasma sintering (SPS) process. All composites exhibited a better mechanical performance than the monolithic SiC, improving the flexure strength and the fracture toughness up to 70% and 160%, respectively, when adding 5 vol.% of rGO. In addition, graphene-based composites also showed up to a 70% enhanced wear resistance and electrical functionality, opening new uses in promising advanced applications.

3:10 PM

(ICACC-S1-045-2016) Processing and Properties of Tyranno ZMI Fiber/$TiSi_2$-Si Matrix Composites

T. Aoki*[1]; T. Ogasawara[1]; 1. Japan Aerospace Exploration Agency, Japan

A Tyranno ZMI fiber/$TiSi_2$-Si matrix composite was fabricated via melt infiltration (MI) of a Si-16at%Ti alloy at 1375°C under vacuum. The Si-Ti alloy was used as an infiltrant to conduct MI processing below 1400°C and inhibit the strength degradation of the amorphous SiC fibers. The alloy matrix formed was dense and comprised primarily of $TiSi_2$-Si eutectic structures. The $TiSi_2$-Si matrix composite melt-infiltrated at 1375°C showed a pseudo-plastic tensile stress-strain behavior followed by final fracture at ~290 MPa and ~0.9% strain. When the MI temperature was increased to 1450°C, however, substantial reduction in the stiffness and ultimate strength occurred under tensile loading. Microstructural observations revealed that these degradations were attributed to the damages that occurred on the reinforcing fibers and pyrolytic carbon interfaces during the MI process. The present experimental results clearly demonstrated the effectiveness of the low-temperature MI process in strengthening Tyranno ZMI fiber composites and reducing the processing cost.

3:30 PM

(ICACC-S1-046-2016) Development of CNTs reinforced bulk polycrystalline ceramics, possessing uniform CNTs distribution, via engineered sol-gel based processing route

M. K. Satam*[1]; S. Vishwanathe[1]; T. Bhandari[1]; P. Joseph[1]; S. Galaveen[1]; L. Gurnani[1]; K. Ravikanth[2]; P. Patro[2]; T. Mahata[2]; A. Mukhopadhyay[1]; 1. IIT Bombay, India; 2. BARC, India

The usual route for developing bulk ceramic-CNT composites involves physical mixing of ceramic starting powder and CNTs, which, in addition to the general challenges associated with the CNTs dispersion, leads to the clustering of CNTs just along the matrix grain boundaries upon sintering, with almost nothing present within the grains. In order to address these issues, we report here the development of an innovative processing route for CNTs reinforced oxide (Al_2O_3), as well as boride (ZrB_2), based ceramics, which involves incorporation of well-dispersed CNTs in the matrix sol under ultrasonication, followed by rapid gelation to 'freeze' the CNTs in dispersed state. Subsequent calcination and sintering of the composite gel powders have allowed the development of the desired microstructures, with the CNTs reinforcing the interiors of the matrix grains, along with presence along the grain boundaries; a microstructure type, not achieved upon physical mixing of CNTs with the ceramic powders. Accordingly, the bulk composites developed using the powders prepared by incorporating the CNTs within the gels possess significantly improved mechanical properties in terms of fracture toughness and flexural strength. Based on the results and analysis, a correlation between the microstructure development and mechanical properties will be established.

3:50 PM

(ICACC-S1-047-2016) Hertzian indentation response of TiC/316-L stainless steel cermets

K. P. Plucknett*[1]; 1. Dalhousie University, Canada

Titanium carbide (TiC) based cermets are commonly used as wear and corrosion resistant components, due to its high melting point, high strength and low density. In the present work, stainless steel binders (grade 316-L) have been utilised for the preparation of TiC-based cermets, with the steel content varied from 5 to 30 vol. %. Samples were fabricated using a simple vacuum melt-infiltration procedure, at temperatures between 14750C and 15500C, held for up to 240 minutes. The use of Herztian indentation, with various applied loads ranging from 250 to 2000 N, and contact sphere diameters from 3/64" (1.191mm) to 5/32" (3.967mm), are studied. The 'pile-up' effect were found after the indentation test, and indentation damage induced using different loads and contact radii were measured and analyzed by optical profilometry. Indentation stress-strain curves were produced from data and an elastic-plastic response of the material was detected. Preliminary results of finite element modeling of this kind of material will also be reported.

4:10 PM

(ICACC-S1-048-2016) Pre-sliding Effect on Friction Mechanism of Diamond-like Carbon in Water: A Theoretical Study

S. Bai*[1]; J. Xu[2]; Y. Higuchi[2]; N. Ozawa[2]; K. Adachi[3]; S. Mori[1]; K. Kurihara[4]; M. Kubo[2]; 1. New Industry Creation Hatchery Center, Tohoku University, Japan; 2. Institute for Materials Research, Tohoku University, Japan; 3. Graduate School of Engineering, Tohoku University, Japan; 4. Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Japan

Diamond-like carbon (DLC) in water lubrication is a clean system for an earth friendly environment. It shows low friction properties and reduces the emission of CO_2. Furthermore, the friction coefficient of DLC in water changes by the pre-sliding. However, the

details of the change in friction coefficient of DLC in water on an electronic and atomic scale are still unclear. Our tight-binding quantum chemical molecular dynamics (TB-QCMD) method is very effective for clarifying tribo-chemical reactions on friction mechanism during friction process, because it enables large-scale long calculations on an electronic and atomic scale [1, 2]. In this study, tribo-chemical reaction of DLC films in water lubrication is investigated by our TB-QCMD code. The results show that the C-H and C-OH bonds are generated on the DLC surface without pre-sliding due to the dissociation of water molecules during friction. Furthermore, C-O-C generation on the DLC surface is observed with pre-sliding. The structure change from sp^3 carbon (Csp^3) to sp^2 carbon (Csp^2) on the surface by C-O-C bond leads to rich Csp^2 on the DLC surface. We suggest that low friction properties of DLC films in water lubrication is caused by this structure change.

4:30 PM

(ICACC-S1-049-2016) High porosity of 4A zeolite/magnesium phosphate material with uniform open-pore structures

L. Liu*[1]; J. Li[1]; X. Li[2]; X. Wang[1]; 1. China University of Geosciences(Beijing), China; 2. Bohai Petroleum Research Institute. CNOOC, China

High-porosity composite material of 4A zeolite/magnesium phosphate (M-4A) was obtained by the pre-foaming method. In the pre-foaming method, sintering treatment was not required. Experimental and theoretical studies were reported on distribution of pores, porosity and Cd2+ adsorption on 4A molecular sieve zeolite at 301 K, and characterized by XRD, SEM and ICP. The results of this study show that the 4A zeolite was highly dispersed on the surface of uniform alignment pores, and the average pore size of M-4A is about 180 μm. When the ratio of 4A zeolite to solid content (MgO and MAP) was increased from 0.2 to 0.6, the compressive strength and bulk density of M-4A increased. With the addition of 4A zeolite up to 1.0, the compressive strength and bulk density were all decreased to a stable value. In addition, measurement of open porosities according to Archimede sprinciple, were used. The result show a relatively high porosity in the range of 78.5–81.5% is obtained for the samples with the increases in the addition of 4A zeolite. The compressive strength and bulk density of optimized sample was 1.15 ± 0.05 MPa and 482.5 ± 5 g/cm^3 respectively, and the porosity was 81.33% correspondingly. For all samples of M-4A, the absorption of Cd^{2+} exceed 99.2%.

S2: Advanced Ceramic Coatings for Structural, Environmental, and Functional Applications

Coatings to Resist Oxidation, Corrosion, and Erosion

Room: Coquina Salon H

Session Chairs: Eugene Medvedovski, Consultant; Peter Mechnich, German Aerospace Center (DLR)

1:30 PM

(ICACC-S2-037-2016) Boride-Based Thermal Diffusion Coatings for Tribo-Corrosion Applications (Invited)

E. Medvedovski*[1]; J. Jiang[2]; M. Robertson[2]; 1. Endurance Technologies Inc., Canada; 2. NRC Canada, Canada

Engineering components and tubing systems for the down-hole applications in the oil production should withstand severe friction, sliding abrasion and corrosion actions. To resolve these issues, the hard boride-based coatings on steels obtained through the thermal diffusion process can be applied on the entire working surfaces of large size and complex shape products. The behavior of these coatings obtained at Endurance Technologies Inc. has been studied in the friction-abrasion, friction-corrosion and friction-abrasion-corrosion conditions simulating oil production service conditions. The synergistic actions of harsh conditions results in a higher rate of materials destruction. The obtained boride coatings demonstrated significantly lower wear losses with no delamination and spalling than untreated steels and Ni- and Cr-based coatings. Successful application of the products with the boride protective coatings is reported.

2:00 PM

(ICACC-S2-038-2016) Evaluating the Effectiveness of Coatings for Interconnections in Solid Oxide Fuel Cells: A Diffusion Model

S. Basu*[1]; U. Pal[1]; S. Gopalan[1]; 1. Boston University, USA

Chromium poisoning of the cathode due to oxidation of metallic interconnections and subsequent formation of vapor phase chromium containing species is a well-known problem. The application of ceramic coatings on the interconnections to prevent this deleterious phenomenon is currently being extensively investigated. Copper manganese spinel coatings were deposited on Crofer 22 APU substrates by electrophoretic deposition (EPD). Thermo-gravimetric measurements under oxidizing conditions were carried out to study the effectiveness of the coatings as diffusion barriers. A diffusion model, highlighting the expected para-linear oxidation kinetics will be presented to guide the interpretation of the thermo-gravimetric data, and to correctly measure the effective diffusivities of chromium and oxygen in the coatings.

2:20 PM

(ICACC-S2-039-2016) Erosion resistance characteristics of advanced atmospheric plasma spray thermal barrier coatings

D. Shin*[1]; A. Hamed[1]; 1. University of cincinnati, USA

Modern aero-gas turbine engine components operate in extremely harsh environments where combination of high temperature, steep temperature gradients, fast temperature transient and high aero thermal, mechanical loadings are presents. Impacts by the erosive particles causes critical damage to the thermal barrier coatings (TBCs). In this study, particle erosion resistance characteristics of advanced thermal barrier coatings for gas turbine engine components are investigated using specially designed high temperature particulate wind tunnel. The work is focused on testing atmospheric plasma spray 7YSZ and Gadolinium Zirconate ceramic coatings applied on MCrAlY bond coat and IN718 substrate. Nominal 27 micron Aluminum Oxide and A3 Medium test dust are used as erodent particles. To simulate gas turbine operating conditions, the tests are conducted in gas temperature between 1000 F and 2500 F, gas velocities up to 1200 ft/s and several particle impact angles. Erosion rates, SEM surface images and surface roughness are presented and compared for the tested TBCs over the range of test conditions.

2:40 PM

(ICACC-S2-040-2016) Novel coatings for superheater tubes for waste-to-energy plants

S. Molin*[1]; M. Chen[1]; L. Mikkelsen[2]; P. Hendriksen[1]; 1. Technical University of Denmark, Denmark; 2. Babcock and Wilcox Vølund A/S, Denmark

Waste-to-energy technologies are important in Europe due to the new EU legislative banning on open storage of waste and thus incineration of waste to produce district heating and electricity is becoming more and more important in developed countries. Efficiency and lifetime of the plants can be improved by mitigating high temperature corrosion phenomena. In this work different coatings will be deposited on superheater tubes and their influence on corrosion in relevant simulated conditions will be assessed. Coating materials will be based on reactive elements (e.g. Ce, Y, La, Gd) which have proven anti corrosion properties. Coated alloys will be tested at temperatures between 500°C and 600°C with exposure to possible contaminants present in flue gases in waste incineration plants. This project is supported by an Industrial Postdoc project "Improved materials for heat exchangers in waste-to-energy plants" granted by InnovationsFonden, Denmark.

3:20 PM

(ICACC-S2-041-2016) Self-healing glass coating for high temperature applications

T. Carlier*[1]; F. Mear[1]; R. Podor[3]; J. Blach[2]; S. Saitzek[2]; A. Ferri[2]; L. Montagne[1]; 1. Université Lille Nord de France, UCCS UMR CNRS 8181, France; 2. Université d'Artois, UCCS UMR CNRS 8181, France; 3. Institut de Chimie Séparative de Marcoule, UMR 5257 CEA-CNRS-UM2-ENSCM, France

Glass-ceramics are a technological solution to achieve efficient materials to operate at high temperatures, such as for enamel protective coatings applications. To overcome cracking of the glass when subjected to thermal cycles, self-healing is shown to be a promising solution. The self-healing property is defined as the capacity of a material to recover its mechanical integrity and initial properties after destructive actions of external environment or under internal stresses. Based on this process, an innovative approach is to develop self-healing glassy thin films for protective coating applications such as in the aerospace field. The present study is based on the heterostructure deposition of glass-ceramics and active particles layers by Pulsed Laser Deposition (PLD). The properties of the deposited films depend on many parameters during growth. We have shown that highly homogeneous layers are obtained under high vacuum, at room temperature, using a pulse energy of 225 mJ, with a target-substrate distance varying from 3.5 to 5.5 cm. The characterization of the multi-layers films has been studied using different techniques: (a) film thickness by ellipsometry ; (b) homogeneity by XPS, ToF-SIMS; and (c) structural characterization by ATR-FTIR spectroscopy. The efficiency of the self-healing effect is demonstrated by an *in-situ* experiment performed into an environmental scanning electron microscope (HT-ESEM).

3:40 PM

(ICACC-S2-042-2016) Structure features of reaction-cured glass-ceramic coatings in system (SiO_2-B_2O_3)-SiB_4

V. Denisova*[1]; S. S. Solntsev[1]; M. R. Orlov[1]; P. N. Medvedev[1]; 1. Federal State Unitary Enterprise All-Russian Institute of Aviation Materials, Russian Federation

The novel heat-resistant materials, particularly, structurally stable nickel alloys based on Ni-Cr-Co system, have been developed to increase the operating temperatures of combustion chamber for about 150-200 degrees Celsium in modern and advanced gas-turbine engines. Solving the problem of heat-resistant alloys oxidation at elevated temperatures (over 1000 degrees Celsium) is now possible by appliance of advanced heat-resistant reaction-cured enamel coatings. The identifying feature of this kind of coatings if the formation ability at temperatures lower or equal to operating temperature. Heat-resistant reaction-cured glass-ceramic coatings were synthesized. Such high-melting materials, as SiB_4, $MoSi_2$ and some others were used as modifying additives. The reduction of coatings' formation temperature was distinguished for coatings with modifying additives relatively to coatings without modifying additives. Heat-resistant coatings based on glasses in BaO-Al_2O_3-SiO_2 glass system with modifying additives, such as hard-melting silicate compounds, were synthesized. These coatings are notable for high heat-resistance and thermal stability at temperatures up to 1150 degrees Celsium. High adherence of coatings to steel and nickel alloys was achieved.

S3: 13th International Symposium on Solid Oxide Fuel Cells (SOFC): Materials, Science and Technology

Electrode Materials / Sealing Materials

Room: Crystal

Session Chairs: Ayhan Sarikaya, Saint-Gobain; Federico Smeacetto, Politecnico di Torino

1:30 PM

(ICACC-S3-034-2016) Using Precursor Solution Desiccation, Nano-Ceria Pre-Infiltration, and/or Organic Precursor Solution Additives to Improve the Electrochemical Performance and Stability of Infiltrated Solid Oxide Fuel Cell Cathodes (Invited)

T. E. Burye[1]; B. J. Bocklund[1]; J. D. Nicholas*[1]; 1. Michigan State University, USA

Infiltrated Mixed Ionic Electronic Conducting (MIEC) oxide nano-particles are commonly used to improve the performance of Solid Oxide Fuel Cell (SOFC) cathodes. This talk will describe how infiltrate precursor solution desiccation, nano-ceria pre-infiltration, and/or organic precursor solution additives can be used to control the size, phase purity, and microstructural stability of both stoichiometric and A-site deficient $La_{0.6}Sr_{0.4}Co_xFe_{1-x}O_{3-\delta}$ (LSCF) infiltrate. Further, this talk will describe how these infiltrate tailoring approaches can be used to produce LSCF-infiltrated $Ce_{0.9}Gd_{0.1}O_{1.95}$ (GDC) cathodes that display average LSCF particle sizes of 21 nm and open-circuit polarization resistance values of 0.1 Ωcm^2 at 540°C, compared to 48 nm and 640°C for conventionally infiltrated LSCF-GDC cathodes. This talk will also explore the mechanisms behind these infiltrate tailoring approaches and demonstrate that infiltrate-tailored SOFC cathodes can achieve 540ºC degradation rates lower than conventionally infiltrated LSCF-GDC cathodes.

2:00 PM

(ICACC-S3-035-2016) Effects of copper dopant on the characteristics of cathode materials for intermediate temperature solid oxide fuel cells (Invited)

S. Wang*[1]; Y. Hsu[1]; Y. Liu[1]; 1. National Taipei University of Technology, Taiwan

In this study, copper ions doped into $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-d}$, $LaCo_{1-x}Cu_xO_{3-\delta}$, $LaCo_{0.4}Ni_{0.6-x}Cu_xO_{3-\delta}$, $Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$, and $Ca_3Co_4O_{9-\delta}$ cathode materials were explored in order to enhance the electrode performance of solid oxide fuel cells (SOFCs). It was found that the electrical conductivity of the cathodes increased with the Cu^{2+} content. The Cu^{2+}-doped cathode materials revealed lower sintering temperature and lower TEC as compared with the un-doped cathodes. Anode supported intermediate temperature-SOFCs were then built to evaluate the cell performance. The cathodes were screen-printed on anode-supported substrates incorporating a SDC electrolyte layer and a three-layer anode composed of a current collector layer of NiO and two functional layers of NiO-SDC composites. The impedance of the cells revealed that the Cu^{2+}-doped cathodes exhibited greater electrochemical catalytic activity for oxygen reduction and thus escalated the maximum power density. It is evident that the doping of Cu^{2+} ions in cathode materials is capable of enhancing the electrochemical performance of the cells.

2:30 PM

(ICACC-S3-036-2016) Role of Cr : Fe variation on the chemical and structural stability of $(La_{0.8}Sr_{0.2})_{0.95}Cr_{1-x}Fe_xO_3$ - 10Sc1CeSZ composite

S. Gupta*[1]; P. Singh[1]; 1. University of Connecticut, USA

This study investigates the role of Cr: Fe ratio on the stability and processing of iron doped lanthanum strontium chromite ($(La_{0.8}Sr_{0.2})_{0.95}Cr_{1-x}Fe_xO_3$; x~0.1-0.3) and stabilized zirconia

(10Sc1CeSZ) composite for high temperature electrochemical devices such as oxygen transport membrane (OTM) and solid oxide fuel cell (SOFC). Processing and operating conditions examination included exposure of materials to the temperature range of 1000-1400°C and oxygen partial pressure range of 0.21-10^{-12} atm for up to 500h. Processing ability in terms of sintering and densification of $(La_{0.8}Sr_{0.2})_{0.95}Cr_{1-x}Fe_xO_3$ (LSCF) increased with increase in Fe doping level. In contrast, surface morphology changes and interaction between LSCF perovskite and 10Sc1CeSZ was observed to increase with Fe doping level also resulting in $SrZrO_3$ phase formation. Highest stability with little to no changes in the surface/bulk/interface is identified for x~0.1 for upto 500h in oxidizing and reducing atmospheres. Chemical interaction and morphological evolution has been examined using scanning and transmission electron microscopy (SEM and TEM), and in-situ X-ray diffraction (RT-1200°C). Reaction mechanism have been investigated based on experimental observations, defect-chemistry and thermodynamics.

2:50 PM

(ICACC-S3-037-2016) Evaluation of A-site Non-stoichiometry Lanthanum Strontium Cobalt Ferrite as Cathode Material for Intermediate Temperature Solid-Oxide Fuel Cell

L. Ge*[1]; A. L. Lipson[1]; J. Carter[1]; B. Ingram[1]; 1. Argonne National Lab, USA

Lanthanum strontium cobalt ferrite (LSCF) perovskite has been identified as promising cathode candidate for intermediate temperature (IT) solid oxide fuel cell (SOFC) applications, due to its mixed ionic and electronic conductivity at operating temperatures (500-700 °C). In particular, A-site deficient LSCF has shown better electrochemical performance compared to its stoichiometry counterpart. However, non-uniformity in electrical, electrochemical, and morphological characteristics found in different powders used for fabricating cell and stack components has been a continuing challenge for SOFC manufacturers. In this study, a wide variety of physical and chemical characterizations on $(La_{0.6}Sr_{0.4})_{0.95}Co_{0.2}Fe_{0.8}O_{3-d}$ powders were performed to investigate the correlation between the electrochemical performance and materials properties. This effort will help in defining tolerances of key materials properties for optimal cell performance.

3:30 PM

(ICACC-S3-038-2016) Autonomic self-repairing glassy materials for high temperature applications (Invited)

F. O. Mear*[1]; S. Castanié[1]; T. Carlier[2]; R. Podor[3]; L. Montagne[1]; 1. Lille 1 University, France; 2. University Lille, France; 3. Marcoule Institute for Separative Chemistry, France

The self-healing in materials science is defined as the ability to recover the mechanical integrity and initial properties of a material after destructive actions of external environment or under influence of internal stresses. The self-healing concept has been developed in many application fields such as polymers for coatings, microelectronic packaging, medical uses, concrete or cementitious structures, and composites materials for aerospace applications. In this lecture is presented our recent work on self-healing processing in glassy materials. We show that glass and glass-ceramic enable both non-autonomous and autonomous self-healing, provided that their compositions are adapted, and depending on the environment parameters. The submicronic size of the cracks excluded the analysis of the healed zone by conventional methods like SEM-EDX, X-ray diffraction or vibrational spectroscopy. Recent results from synchrotron imaging (coupled with micro-fluorescence and diffraction) on self-healing processing in glassy materials will be presented. We will illustrate with some examples of self-healing involving glasses in the high-temperature sealing of SOFCs. New original healing architecture will be also presented, based on alternated layers of glass and healing compounds deposited by Pulsed laser Deposition.

4:00 PM

(ICACC-S3-039-2016) Electrical and Mechanical Properties of Phologpite mica/BaO-Al_2O_3-B_2O_3-SiO_2-Based Glass Sealants for Solid Oxide Fuel Cell

C. Liu*[1]; W. Shong[1]; R. Lee[1]; 1. Institute of Nuclear Energy Research, Taiwan

The BaO-Al_2O_3-B_2O_3-SiO_2-based glass, designated as GC9, was developed by the Institute of Nuclear Energy Research (INER) for use as a high-temperature seal in solid oxide fuel cell (SOFC) applications. In this study, we investigated the properties of electrical, mechanical and hermetical of the phologpite mica/GC9 glass hybrid sealants. Different weight fractions(x) of phologpite micas, specifically for x=0, 0.1, 0.2, were mixed into the GC9 glass powders to improve the ductility of the sintered phologpite mica/GC9 glass blends. The coefficient of thermal expansion (CTE), viscosity, fracture strength, electric resistance, and leak rate of the specimens were measured by using dilatometer, parallel plate viscometer, ring-on-ring test, two-point and four-wire method, and pressure leakage equipment, respectively. The results showed that the CTE of the phologpite mica/GC9 glass blends can be modified by adjusting the weight fraction of phologpite mica. As the weight fraction of phologpite mica increases, the ductility of the blends increases while the fracture strength decreases. The electric resistance of the glass blends increased insignificantly during a long-term test at 800°C. At a weight fraction of x=0.2, it still keeps at a low average leak rate below 3.0×10^{-4} mbar•l/s/cm, for a 50th-thermal cycling test at 800°C in air.

4:20 PM

(ICACC-S3-040-2016) New Ba-free glass-ceramic sealant for SOCs application: characterization and performance

A. Sabato*[1]; G. Cempura[2]; D. Montinaro[3]; A. Chrysanthou[4]; M. Salvo[1]; M. Ferraris[1]; F. Smeacetto[1]; 1. Politecnico di Torino, Italy; 2. AGH University of Science and Technology, Poland; 3. SOLID POWER, Italy; 4. University of Hertfordshire, United Kingdom

A new Ba-free glass-ceramic sealant was designed, characterised and tested. The crystallization and the sintering behaviour was investigated using Differential Thermal Analysis (DTA) and Heating Stage Microscopy (HSM). DTA analyses have been carried out at different heating rates to evaluate the activation energy for crystallization by using the Kissinger method and the Matusita and Sakka equation. The thermo-mechanical and thermo-chemical compatibility between the glass-ceramic and both uncoated and Mn-Co spinel-coated stainless steel has been examined. The joining process was carried out at 850°C for 30 min in air. SEM-EDS analysis shows good compatibility between the glass-ceramic and the interconnect. By conducting X-Ray diffraction (XRD) and Selected Area Electron Diffraction (SAED) analysis of the glass-ceramic, Diopside has been identified as the crystalline phase along with a glassy phase. Steel/glass-ceramic/uncoated steel was thermally tested at 800°C up to 1100 hrs in dual atmosphere (air and Ar/H_2). There was no leakage following the long term test confirming the gas tightness of the sealant. The samples were then used for post-mortem analyses to understand the thermal behaviour. The compatibility between the glass-ceramic sealant and the stainless steel (bare and coated) after dual atmosphere tests is reviewed and discussed by means of SEM-EDS and TEM-SAED techniques.

4:40 PM

(ICACC-S3-041-2016) High temperature mechanical properties of glass-ceramics sealants for SOFC

S. Rodríguez-López[2]; J. Wei[1]; N. H. Menzler[1]; S. Gross-Barsnick[1]; J. Malzbender[1]; M. Pascual*[2]; 1. Forschungszentrum Jülich GmbH, 52425, Germany; 2. Institute of Ceramics and Glass, CSIC, Spain

Glass-ceramics are the most widely used materials for sealing p-SOFCs. However, they present some thermo-mechanical problems derived from their inherent fragility. Recent research has been oriented towards the improvement of the long-term mechanical stability, especially with respect to thermal cycling and prolonged

operation. This work is focused on the development of glass-ceramic compositions, with high mechanical resistance for sealing lightweight p-SOFCs. This type of anode-supported cell has even stronger requirements for the thermo-mechanical resistance. The RO-SiO_2-MgO-B_2O_3 (R=Ba, Sr) glass system has been chosen and, in order to evaluate the suitability of the glass-ceramic seals, properties such as gas-tightness, coefficient of thermal-expansion, viscosity, electrical resistance and adherence have been studied after extended periods of time at the typical SOFC working temperature (800°C). The mechanical characterization of the glass-ceramic materials at room temperature includes bending strength, hardness and Young's Modulus. The characterization of glass-ceramics and joints at high temperature was carried out through bending tests of sintered bars and joined bar type specimens (interconnect-seal-interconnect). Based on the obtained results, the thermo-mechanical behavior of glass-ceramics and interphases and the degradation mechanisms after thermal ageing and thermal cycling are discussed.

S5: Next Generation Bioceramics and Biocomposites

Bioceramics II

Room: Coquina Salon F

Session Chairs: Jeremy Soulie, Institut National Polytechnique de Toulouse; Alastair Cormack, Alfred University; Mohamed Rahaman, Missouri University of Science & Technology

1:30 PM

(ICACC-S5-009-2016) Development of Bioactive Glass Scaffolds with Improved Flexural Strength for Bone Repair

M. N. Rahaman*[1]; W. Xiao[1]; M. A. Zaeem[1]; 1. Missouri University of Science & Technology, USA

There is a need to develop synthetic scaffolds to repair large defects in load-bearing bones. Bioactive glass has attractive properties as a scaffold material for bone repair but its brittle mechanical response is a concern. Previously, we created bioactive glass (13-93) scaffolds with a uniform grid-like architecture which showed a compressive strength comparable to human cortical bone but a flexural strength much lower than cortical bone. In the present study, finite element modeling (FEM) was used to re-design the architecture of the scaffold to improve its flexural strength. Then scaffolds with the requisite architectures were created by a robotic deposition method and tested in four-point bending to validate the FEM simulations. Scaffolds with a gradient architecture had a flexural strength that was more than twice the value for the uniform grid-like architecture. These scaffolds could provide more reliable implants for structural bone repair.

1:50 PM

(ICACC-S5-010-2016) Medical Initiatives from the Nuclear Community: Porous Wall Hollow Glass Microspheres (PWHGMs) (Invited)

G. Wicks*[1]; 1. Applied Research Center, USA

The Nuclear Community has developed various specialized and one-of-a-kind technologies for a variety of applications, both inside as well as outside extreme environments. Many of these innovations can be termed "multi-use technologies", which have the potential for many other uses in a variety of other fields. Examples of these technology areas include digital radiography, microbiology, sensors/ robotics, advanced materials, and ceramics/ glass science. One specific example includes the development of a unique product called Porous Wall Hollow Glass Microspheres (PWHGMs), which was developed originally for hydrogen isotopes separations and storage. This technology was awarded an R&D 100 Award in 2011, awarded 'Top Honors' at a Symposium on Discovery and Innovation in 2012, and has been patented and also licensed for uses in other fields. These other areas include energy storage systems/ advanced batteries, security, environmental remediation and medicine. A discussion of the unique properties of these materials will be given along with some efforts as improved MRI contrast agents, a drug deliver platform, and other applications.

2:20 PM

(ICACC-S5-011-2016) Using Light to Measure Temperature: Lanthanide-doped Nanoparticles for Nanothermometry (Invited)

E. Hemmer*[1]; F. Legaré[1]; F. Vetrone[1]; 1. INRS, Canada

Thermal singularities in biological tissues or cells can be a first indicator for diseases such as cancer. Seeking new diagnostic approaches for the earliest possible detection of a disease, the measurement of these thermal singularities by use of nanoparticles has been suggested evolving into the field of nanothermometry. Lanthanide (Ln^{3+}) doped nanoparticles are well known for the intrinsic temperature dependence of their optical properties, such as emission intensities or lifetimes, which makes them highly interesting as nanothermometers. Further surface modification with a thermoresponsive polymer (pNIPAM) opens new pathways towards novel cellular nanothermometers: The linkage of Er^{3+}/Yb^{3+}:$NaGdF_4$ nanoparticles (emitting visible light after near-infrared (NIR) excitation) with an organic dye through pNIPAM provides donor-acceptor-pairs allowing for a temperature-dependent energy transfer from the Er^{3+}-ions to the organic dye. Moreover, NIR light is of particular interest for biomedical applications due to its increased tissue penetration when compared to visible or ultraviolet light. Thus, we are aiming for the development of novel nanothermometers taking advantage of the emission of NIR light under NIR excitation. Therefore, Er^{3+} and/or Ho^{3+}-doped $NaGdF_4$ nanoparticles were synthesized, and the nanostructures' suitability as ratiometric NIR-based nanothermometers will be discussed.

2:40 PM

(ICACC-S5-012-2016) Exciton dynamics between quantum dots and metal oxide semiconductors (Invited)

A. Vomiero*[1]; 1. Lulea University of Technolgy, Sweden

Due to their unique optical features, semiconductor quantum dots (QDs) are often presented as the ultimate frontier as sensitizers for photoelectrochemical solar cells and LEDs. In excitonic solar cells, the QD absorbs the incident radiation, an exciton is created, and charge separation occurs at the interface between the QD and the electron transporter. The control and proper modulation of exciton dynamics is critical in determining the performance of the device by regulating charge generation, separation and collection, and intense research is developed to optimize the matching between QDs and wide bandgap semiconductors (TiO2, ZnO, SnO2, etc.). The most interesting results in terms of device performances have been obtained by using poly-dispersed, *in situ* generated QDs. This approach allows obtaining naked QDs directly grown on the porous structure of the metal oxide photoanodes, thus guaranteeing an intimate contact between the two interfaces. Moreover, the deposition of networks of QDs presenting absorption features able to collect a wider region of the solar spectrum is possible by tuning the composition of QDs using mixed. We will present an overview of photoelectrochemical systems composed of metal oxide semiconducting photoanodes sensitized with semiconducting QDs and we will discuss possible strategies to tailor the optical properties of the system to maximize its photoconversion efficiency.

3:20 PM

(ICACC-S5-014-2016) Using Molecular Dynamics to Probe the Structure and Reactivity of Bioactive Glasses (Invited)

A. Cormack*[1]; 1. Alfred University, USA

Structural characterization of bioactive glasses, like all inorganic glasses, at the atomic scale is difficult because of the inherent lack of periodicity. Atomistic computer simulation techniques, on the other

hand, have been employed with considerable success. In this presentation, we will describe the elucidation of the structure of bioactive glasses using molecular dynamics. In particular, we will discuss the structural features, both in the bulk glass, as well as on the surface, which impact the reactivity of bioactive glasses with water.

3:40 PM

(ICACC-S5-015-2016) New bioactive, bioresorbable magnetic nanoparticles: A new platform for theranostics (Invited)

A. Tampieri*[1]; A. Adamiano[1]; S. Sprio[1]; M. Sandri[1]; M. Iafisco[1]; M. Montesi[1]; S. Panseri[1]; 1. National Research Council of Italy, Italy

Magnetic materials are receiving increasing attention for new potential applications in medicine. Also, magnetic nanoparticles are being increasingly employed as support materials for enzyme immobilization, drug-delivery systems (DDS), contrast agents for magnetic resonance imaging as well as heat mediators for hyperthermia-based anti-cancer treatments. The big challenge is the production of magnetic materials with good biocompatibility and biodegradability, as the long-term cytotoxic effect of the currently used iron oxides are not yet completely assessed. Recently we developed a novel biocompatible and bioresorbable superparamagnetic nano-apatite substituted with Fe^{2+}/Fe^{3+} ions (FeHA). The biocompatibility of FeHA nanoparticles opens to a conceptually new type of biomaterial enhancing hard tissue regeneration, based on magnetic stimulation of mesenchymal stem cells. Moreover FeHA can replace iron oxides in theranostics. In particular, the hyperthermia of FeHA opens to new thermo-sensitive DDS and/or to anti-cancer therapies. In addition, magnetic targeting of stem cells offers exciting opportunities for new cell-based therapies. Cells can be guided to target sites by using external magnetic fields to improve retention in the injured organs. FeHA NPs could be also easily functionalized with drugs, growth factors, vectors and miRNA opening new promising prospects in nanomedicine.

4:00 PM

(ICACC-S5-013-2016) Molecular Biomimetic Approaches for Hard-to-Soft Interfaces (Invited)

C. Tamerler*[1]; 1. UNIVERSITY OF Kansas, USA

In adapting newer and better biomaterials that are similar to their canonical counterparts, integration at the biomaterial interfaces has been a critical roadblock. Biological systems are guided by molecular interactions occurring between the material and cell surface. There has been a proliferating interest in creating advanced bio-interfaces resolving protein modulated material surfaces that allow favorable interactions with the surrounding biological systems. Smaller protein domains, i.e. peptides, have been utilized as the key building blocks to mimic the molecular recognition as the basis of molecular scale interactions. Our approach includes decoding the peptide-material interactions towards generating controllable interfaces. Here we will describe to engineer chimeric molecules that can have controlled surface organization at the implantable material interface while keeping the desired orientation to present a bioactive signal to the cells to direct their behavior. Our examples will include: i) to utilize antimicrobial peptides in controlling bacteria-surface interactions at the interfaces to prevent biofilm formation and consequent implications such as implant failure due to bacterial infections, ii) to direct cell-to-implant interactions by chimeric peptides that are displayed at the material interfaces to achieve guided stem cell differentiation.

4:20 PM

(ICACC-S5-016-2016) Sol-gel elaboration of new calcium pyrophosphate glasses for bone regeneration (Invited)

J. Soulie*[1]; P. Gras[1]; D. Laurencin[2]; O. Marsan[1]; O. Varlet[1]; C. Charvillat[1]; C. Rey[1]; C. Combes[1]; 1. INPT, France; 2. Université de Montpellier, France

Since the invention of Bioglass®, bioactive glasses for bone regeneration have been extensively studied. The success of these silica-based glasses has opened the way to other compositions and particularly, to phosphate-based glasses, in order to reach new dissolution kinetics. Although several sol-gel reactions has been developed to elaborate phosphate glasses thanks to orthophosphate precursors, two problems can be pointed out : i) the difficulty of reaching a "gel" state, ii) the cost of precursors. Considering these results, our study is focused on the synthesis of phosphate glasses by soft chemistry using pyrophosphate precursors. Indeed, this entity has been demonstrated to favor bone regeneration when added to orthopedics cements, but to the best of our knowledge there is no description of sol-gel derived pyrophosphate glasses in the literature. In this work, glasses have been elaborated in aqueous solutions, followed by centrifugation, washing steps (gel step) and finally a thermal treatment. The influence of synthesis parameters on both morphological and structural characteristics of materials has been studied. It has been found that both glasses and glass-ceramics could be obtained depending on formation conditions. The nature of the phosphate entities is confirmed to be linked to this parameter and to play a critical role in the structure formation.

S6: Advanced Materials and Technologies for Direct Thermal Energy Conversion and Rechargeable Energy Storage

Direct Thermal Energy Conversion

Room: Tomoka A

Session Chairs: Hua-Tay Lin, Guangdong University of Technology; Gabi Schierning, University of Duisburg-Essen

1:30 PM

(ICACC-S6-029-2016) Energy Conversion and Storage Requirements for Hybrid Electric Aircraft (Invited)

A. Misra*[1]; 1. NASA Glenn Research Center, USA

Among various options for reducing greenhouse gases in future large commercial aircraft, hybrid electric option holds significant promise. In the hybrid electric aircraft concept, gas turbine engine is used in combination with an energy storage system to drive the fan that propels the aircraft, with gas turbine engine being used for certain segments of the flight cycle and energy storage system being used for other segments. The paper will provide an overview of various energy conversion and storage options for hybrid electric aircraft. Such options may include fuel cells, batteries, supercapacitors, multifunctional structures with energy storage capability, thermoelectric, thermionic or a combination of any of these options. The energy conversion and storage requirements for hybrid electric aircraft will be presented. The role of materials in energy conversion and storage systems for hybrid electric aircraft will be discussed.

2:00 PM

(ICACC-S6-030-2016) Nanocrystalline bulk silicon for direct thermal energy conversion (Invited)

G. Schierning*[1]; 1. University of Duisburg-Essen, Germany

Silicon is the second most abundant element of the earth crust and, as a crystal, the most important semiconductor of our time. Hence, the good scalability of silicon-based technology is driving force to explore novel fields of application. While in its single or polycrystalline embodiments, silicon is per se not a good choice for direct thermal energy conversion, its thermoelectric figure of merit can be boosted by the transition from polycrystalline to nanocrystalline variants. Alloying or the implementation of nanoinclusion phases further help to improve the figure of merit. The nanocrystalline bulk material is hereby obtained by a bottom-up approach which uses tailored silicon nanopowder from a scalable gas phase process as raw material. Applying a spark plasma sintering (SPS) technique, small grain sizes have been maintained despite of consolidation. But SPS imposes some characteristic microstructural features into the

nanocrystalline bulk, especially if a thermoelectrically optimized powder is being processed. Since the electric current directly penetrates the sample during the compaction process, the generation of current paths along with density fluctuations may be observed. Further, the Peltier effect leads to a significant redistribution of heat within the sample at the sample-electrode interfaces. Nonetheless, SPS is widely used for thermoelectric materials and the scale-up possible without drawbacks.

2:30 PM

(ICACC-S6-031-2016) Black nano-ceramics as high-temperature solar absorbing material for next-generation concentrating solar power (Invited)

R. Chen*[1]; 1. University of California, San Diego, USA

Concentrating solar power (CSP) is becoming an increasingly important part of the renewable energy portfolio. However, further cost reduction is needed to make CSP competitive with traditional energy technologies. Higher operation temperature is considered a plausible avenue leading to higher power conversion efficiency and lower cost, but tremendous technical challenges remain due to the higher temperature. One of the main issues is the lack of a high-performance solar absorbing material that is durable at high temperature (750 °C or above). In this presentation, we will describe our recent work on the development of a class of black oxide nanoparticles as high-temperature solar absorbing materials. The nanoparticles and the solar absorbing coatings are made from scalable processes. Our coatings show high solar absorption efficiencies (>90%). More importantly, when exposed to high temperature, the coatings are more stable than the state-of-the-art material. Our findings suggest that the materials and processes developed here are promising for solar absorbing coating for next-generation high-temperature CSP systems.

3:20 PM

(ICACC-S6-032-2016) Enhanced thermal conductivity of polyethylene glycol/ expanded vermiculite shape-stabilized composite phase change materials with multi-wall carbon nanotubes for thermal energy storage

Y. Deng*[1]; J. Li[1]; T. Qian[1]; W. Guan[1]; 1. China University of Geosciences, China

Enhanced thermal conductivity of polyethylene glycol (PEG)/ expanded vermiculite (EVMT) shape-stabilized composite phase change materials (ss-CPCM) with multi-wall carbon nanotubes (MWCNTs) was prepared by vacuum impregnation method. The maximum mass percentage for PEG retained in ss-CPCM was more than 70% due to specific non-uniform flat layers pore structure of EVMT. The thermal conductivity of ss-CPCM containing 0.2 wt.% and 0.3 wt.% MWCNTs was 0.505 W/m K and 0.635 W/m K, respectively. The enhancing level was as high as 20.8% and 51.9%. The corresponding latent heats decreased 1.45% and 11.39% for melting process and 5.96% and 14.28% for freezing process, which still had large value (75.86-101.60J/g). Moreover, the MWCNTs reduced the supercooling effect for ss-CPCM. In addition, the SEM and FT-IR analysis results indicated that the melted PEG was adsorbed on the surface and completely dispersed into the pores of EVMT and no chemical changes took place during the heating and cooling process. XRD results showed that the crystal structure of PEG was not destroyed after impregnation whereas the crystallization process of PEG was greatly restrained.

3:40 PM

(ICACC-S6-033-2016) High temperature solar selective absorber coatings consisting of alternating W and HfO_{2-x} nanolayers

C. Hsueh[1]; C. Chen[1]; I. Chang[1]; J. Ting*[1]; 1. National Cheng Kung University, Taiwan

Optical coatings consisting of alternating W and HfO_{2-x} nanolayers have been investigated theoretically and experimentally. Tungsten was selected because of its high melting point and high infrared reflectance. HfO_{2-x} was chosen due to its large band gap and good thermal stability. Furthermore, the refractive index and extinction coefficients of HfO_{2-x} could be tuned by adjusting the oxygen defect concentration. Computer simulation using COMSOL software was first performed to study the effects of layer thickness and number of layers, and refractive indices and extinction coefficients of the HfO_{2-x} on the optical properties of resulting coatings. The simulated results were then used as the guideline for the fabrication of high temperature solar selective absorber coatings, and compared to the experimental results. Experimentally, alternating W and HfO_{2-x} nanolayers were deposited on stainless steel substrates using an RF sputter deposition method. The characteristics of the obtained coatings were examined before and after heat treatment at 800, 900 and 1000 °C: X-ray diffraction, micro-Raman spectroscopy, ellipsometry, field emission scanning electron microscopy, X-ray photoelectron spectroscopy, UV-vis spectroscopy, and IR spectroscopy. The effects of the material characteristics on the optical performance are presented and discussed.

4:00 PM

(ICACC-S6-034-2016) Electrical and Thermal Effects of Contacts in Thermoelectric Characterization by Harman Method

B. Kwon*[1]; I. Roh[1]; D. Hyun[1]; C. Park[2]; J. Kim[1]; 1. Korea Institute of Science and Technology, The Republic of Korea; 2. Seoul National University, The Republic of Korea

Harman method measures the thermoelectric figure of merit rapidly and readily based on the voltage responses determined by ohimic resistance and the Peltier effect. However, the Harman method relies on the assumptions of one-dimensional electrical potential distribution, negligible contact resistance, and an adiabatic condition. As it is difficult to satisfy all these requirements, the understanding of available parasitic effects is critical. A direct welding of thin lead wires and the sample reduces the contact resistance and the heat loss, however creates a complex electrical potential distribution due to current spreading. The use of plate-type electrodes ensures one-dimensional electrical potential distribution, while the contact resistance at the plate and sample interface becomes important. Here, we discuss how the contacts influence the Harman method electrically and thermally, and a correction scheme for this issue. We study the electrical potential distribution and heat loss during the Harman measurement employing a finite element model. To validate the model, we measure the thermoelectric properties of Bi-Te based alloys having various geometries, which is equivalent to varying the electrical and thermal resistances of the samples.

4:20 PM

(ICACC-S6-035-2016) Wettability Study of Borosilicate Glass Over Metal Substrates for Development of Glass-Metal Joints

R. Chhibber*[2]; R. Joshi[1]; 1. IIT Jodhpur, India; 2. Indian Institute of Technology Jodhpur, India

One of the major challenges in fabricating a Glass-Metal Joint is the wettability of glass over the metal surface. The present work aims at studying the wettability of borosilicate glass over metal substrates for development of glass-metal joint. The borosilicate glass-metal joint specimens were fabricated with different metal substrates having variation in surface roughness and exposed to same pre-oxidation time. The wettability study was carried out using contact angle measurement technique over these specimens. The contact angle decreased with increase in oxide layer thickness for stainless steel SS 304 and for Copper substrate. It was found that the measured contact angle values increased with increase in surface roughness of the metal substrate. It is concluded that surface roughness of the metal substrate affects the wettability of glass over metal substrate.

S7: 10th International Symposium on Nanostructured Materials: Functional Nanomaterials and Thin Films for Sustainable Energy Harvesting, Environmental and Health Applications

Synthesis, Functionalization & Assembly of Nanostructures III

Room: Coquina Salon A

Session Chairs: Csaba Balazsi, Bay Zoltan Nonprofit Ltd. for Applied Research; Roger Narayan, UNC/NCSU Joint Dept of Biomedical Engineering

1:30 PM

(ICACC-S7-041-2016) Molecular self-assembly of ultrathin 2D metal oxide nanosheets – a bottom-up approach on graphene analogues synthesis (Invited)

Z. Sun*[1]; 1. Queensland University of Technology, Australia

Two-dimensional (2D) transition metal oxide systems present exotic electronic properties and high specific surface areas, and also demonstrate promising applications ranging from electronics to energy storage. Yet, in contrast to other types of nanostructures, the question as to whether we could assemble 2D nanomaterials with an atomic thickness from molecules in a general way, which would give them some amazing properties such as those of graphene, still remains unresolved. In this presentation, we will report a generalized and fundamental approach to molecular self-assembly synthesis of ultrathin 2D nanosheets of transition metal oxides by rationally employing lamellar reverse micelles. It is worth emphasizing that the synthesized crystallized ultrathin transition metal oxide nanosheets possess confined thickness, high specific surface area, and chemically reactive facets, so that they could have promising applications in nanostructured electronics, photonics, sensors, and energy conversion and storage devices.

2:00 PM

(ICACC-S7-042-2016) Utilizing chemical nanotechnologies in Improving consolidation and thermal conductivity of the adsorbent layer for absorption heat pump

S. Cho[1]; T. Hwang*[1]; 1. Korea Institute of Industrial Technology, The Republic of Korea

There is an increasing interest in the development and use of adsorption heat pumps due to their economic and environmental benefits, since they enable the use of solar energy or waste heat for the applications such as district networks and cogeneration plants. Solid/vapor adsorption systems were first commercialized in the 1920s and hold great promise for overcoming the limitations of the engine-driven vapor compression and the liquid/vapor absorption systems. Improving the performances of adsorption heat pumps inevitably includes developments in adsorbent materials together with the design of more efficient absorbers and heat exchangers. A possibility to enhance both heat and mass transfer characteristics of an adsorption heat exchanger is to apply the adsorbent directly to its surface in form of a consolidated layer. The binding of ready-prepared adsorbent particles on the metal surface is still valid due to its simplicity and productivity. In this case, chemical nanotechnologies could readily be employed to provide inorganic binders for the consolidation of mesoporous particles into an adsorbent layer and also metallic nano-phase in the layer to improve thermal conductivity thereof. In this paper, the processing ideas and improved properties of the prepared adsorbent layer will be presented and discussed.

2:20 PM

(ICACC-S7-043-2016) Shape-Induced Advancement of Nanocubes for Miniaturization of High Performance Devices (Invited)

K. Kato*[1]; K. Mimura[1]; Q. Ma[1]; M. Osada[2]; H. Imai[3]; S. Wada[4]; H. Haneda[2]; 1. National Institute of Advanced Industrial Science and Technology (AIST), Japan; 2. National Institute for Materials Science, Japan; 3. Keio University, Japan; 4. University of Yamanashi, Japan

Nanocrystals with an anisotropic shape of cube are candidates as building blocks for functional architectures. Such materials also receive attention because of their intrinsic size-dependent properties and resulting applications. Here, we demonstrate synthesis and characteristics of $BaTiO_3$, $SrTiO_3$ and CeO_2 nanocubes and the ordered assemblies. The importance of shape as well as size distribution is clarified for the bottom-up development of 3D hierarchial architectures. Recently, {100}-dominant $BaTiO_3$ and $SrTiO_3$ nanocubes with narrow size distributions and robust diversity in compositions were obtained. $BaTiO_3$ films made up of ordered nanocube assemblies were fabricated on various substrates. Regardless of the substrate, the nanocubes exhibited {100} orientations and a high degree of face-to-face ordering, which remained even after heat treatment at 850°C. The supracrystal films exhibited distinct dielectric behaviors with high permittivity. On the other hand, {100}-dominant CeO_2 nanocubes have been reported to show higher oxygen storage capacity compared with the conventional nanoparticles. In addition, Pt dots adsorbed on the {100} surface did not corporate but kept the high catalytic activity against a number of oxidation and reduction cycles. CeO_2 nanocube assemblies with nano-sized open spaces surrounded by enhanced surfaces would open new surface-dominant devices.

2:40 PM

(ICACC-S7-044-2016) Scalable low-cost routes to complex thin and ultra-thin metal - oxide nanocomposite coatings

G. Westin*[1]; 1. Uppsala University, Sweden

The development of catalysts for solar fuels, solar cells and photo-assisted water and air cleaning require robust, routes capable of producing advanced complex materials. These multi-functional devices should both be effective in absorbing photons for generation of holes and electrons, charge transport and catalysis of surface reactions and be stable. Quantum confinement in typically less than 3-4 nm sized oxide systems may also be utilized for improved charge separation and transport properties which puts high demands on the precision of the processing routes, although they still need to be of low cost. For such tough combination of demands solution based routes are probably the best suited for many systems, but there is a need for further development of these processes before they can be fully exploited for industrial scale manufacture of complex tailored materials. Here is discussed two solution based processing routes to metal-oxide complex thin- and ultra-thin films on various flat and complex nano-structured substrates using either reactive alkoxides or organically modified salts. Efficient processing of multi-metallic metal particles in multi-metallic oxide matrixes, e.g. Pt-Ni nano-particles and doped Fe2O3 will be described with an emphasis towards systems of relevance for photo-assisted solar fuel generation.

Synthesis, Functionalization & Assembly of Nanostructures IV

Room: Coquina Salon A

Session Chairs: Gunnar Westin, Uppsala University; Kazumi Kato, National Institute of Advanced Industrial Science and Technology

3:20 PM

(ICACC-S7-045-2016) Biology Enabled Nanotechnology: From Surfaces to Biologically Integrated Hybrid Materials (Invited)

C. Tamerler*[1]; 1. University of Kansas, USA

In recent years, there is proliferating interest in creating advanced bio-interfaces resolving protein modulated material surfaces that allow as well as enhance favorable interactions with the surrounding biological systems. Smaller protein domains, i.e. peptides, have been utilized as the key fundamental building blocks to mimic the molecular recognition as the basis of molecular scale interactions. Following Nature's molecular footsteps, we explore tuning molecular interactions at bio-nano interfaces to create integrated bio-hybrid systems. In this presentation, we summarize our approach on decoding the peptide-material interactions to design tunable bi-nano interfaces. Next, using these foundations, we will demonstrate controlling the biological activity at soft-hard interfaces. Our examples will include the self-organization of engineered peptides conjugated to functional proteins, e.g. redox enzymes and fluorescence proteins to form controlled assemblies with single to multiple layer organization. We will finally describe the modularity of our approach in designing polymer nanofibers integrated with nanoparticles assembled with engineered peptides that are genetically conjugated to photoactive biomarker proteins. The integration of biological building blocks may allow harnessing the diversity and protein functions to generate smart bio-hybrid materials for wide range of applications.

3:50 PM

(ICACC-S7-046-2016) Engineered bioactive hydroxyapatite nanostructured composites (Invited)

C. Balazsi*[1]; K. Balazsi[2]; 1. Bay Zoltan Nonprofit Ltd. for Applied Research, Hungary; 2. Centre for Energy Research HAS, Hungary

Hydroxyapatite is a most popular material for application in bone regeneration for its excellent bioactivity, biocompatibility and osteoconductivity. Cellulose is the major component in the rigid cell walls in plants, a linear polysaccharide polymer with many glucose monosaccharide units. The synthesis of hybrid ceramic polymer nanofibers by means of electrospinning is a major breakthrough in biotechnology-related nanomanufacturing. Electrospinning is a long time known method to produce nano and micro polymer fibers. The very large surface area and flexibility in surface functionalities make the polymer nanofibers to be optimal candidates for many applications. In this work, nano HAp and CA are combined to form novel hybrid 3D scaffolds mimicking the extracellular matrix (ECM) architecture by electrospinning. CA / nano HAp scaffolds were proved to adhesion and growth of osteoblasts of bone cells. From these studies suggest that both the morphology and structure of the CA-HAp composite scaffolds play important roles in the enhance apatite mineralization. Based on our observations, these scaffolds are considered as a promising candidate for bone tissue engineering application.

4:10 PM

(ICACC-S7-047-2016) Additive Manufacturing of Small-Scale Systems for Medical Applications (Invited)

R. Narayan*[1]; 1. North Carolina State University, USA

Laser-based processing of inorganic-organic hybrid materials may be used to develop complex small-scale tools for medical diagnosis and treatment. For example, two photon polymerization has been used to prepare microneedles for transdermal drug delivery, tissue engineering scaffolds, and other small-scale medical devices. Unlike conventional fabrication methods, two photon polymerization is an additive manufacturing method that uses spatial and temporal overlap of photons for photopolymerization of photosensitive materials within highly-localized volumes. A medical device with an arbitrary geometry is created by polymerizing the material along the laser trace. Several classes of inexpensive inorganic-organic hybrid materials and other photosensitive materials may be processed with two photon polymerization. In this presentation, the development of novel classes of photosensitive materials as well as chemical characterization, mechanical characterization, and biologically-relevant in vitro characterization of two photon polymerization-fabricated small-scale medical devices will be presented

4:30 PM

(ICACC-S7-048-2016) Self-Assembled Graphitizing Coatings for the Rational Design of Photocatalysts

J. Claverie*[1]; J. Zhang[1]; L. Hong[2]; 1. University of Quebec at Montral (UQAM), Canada; 2. Beijing Institute of Nanoenergy and Nanosystems,, China

A self-assembly approach has been designed for the preparation of polymeric graphitizing coatings on a variety of inorganic materials. Upon heat treatment, the coating is converted into graphene-like material (D/G ≈ 0.8), with thickness precisely tunable from 0.6 nm up to 10 nm. This technology was applied to the formation of hierarchical TiO_2 nanobelt photocatalysts with plasmonic enhancemen provided by either Au nanoparticles or carbon quantum dots. Water-splitting activity as well as organic dye photocatalytic decomposition were measured for a variety of photocatalysts having all the same amount of TiO_2, Au and carbon but different architectures. Highly active catalysts in the visible range were thus discovered. In conclusion, this self-assembly technique enables the precise tuning of the position and thickness of graphene-like carbon. By controlling these parameters, novel highly-active photocatalysts can be unravelled.

4:50 PM

(ICACC-S7-049-2016) Laser desorption/ionization (LDI) mass spectrometry based on nanomaterials for biomedical applications

J. Pyun*[1]; 1. Yonsei Univ, The Republic of Korea

In conventional MALDI-TOF mass spectrometry, analyte molecules are known to be ionized bymixing with organic matrix molecules. As the organic matrix molecules are ionized, they generate unreproducible mass peaks such that MALDI-TOF massspectrometry is nearly impossible in the low mass-to-charge (m/z) range (< 1000). In this work, laser desorption/ionization (LDI) mass spectrometry was presented using solid-matrices based on nanomaterials: (1) Top-down synthesized TiO_2nanowires were synthesized as arrays using a modified hydrothermal processdirectly on the surface of a Ti plate; (2) The nylon nanoweb with TiO_2 particles was prepared by the simultaneouslyelectrospinning a nylon nanoweb and electrospraying TiO_2nanoparticles; (3) The parylene-matrix chip was fabricated by the deposition of a partiallyporous parylene-N thin film on a dried organic matrix array. The mass spectrometry of multiple analyteswas demonstrated in the low molecular weight range using eight amino acids.Additionally, model peptides. The biomedical application of LDI mass spectrometry was demonstrated for (1) the detection of chemical and biological warfare agents, (2) the newborn metabolite analysis and (3) the antibiotics-resistant bacteria screening.

5:10 PM

(ICACC-S7-050-2016) Zinc Oxide Based Materials: Preparation, Characterization, Properties and Application (Invited)

Z. Crnjak Orel*[1]; 1. National Institute of Chemistry, Slovenia

The preparation of stable and non-agglomerated ZnO particles of different shapes and sizes will be presented. Experiments

were performed in reactor at controlled temperature. The starting concentration of precursors, type of solvents and pH influence the size and morphology of particles. The morphological and crystalline properties were characterized by IR, XRD, SEM and HRTEM. We will present the growth mechanism of ZnO particles. It follows the non-classical crystallization concept which was observed by combining of advanced in-situ SAXS method and ex-situ electron microscopy (FE-SEM and TEM). The mechanism predicts the self-assembling of nanobuilding units (5-10 nm) into larger microstructures with prompt crystallization. At the same time, the growth based on the direct attachment of ions from the solution also occurs in minor extension. The synthesized ZnO nanoparticles were further used for the preparation of polymer/inorganic-material-based nanocomposites. We found that the presence of a very small quantity of ZnO based nanomaterial in the PMMA showed sufficient UV shielding (efficiently absorb UV light up to 370 nm) and at the same time good transparency in the visible-light region. Thermal stability of the ZnO/PMMA nanocomposites is considerably improved The synthesized ZnO on a K glass were further used for the preparation of solar cells and for photoelectrochemical water splitting.

5:30 PM

(ICACC-S7-051-2016) Current challenges in zeolite synthesis (Invited)

M. T. Wolberg*[1]; C. Kirschhock[1]; J. Martens[1]; 1. KULeuven, Belgium

Since decades zeolites catch the interest of industry as well as academy for an ever expanding field of applications. Even so, many open scientific questions remain. In particular understanding the formation of zeolites on molecular level is still an unsettled but essential challenge. Thorough mechanistic study is hindered by the common occurrence of complex gels during traditional zeolite synthesis. Only in a few cases synthesis and in presence of organic structure directing agents (SDAs) clear synthesis solutions are available for detailed characterization. A comparable system in the purely inorganic case, usually used to obtain alumosilicate zeolites with cation exchange properties, is still lacking. A new synthesis route is discovered using hydrated alkali silicate ionic liquids (HSIL). The extraordinarily low water content and fully clear nature of these inorganic liquid crystal systems, offer unprecedented opportunities for thorough mechanistic studies. Another, economically exceptionally attractive synthesis strategy based on inter-zeolite-transformation offers a facile route to numerous frameworks in a cheap and easy manner. Investigation of these systems reveal the peculiar structure directing role of alkaline cations and the role of suitable aluminosilicate connectivity in the precursor material.

5:50 PM

(ICACC-S7-052-2016) Synthesis and Characterization Of ZnO Nanorods and CdSe Quantum Dots for Optoelectronic Applications

D. K. Choi*[1]; E. A. Mgbemeje[1]; S. Y. Lee[1]; 1. Chonbuk National University, The Republic of Korea

We spin coated CdSe quantum dots on ZnO nanorods to extend photo absorption range of solar cell electrode and photo detector. ZnO nanorods were synthesized on corning glass(7059) by hydrothermal method and CdSe quantum dots were synthesized by high injection process. The characterizations of ZnO nanorods, CdSe quantum dots and CdSe spin coated ZnO nanorods were investigated through morphology, component analysis, crystal structure, photo absorption, photo luminescence spectra(PL), hall effect and current-voltage characteristics. PL spectra of ZnO nanorods that annealed at 400 for 30 min. reduced largely in deep-level emission intensity compared to as-grown ZnO nanorods. Growth temperature, time, amount of Se precursor and cooling rate were some pertinent factors needed to extend the photo absorption range in high injection CdSe synthesis . By decreasing growth temperature, growth time and amount of Se precursor, PL spectra of CdSe quantum dots shifted to blue range. ZnO nanorods spin-coated with CdSe quantum dots were identified as n-type semiconductor and their PL spectra intensity increased in wavelength from 530 to 570 nm compared to ZnO nanorods. Photo absorption of ZnO nanorods spin-coated with CdSe quantum dots decreased in near-UV range. I-V characteristics of ZnO nanorods spin-coated with CdSe quantum dots were not changed.

S8: 10th International Symposium on Advanced Processing and Manufacturing Technologies for Structural and Multifunctional Materials and Systems (APMT10)

Novel Ceramic Processing III

Room: Coquina Salon B

Session Chairs: Olivier Guillon, Forschungszentrum Juelich; Hisayuki Suematsu, Nagaoka University of Technology

1:30 PM

(ICACC-S8-038-2016) Polymer-Derived Advanced Ceramics —- Synthesis and Microstructure-Property Relation (Invited)

R. Riedel*[1]; 1. TU Darmstadt, Germany

The polymer to ceramic transformation process enabled significant technological breakthroughs in ceramic science and technology, like the development of ceramic fibers, coatings or ceramics stable at ultra-high temperatures with respect to decomposition, crystallization, phase separation and creep. In recent years, several important advances have been achieved such as the discovery of a variety of functional properties associated with PDCs. Particularly, novel insights into their structure at the nanoscale level has contributed to the fundamental understanding of the various useful and unique features of PDCs related to their high chemical durability or high creep resistance or semiconducting behavior. From the processing point of view, preceramic polymers have been used as reactive binders to produce technical ceramics, they have been manipulated to allow for the formation of ordered pores in the meso-range, they have been tested for joining advanced ceramic components and others. Consequently, possible fields of applications of PDCs have been significantly extended by the recent research & development activities. Several key engineering fields suitable for PDCs will be discussed in this presentation including high temperature resistant materials, hard materials, chemical engineering, or functional materials in electrical engineering as well as in micro/nano-electronics.

2:00 PM

(ICACC-S8-039-2016) Novel MAX-Polymer Multifunctional Composites

S. Ghosh*[1]; R. Dunnigan[1]; M. Habib[1]; S. Gupta[1]; 1. University of North Dakota, USA

$M_{n+1}AX_n$ (MAX) phases (over 60+ phases) are thermodynamically stable nanolaminates displaying unusual, and sometimes unique, properties. These phases possess a $M_{n+1}AX_n$ chemistry, where n is 1, 2, or 3, M is an early transition metal element, A is an A-group element, and X is C or N. The MAX phases are highly damage tolerant, thermal shock resistant, readily machinable, and with Vickers hardness values of 2–8 GPa, are anomalously soft for transition metal carbides and nitrides. MAX phases display nonlinear, hysteretic, elastic behavior due to kink band formation in the basal planes. The W_d (energy dissipated per unit volume per cycle) of these crystalline solids are comparable to most woods. The composites of MAX phases with metals (MAXMET) are also important from both fundamental and applied perspective. In this paper, we will report for the synthesis and characterization of novel MAX-Polymer composites. It is expected that these novel composites can be used for multifunctional applications.

2:20 PM

(ICACC-S8-040-2016) In-situ X-ray Computed Micro-tomography of Defect Evolution in Polymer Impregnation and Pyrolysis Derived Ceramic Matrix Composites

N. M. Larson*[1]; C. G. Levi[1]; F. W. Zok[1]; 1. University of California, Santa Barbara, USA

Current matrix processing methods have proven ineffective in producing SiC/SiC ceramic matrix composites (CMCs) that can operate for extended time periods at 1500°C in engines. To utilize SiC/SiC composites at their full potential, new matrix processing routes must be developed. The current study aims to investigate defect evolution in polymer impregnation and pyrolysis (PIP) derived CMCs. During the polymer infiltration, pores form due to flow speed variations in non-uniformly packed fiber beds. The relationship between the infiltration parameters and resulting 3D pore structure will be discussed. Furthermore, preceramic polymers undergo significant volume loss throughout pyrolysis, resulting in a very porous and heavily cracked matrix microstructure. The evolution of this microstructure throughout pyrolysis was characterized via in-situ 3D tomography in a thermally and environmentally controlled hot cell. Preliminary results of this in-situ microstructure evolution study will be presented in conjunction with the corresponding chemical evolution characterized via thermogravimetric mass spectrometry.

2:40 PM

(ICACC-S8-041-2016) Electrical Conductivity of Dense, Bulk SiOC Ceramics

J. Eom*[1]; Y. Kim[1]; K. Kim[2]; 1. University of Seoul, The Republic of Korea; 2. Kunkuk University, The Republic of Korea

Crack-free, dense SiOC ceramics with 6-7 mm thickness and a 30 mm diameter were successfully fabricated from commercially-available polysiloxane without any fillers. The effect of sintering temperature on the electrical conductivity of bulk SiOC ceramics was investigated. The electrical conductivity of SiOC ceramics increased from 0.4 $\Omega^{-1}cm^{-1}$ to 7.1 $\Omega^{-1}cm^{-1}$ at RT with increasing sintering temperatures from 1450 to 1650°C. The electrical conductivity of SiOC ceramics fabricated at 1550°C gradually increased with increasing temperatures from 4 to 300 K. Raman spectroscopy suggests the presence of graphictic carbon species in the amorphous SiOC matrix. High resolution transmission electron microscopy (HRTEM) observation shows the presence of nano-crystalline graphitic flakes in all specimens and the presence of nano-crystalline SiC in the SiOC ceramics sintered at 1650°C. The Raman spectroscopy and HRTEM revealed the increase in electrical conductivity of the SiOC ceramics with increasing sintering temperature is attributed to a structural modification leading to ordering of the graphitic domains (transformation of sp^3 into sp^2) and a possible contribution of nano-crystalline SiC grains precipitated from the amorphous SiOC.

3:20 PM

(ICACC-S8-042-2016) Defect Control of SiC Polycrystalline Fiber Aiming for Higher Strength (Invited)

T. Ishikawa*[1]; H. Oda[2]; 1. Tokyo University of Science, Yamaguchi, Japan; 2. Ube Industries, Ltd., Japan

Tyranno SA (Ube Industry) and Hi-Nicalon Type S (NGS) are well-known as a SiC-polycrystalline fiber with highest heat-resistance and excellent mechanical properties, and thus actively evaluated for the aerospace applications as SiC/SiC composites. The structural performances of the composites are dominated by the fiber strength. Hence, an increase in the fiber strength would be important. So, a clarification of the relationship between the strength and fine structure of the fiber is needed. Using these observations, we have to control the fine structure of each fiber element. These SiC-polycrystalline fibers are synthesized by further heat-treatment of amorphous SiC-based fibers, which are synthesized from derivatives of polycarbosilane. During the aforementioned further heat-treatment, the decomposition reaction of the amorphous SiC-based fiber and the sintering of the decomposed fiber proceed as well, accompanied by the release of CO gas and compositional changes, to obtain the dense structure. Since these changes proceed in each fiber filament, a strict control should be needed to minimize residual defects on the surface and in the inside of each fiber element. Actually, the present SiC-polycrystalline fibers contain some defects. By a decrease in the defects, much higher strengths will be expected. In this paper, the controlling factors of the fiber strength and their important things will appear.

3:50 PM

(ICACC-S8-043-2016) Facile obtainment of luminescent glass-ceramics by direct firing of a preceramic polymer and oxide fillers

E. Bernardo*[1]; L. Fiocco[1]; Z. Babakhanova[2]; 1. University of Padova, Italy; 2. Tashkent Chemical-Technological Institute, Uzbekistan

Rare-earth (RE) doped glass-ceramics represent very interesting luminescent materials. The thermal annealing of a glass causes the controlled precipitation of several crystalline phases, in which RE may be variously distributed, also with different oxidation states, e.g. Eu^{2+} and Eu^{3+}. The present investigation demonstrates the feasibility of Eu-doped alumino-boro-silicate glass-ceramics by direct firing in air, at 1000-1200 °C, of a silicone polymer, filled with nano- and micro-sized particles, instead from glass melting and annealing. $SrCO_3$ or $BaCO_3$ micro-particles, mixed with nano-sized γ-Al_2O_3, were found to react with amorphous silica, available from the oxidative decomposition of a commercial silicone, yielding a strontium or a barium alumino-silicate phase. Boric acid micro-particles contributed both to the development of a liquid phase upon firing (promoting ionic interdiffusion) and to the formation of a La-borate phase, by interaction with La_2O_3 micro-particles. The blue and red luminescence is attributed to the distribution of Eu^{2+} and Eu^{3+} ions, from nano-sized Eu_2O_3 filler, in alumino-silicate and borate phases, respectively.

4:10 PM

(ICACC-S8-044-2016) On the Development of MAX Reinforced Metal Matrix Composites

M. Habib[1]; R. Dunnigan[1]; S. Ghosh*[1]; S. Gupta[1]; 1. University of North Dakota, USA

$M_{n+1}AX_n$ (MAX) phases (over 60+ phases) are thermodynamically stable nanolaminates displaying unusual, and sometimes unique, properties. These phases possess a $M_{n+1}AX_n$ chemistry, where n is 1, 2, or 3, M is an early transition metal element, A is an A-group element, and X is C or N. The MAX phases are highly damage tolerant, thermal shock resistant, readily machinable, and with Vickers hardness values of 2–8 GPa, are anomalously soft for transition metal carbides and nitrides. MAX phases display nonlinear, hysteretic, elastic behavior due to kink band formation in the basal planes. The W_d (energy dissipated per unit volume per cycle) of these crystalline solids are comparable to most woods. The composites of MAX phases with metals (MAXMET) are also important from both fundamental and applied perspective. In this study, recent results on mechanical and tribological behavior of MAX-Al, MAX-Sn, and MAX-Zn composites will be demonstrated. There is a huge potential that these materials can be used for different tribological and engineering systems, for example, air-foil bearings, gas turbine seals, cylinder wall/piston ring lubrication for low-heat rejection diesel engines, various furnace components, among many others. In this presentation, we will report novel metal matrix composites by adding MAX phases as additives.

4:30 PM

(ICACC-S8-045-2016) Fabrication of SiC_f/SiC composites using electrophoretic deposition combined with ultrasonication followed by hot pressing

D. Yoon[1]; P. Fitriani[1]; S. Chae[1]; K. Raju[1]; A. Sharma*[1]; 1. Yeungnam University, The Republic of Korea

Because of the wide possible applications of continuous SiC fiber-reinforced SiC composites (SiC_f/SiC) under extreme conditions, such as for aerospace and nuclear reactor, much attention is being focused on the fabrication of SiC_f/SiC. However, the main current limitation for producing a dense SiC_f/SiC composite is the lack of a suitable manufacturing technique, although a range of techniques have been used to infiltrate the matrix phase into the fine voids of a fiber-preform. To develop a more suitable way to infiltrate a matrix phase composed of ceramic particles into a tightly woven preform, both AC and DC electrophoretic deposition (EPD) combined with ultrasonication were examined. Associated with the fabrication of dense SiC_f/SiC composites having a planar shape as well as tubular shape by hot pressing, experimental results on the controlling of slurry properties, designing a new mold for tube fabrication, the efforts to increase the degree of infiltration along with the resultant composite properties will be presented.

4:50 PM

(ICACC-S8-046-2016) Study on thermal properties of Al_2O_3 ceramic substrate composite reinforced by Si_3N_4

S. Wang*[1]; D. Zhang[1]; W. Wang[1]; X. Ouyang[1]; 1. Shantou university, China

With the miniaturization and chip-type tendency of electrical components, low temperature co-fired ceramic technology becomes a primary process for electrical packaging. Si_3N_4 possess similar thermal conductivity to AlN (320W/mK) and good matching thermal expansion coefficient with Si chip, good insulation and good mechanical property. It is taken as a potential material for high-speed circuit and high-power components packaging. Unfortunately, it is too expense to be used as substrate. In this paper, combining with the low cost feature of Al_2O_3 and high thermal conductivity of Si_3N_4, silicon nitride powder (Si_3N_{4p}) and whisker (Si_3N_{4w}) were took as the reinforcement phases to enhance the thermal ability of Al_2O_3 ceramic composite respectively. The Al_2O_3/glass /Si_3N_{4p} and Al_2O_3/glass/Si_3N_{4w}, were hot-pressed at 850. The composite were characterized by SEM, XRD. The thermal conductivity of the composites was determined by laser-flash method. The experiment results showed that the thermal conductivity of the composite rises with the increasing volume fraction of Si_3N_4. When adding 30vol%Si_3N_{4p} or 30%Si_3N_{4w} into Al_2O_3/30glass composites, the thermal conductivity of the composite was increased from 4.51 W/mK to 6.73W/mK or 9.31W/mK, respectively. It demonstrates that the Si_3N_4 whisker has a more effective influence on thermal conductivity of the ceramic composite, compared with Si_3N_4 powders.

S9: Porous Ceramics: Novel Developments and Applications

Innovative Characterization Methods for Porous Ceramics

Room: Coquina Salon G

Session Chair: Gian Soraru, University of Trento

1:30 PM

(ICACC-S9-001-2016) Gaining novel Insights into transport paths within porous Materials: Combining the powerful NMR and X-CT Tomography Techniques (Invited)

K. Rezwan*[1]; 1. University of Bremen, Germany

The conditioning of novel porous ceramic structures and their surfaces for applications in important fields of energy, environmental and chemical processing is of pivotal interest. While ceramic materials feature a high corrosion and high-temperature resistance, they are far more demanding to be manufactured and to be conditioned than metals or polymers. With the aid of recently established new ceramic manufacturing techniques, porous structures with pore sizes in the micro- (< 2nm), meso- (2 – 50 nm) and macropore (> 50 nm) range were generated for targeted applications. The characterisation of the transport paths within the opaque, three-dimensional structures, however, is highly challenging and requires imperatively the establishment of novel analytical methods. Thus, we have combined two powerful techniques; nuclear magnetic resonance (NMR) for spatial analysis of the liquid phase distribution and dynamic flow processes, whereas X-ray tomography (X-CT) is applied for quantitative analysis of the ceramic structure. Our preliminary results obtained from the systematic combination of these two powerful methods will be presented and discussed in this talk.

2:00 PM

(ICACC-S9-002-2016) Evaluating Porosity in Cordierite Diesel Particulate Filter Materials: Advanced X-ray Techniques and New Statistical Analysis Methods (Invited)

G. Bruno*[1]; A. Kupsch[1]; A. Staude[1]; A. Lange[1]; Y. Onel[1]; K. Ehrig[1]; B. Mueller[1]; M. Hentschel[1]; 1. BAM Federal Institute for Materials Research and Testing, Germany

Bi-continuous porous ceramics for filtration applications possess a particularly complicated microstructure, whereby porosity and solid matter are intermingled. Mechanical, thermal, and filtration properties can only be precisely estimated if the morphology of both solid matter and porosity can be quantitatively determined. Using 3D computed tomography (CT) at different resolutions, and several X-ray refraction-based techniques, we quantitatively evaluated porosity and pore orientation in cordierite diesel particulate filter ceramics. Moreover, applying both Fast Fourier Transform (FFT) and a newly developed image analysis algorithm (directional interface variance analysis, DIVA), we quantitatively evaluated porosity and pore orientation. Both the experimental techniques and the statistical approach allow extraction of spatially resolved or average values. Porosity values from synchrotron computed tomography used turn out to agree with mercury intrusion measurements, while pore orientation factors agree with published crystallographic texture data. This latter point also implies that the study of the pore/matter interface is sufficient to describe the morphological properties of these materials.

2:30 PM

(ICACC-S9-003-2016) Characterization of Three-Dimensionally Networked Porous Carbon Material

Y. Kogo*[1]; R. Inoue[1]; E. Kojyo[1]; G. Li[1]; 1. Tokyo University of Science, Japan

A new type of porous carbon material, TNPC (three-dimensionally networked porous carbon), was fabricated, and mechanical properties of the TNPC were examined. The TNPC has open-pore structure with three different average pore size of 7, 10, and 14 μm. The TNPCs have similar pore volume fraction of about 75%, and density of 0.37 g/cm3. Different from form materials, uniform pores are connected each other, and almost no closed pores are observed. Microstructure of the TNPC was observed by optical microscopy, scanning electron microscopy and X-ray computed tomography (X-ray CT). In the mechanical tests, tensile, bending and compressive properties of TNPCs were evaluated. Fracture toughness test was also carried out. In the compression test, the TNPC showed linear elastic behavior close to final fracture. A macroscopic crack extended perpendicular to the loading direction just before the final fracture. This might be attributed to micro-buckling of columns. Such behavior is different from that of bulk carbon material, which shows shear fracture behavior. Compressive strength of the TNPC depends on the pore size. Other mechanical properties also depend on cell size. In this presentation, the effect of pore size on

macroscopic mechanical properties of TNPC will be discussed based on the experimental results.

2:50 PM

(ICACC-S9-004-2016) Observation of internal structures in porous ceramics by micro x-ray CT (Invited)

S. Tanaka*[1]; K. Yasuda[3]; H. Kita[5]; M. Takahashi[6]; Y. Takahashi[10]; S. Honda[2]; T. Mitsuoka[9]; H. Muto[4]; S. Yamamoto[8]; Y. Yoshizawa[7]; 1. Nagaoka University of Technology, Japan; 2. Nagoya Institute of Technology, Japan; 3. Tokyo Institute of Technology, Japan; 4. Toyohashi University of Technology, Japan; 5. Nagoya University, Japan; 6. Ehime University, Japan; 7. AIST, Japan; 8. Asuzac, Japan; 9. NGK Sparck Plug Co. Ltd., Japan; 10. Noritake Co. Ltd., Japan

The porous ceramics has been used in various applications including SOFC, gas filters, catalyst support, etc. The mechanical properties of porous ceramics as well as functional property are strongly influenced by the internal structure as the amount, shape and network of pores, and the wall structure. The objective is to evaluate the internal structures of porous ceramics by micro-focus x-ray computer tomography (μ-CT) and the other microscopy, and to discuss their relevance to fabrication process and influence on mechanical property. Various types of porous ceramics were used as samples. The 3 dimensional networks of pores were observed clearly in various porous ceramics by the μ-CT. Porous Al_2O_3 ceramics, which was prepared from large particles, showed a continuous pore network. The pore sizes varied in the range from several to several hundred micro meter, and they depended on sizes of used particles. For pore forming type, the spherical pores were connected one another with bottle neck pores, and their size of spherical pores were determined by size of pore former. For alumina with 60% in porosity, the large size pores were rely contained, and they affected the mechanical strength and fluctuations. This work was supported in part by METI, Japan.

Innovations in Processing Methods & Synthesis of Porous Ceramics I

Room: Coquina Salon G

Session Chair: Paolo Colombo, University of Padova

3:40 PM

(ICACC-S9-005-2016) Preparation and Properties of Recrystallized Silicon Carbide with Nano-sized SiC Additives Synthesized via Carbothermal Reduction Processing (Invited)

J. Yang*[1]; Y. Deng[1]; 1. Xi'an Jiaotong UIniversity, China

Carbothermal reduction and the recrystallization were combined together. Nano-sized carbon black, micron SiO_2, micron α-SiC and phenolic resin were used as the raw materials. The nano-sized SiC were formed through the carbothermal reduction at the first step. Then the recrystallization was realized through evaporation-condensation process of the nano-sized SiC at the relatively low temperature. The results showed that the morphology and size of the synthesized SiC were controlled by temperature and impurities. The nano-sized SiC enhanced the evaporation condensation process during the recrystallization, resulting in the well development of the necks between the large particles and the great reduce of the recrystallization temperature. With the addition of 10 wt.% nano-sized SiC, the recrystallization could be realized at 1800°C for 4h. The recrystallization time could be significantly shortened with an increase of the temperature at a certain range, and the materials mechanical properties would be improved simultaneously.

4:10 PM

(ICACC-S9-006-2016) Polymer Derived Ceramic Foams by a New Replica Method

G. Soraru*[1]; E. Zera[1]; P. Jana[1]; 1. University of Trento, Italy

SiC, SiOC and SiCN polymer derived ceramic foams have been prepared through a new, low cost and versatile replica method. Unlike the traditional replica method, which is based on the coating of a sacrificial polyurethane foam with a ceramic suspension, the new process described here is based on the direct impregnation of the polyurethane foam with the preceramic polymer. The impregnated low cost PU foam (waste, packing material) is then pyrolyzed in inert atmosphere at 1200°C. Accordingly, SiC, SiOC and SiCN foams, with various density (0.035–0.35 g/cc), porosity (89-99%) and thermal conductivity (0.05–0.1 W/m. K) have been prepared using polycarbosilane, polymethylhydridosiloxane and polysilazane as a starting materials, respectively. Surface analysis by scanning electron microscopy showed that the resultant foams had an open and interconnected porous structure with cell size (100 -1000 microns) and, unlike the ceramic foams made through the conventional replica method, they show a dense strut. Results of the mechanical characterization, thermal stability in inert and oxidizing atmosphere and chemical durability in highly basic solution will also be presented.

4:30 PM

(ICACC-S9-007-2016) Hierarchical and interconnected high porosity mullite ceramics with sericite induced textured structures

X. Wang*[1]; J. Li[1]; W. Guan[1]; L. Liu[1]; 1. China University of Geosciences, China

Porous mullite ceramics were prepared via emulsion templating using commercial powders of calcined kaolin, sericite and alumina as the main raw materials. Natural mineral sericite was successfully used to facilitate the sintering of the macroporous ceramics. The green samples were sintered at 1350-1650 °C for 5 h, and the microstructure and properties of the resultant porous ceramics were characterized. As fabricated, the porous mullite ceramics possess a hierarchical microstructure in which large spherical pores ~20 μm in diameter are lined on their internal walls with small windows with an average diameter of ~3 μm. The short network formed by the interconnected rod-shaped mullite crystals acts as a stiff skeleton, strengthening the highly porous ceramics. The samples sintered at the optimal temperature (1550 °C) have a high open porosity (~73.4%) and a high mechanical strength (~22.1 MPa).

S10: Virtual Materials (Computational) Design and Ceramic Genome

Modeling of Point Defects, Grain Boundaries and Interfaces III

Room: Ponce DeLeon

Session Chair: Yanwne Zhang, Oak Ridge National Laboratory

1:30 PM

(ICACC-S10-031-2016) Computer Simulation of Ionization-Induced Formation of Amorphous Tracks in Ceramics (Invited)

W. J. Weber*[1]; E. Zarkadoula[2]; 1. University of Tennessee, USA; 2. Oak Ridge National Lab, USA

The interaction of ions with solids results in energy loss to atomic nuclei and electrons, and we have integrated computational and experimental approaches to investigate the separate and combined effects of nuclear and electronic energy loss on the response of ceramics to ion irradiation. The loss of energy to electrons results in significant ionization and formation of hot electrons that create a local thermal spike via electron-phonon coupling, and these processes are simulated using large scale molecular dynamics

simulations. Amorphous tracks are readily produced with high energy ions in many ceramic oxides, with a threshold in electronic energy loss for track formation. We have discovered that, in some complex oxides, amorphous tracks can be produced below this threshold due to a synergy between the electronic energy dissipation processes and pre-existing defects. The molecular dynamics simulations have been validated by experimental measurements, and these results provide new insights into the complex processes involved in the coupling of electronic and atomic dynamics. This work was support by U.S. DOE, BES, MSED.

2:00 PM

(ICACC-S10-032-2016) Defect chemistry of $Y_2Ti_2O_7$ pyrochlore from first principles calculations

T. Ogawa*[1]; A. Kuwabara[1]; C. Fisher[1]; H. Moriwake[1]; S. Kitaoka[1]; 1. Japan Fine Ceramics Center, Japan

Environmental barrier coatings (EBCs) protecting Si-based materials in the hot section of aircraft engines have been developed in order to improve fuel efficiency and decrease CO_2 emissions. To suppress the temperature increase by thermal radiation at high temperature, multilayer EBCs composed of Al_2O_3 and $Y_2Ti_2O_7$ have been designed and developed. Although oxygen permeability (diffusion) in $Y_2Ti_2O_7$ is one of the key factors affecting the oxidation resistivity of the coatings, defect creation and migration mechanisms in the material are still not well understood. In this study, we investigated point defect formation in $Y_2Ti_2O_7$ pyrochlore crystal. The defect formation energies of various types of point defects including complex defects were calculated using density functional theory. The results show that the stable defect type changes from V_O^{2+} to an oxygen Frenkel pair and then to V_Y^{3-} as the Fermi level increases from the valence band top. By determining the Fermi level according to the charge neutrality condition with electronic carriers, defect concentrations under different environmental conditions have been evaluated. The Frenkel pair is the predominant defect are a wide range of oxygen partial pressures from 10^{-10} to 10^5 Pa. Our results provide insights into the results of recent oxygen permeation experiments, suggesting that the migration of oxygen atoms is mediated by these complex defects.

2:20 PM

(ICACC-S10-033-2016) Theoretical modeling of the low energy recoil events of Ti_3AlC_2

J. Wang*[1]; J. Wang[1]; 1. Institute of Metal Research, Chinese Academy of Sciences, China

Nano-laminated Ti_3AlC_2 has potential application as nuclear material due to its good radiation damage tolerance. The irradiation resistance is supposed to be related to the layered crystal structure according to previous investigations on the behaviors of point defects under equilibrium conditions. Knowledge of dynamic atomic collisions under radiation is important to understand the generation and evolution of point defect in Ti3AlC2 but was never studied. In this work, we simulated the low energy recoil events in Ti3AlC2 by using the ab initio molecular dynamics (AIMD) modeling. The threshold displaced energies (E_d) of atoms on different lattice sites along or perpendicular to (0001) atomic plane are calculated, and the mechanisms of related defect generation are also revealed. The results show that E_ds of Al and TiII atoms within the weakly bonded layer are obviously anisotropic. In addition, C atoms have the lowest E_ds, which suggest them the most easily knocked on atoms. Besides the Frenkel defect pairs, Ti-Al antisites are also easily formed by the collision of displacement atoms. The present results provide insights into the collision cascade processes occurring in Ti_3AlC_2 under irradiation.

2:40 PM

(ICACC-S10-034-2016) Numerical Simulation of Nano–Porous Network Formation due to Point Defect Accumulation

E. Hernandez*[3]; V. Tikare[2]; L. Wang[1]; 1. UM, USA; 2. SNL, USA; 3. U.S. ARL, USA

Irradiation of certain semiconductors leads to the formation of complex nanoporous networks. We developed a computational model that is able to capture the multi-physical processes that lead to the formation of these structures in an irradiated monatomic material. The model couples deterministic-statistical approaches that enable us to simulate microstructural and compositional evolution. This is achieved by incorporating continuous and discrete order parameters to fully describe the computational domain. The continuum and discrete order parameters are evolved by the rate theory framework and Monte Carlo approaches, respectively. By employing rate theory, Potts Monte Carlo driven microstructural evolution and a kinetic Monte Carlo swelling algorithm we are able to simulate void induced swelling. Radiation damage leads to the formation of point defects, which eventually saturate leading to a stable porous microstructure. As these defects become accumulated, a threshold mechanism is used to nucleate voids out of vacancy rich regions. The model is tested by simulating the influence of radiation dose and rate on the formation and stabilization of the nano–porous networks. Furthermore, the point defect kinetics are studied to determine how they influence the resulting microstructures. The model suggests that slower diffusing point defects lead to a stable and more uniform nano–porous network.

Ceramic Genome and Integrated Materials Computational Engineering I

Room: Ponce DeLeon
Session Chair: Masato Yoshiya, Osaka University

3:20 PM

(ICACC-S10-035-2016) Structural and elastic properties of binary and ternary metal nitride alloys films: experimental study and first-principles calculations (Invited)

P. Djemia*[1]; Q. Hu[2]; L. Belliard[4]; G. Abadias[3]; 1. LSPM-CNRS, Université Paris 13, France; 2. Insitute of Metal Research, Chinese Academy of Sciences, China; 3. Institut P', CNRS-Université de Poitiers-ENSMA, France; 4. UPMC, France

We investigated the structural and mechanical properties of ternary polycrystalline alloys thin films $Zr_{1-x}Ta_xN$ (with $0 \le x \le 1$) deposited by reactive dc magnetron co-sputter deposition from individual Zr and Ta targets in $Ar+N_2$ plasma discharge. The total working pressure was fixed at 0.3 Pa by setting the Ar flow to 16 sccm, while the N_2 flow was adjusted to obtain stoichiometric nitride compounds. The structural properties of the ternary $Zr_{1-x}Ta_xN$ compounds were characterized by X-ray Diffraction and X-ray reflectivity, whereas the picosecond ultrasonics and Brillouin light scattering techniques were employed to measure their acoustic and elastic properties as a function of the Ta concentration, x. Density functional theory and the special quasirandom structure (SQS) method that mimics the random position of atoms were employed to calculate the evolution of the lattice parameter and of the elastic properties, including single-crystal elastic constants and polycrystalline elastic moduli, of $Zr_{1-x}Ta_xN$ with cubic rocksalt structure for rich-Zr content and with hexagonal structure for the Ta-rich content alloys. Binary TaN and ZrN films, with a rocksalt structure, were successfully elaborated on MgO substrates with a cube on cube epitaxial relationship in order to have a single crystal experimental reference that is compared to DFT calculations.

3:50 PM

(ICACC-S10-036-2016) Structural and elastic properties of Ta1-xZrxN and Ti1-xAlxN from first-principles calculations (Invited)

Q. Hu*[1]; P. Djemia[2]; C. Li[2]; R. Yang[1]; 1. Institute of Metal Research, Chinese Academy of Sciences, China; 2. LSPM-CNRS, France

Metal nitrides have drawn much attention for applications involving cutting tools, wear protection and machinery components. Binary nitrides show various crystal lattice structures at ground state. For examples, TiN and ZrN have cubic B1 structure whereas AlN and TaN have respectively hexagonal B4 and Bk structures. This leads to interesting structural transitions, and, consequently, property variations, of the ternary nitrides such as Ta1-xZrxN and Ti1-xAlxN upon increasing composition x. In the present work, we investigated the structural transition of Ta1-xZrxN and Ti1-xAlxN by using a plane-wave pseudopotential method in combination with special quasi-random structure approximation to describe the random distribution of the metal atoms. The critical compositions for the structural transitions were determined. Furthermore, we calculated the elastic constants and elastic moduli of Ta1-xZrxN and Ti1-xAlxN as functions of composition x. With the calculated elastic moduli, the hardnesses of the ternary nitrides were predicted using the hardness model proposed recently by Chen, et al.

4:20 PM

(ICACC-S10-037-2016) Strain triggered self-stiffening in anti-perovskite compounds (Invited)

J. Wang*[1]; 1. Institute of Metal Research, China

Strain-stiffening - an increase of stiffness with tensile strains (non-linear elasticity) is frequently observed in biological materials and elastomers. This would prevent large deformation that could threaten material reliability. In contrast, most solid materials show linear dependences of stress-strain relations at small elastic deformation and display decrement of elastic moduli at large strains. For the first time, we herein predict the particular tensile strain-stiffening mechanism in solid crystalline, the anti-perovskite compounds under tensile deformations. Based on first-principles modeling, we discover valence electron manipulation of the tensile behaviors of studied anti-perovskite materials. The key material parameters that induce strain-stiffening are the significant elastic anisotropy and large Poisson's ratio. The present discovery extends our knowledge on the remarkable strain-stiffening in crystalline solids, and it may provides guideline on design solid materials with improved mechanical stability.

4:40 PM

(ICACC-S10-038-2016) How ICME and MGI fruition benefits the MAX community: A case study on the calculation of (Ti,Cr)2AlC phase diagram

T. Duong*[1]; A. Talapatra[1]; W. Son[1]; H. Gao[1]; M. Radovic[1]; R. Arroyave[1]; 1. Texas A&M University, USA

In 2008, US National Research Council introduced ICME in order to accelerate material researches and developments which was shortly after generalized to MGI. Although there are still many milestones to reach, ICME and MGI have seemed to start reaching its fruition. Showing part of this and its benefit to the MAX community in order to support ICME and MGI and encourage the continuing supports from the MAX community, governmental, and industrial partners is the purpose of the current work. A case study is hence demonstrated. The study involves the utilization of the ATAT code and OQMD database, as ones of ICME and MGI fruition, to efficiently (i.e. quick and inexpensive) sketch out the phase diagram of (Cr,Ti)2AlC, all based on quantum-mechanics basis. This calculated phase diagram could serve as an initial guess for further experimental and accurate computational verification/refinement.

S12: Materials for Extreme Environments: Ultrahigh Temperature Ceramics (UHTCs) and Nano-laminated Ternary Carbides and Nitrides (MAX Phases)

Structure Stability under Extreme Environments II

Room: Tomoka B

Session Chair: Sylvain Dubois, PPRIME Institute

1:30 PM

(ICACC-S12-034-2016) MAX phase materials for nuclear applications (Invited)

K. Lambrinou*[1]; T. Lapauw[2]; J. Vleugels[2]; 1. SCK-CEN, Belgium; 2. KU Leuven, Belgium

The nuclear industry is looking for new materials that can survive the harsh service conditions of both next generation (Gen-IV) and current generation (Gen-III+) nuclear power plants, including design-basis transients (T<1200°C) and beyond design-basis accidents (T>1200°C). MAX phases combine unique mechanical and thermal properties with good corrosion resistance and irradiation tolerance, which makes them promising candidate cladding and structural materials. For example, MAX phases are currently envisaged as coatings on commercial clads for the development of accident-tolerant fuel (ATF) clads for Gen-III+ light water reactors (LWRs). ATF clads must show a step improvement in performance at nominal operating conditions with respect to the currently-used clads, combining good corrosion resistance in hot water/steam and irradiation tolerance while respecting the reactor core neutron economics. MAX phases have a great potential for Gen-IV lead fast reactor (LFR) applications, due to their superb liquid metal corrosion resistance in contact with oxygen-poor lead alloys (Pb, LBE). This work addresses the processing and characterisation of select MAX phases for nuclear applications; these materials are assessed in terms of their mechanical properties, i.e. stiffness, flexural strength, fracture toughness, and high-temperature stability based on the temperature dependence of their dynamic elastic properties and 4-point bending strength.

2:00 PM

(ICACC-S12-035-2016) Towards a better understanding of Ti_3AlC_2 tensile creep properties

E. Drouelle*[1]; V. Gauthier[1]; A. Joulain[1]; J. Cormier[1]; P. Villechaise[1]; S. Dubois[1]; P. Sallot[2]; 1. Institut PPRIME, France; 2. Safran Tech, France

In an aim to reduce fuel consumption, aeronautic companies select new materials to be investigated. Among them, MAX phases deserve to be considered. Indeed, the first mechanical tests performed indicate their good specific properties at high temperatures for half the density of superalloys. In this study, tensile creep tests have been performed on Ti_3AlC_2 samples in the 800-1000°C temperature range for stresses up to 210 MPa. Despite a brittle behavior at room temperature, Ti_3AlC_2 exhibits a brittle-to-ductile transition below 750°C; more than 20% strain can be reached at 1000°C. SEM observations on cross sections enabled to identify cavitation as the main damage mechanism at 900 and 1000°C, eventually assisted by oxidation. TEM observations were performed on a specimen crept at 900°C up to 7.5% strain. Three different types of characteristic microstructures were identified and can be associated to intra-granular deformation: highly dense dislocation networks, stacking faults and eventually numerous original defects parallel to the basal plane. These latter defects, the most representative of the creep microstructure, interrogate the ability of Ti_3AlC_2 to plastically deform during creep. Further tests were performed to assess the contribution of each microstructure on the first steps of specimen deformation and to evaluate the influence of oxidation on creep mechanisms.

2:20 PM

(ICACC-S12-036-2016) Room Temperature Stress-Strain Hysteresis in Ti_2AlC Revisited

R. Benitez[2]; W. Kan[3]; H. Gao[1]; M. O'Neal[2]; G. Proust[3]; M. Radovic*[2]; 1. Texas A&M, USA; 2. Texas A&M University, USA; 3. University of Sydeny, Australia

Room temperature cyclic compressive testing of high purity fine (FG) and coarse (CG) grained Ti_2AlC were carried out in combination with Resonant Ultrasound Spectroscopy (RUS) tests and post mortem Electron-backscatter Diffraction (EBSD). The results show that the room temperature mechanical response of Ti_2AlC can be divided in four stress regions with distinct underlying mechanisms: (a) Region I (FG: 0 to ≈ 175 MPa; CG: 0 to ≈ 100 MPa) characterized by a linear elastic behavior; (b) Region II (FG: from ≈ 175 to ≈ 350 MPa; CG from ≈100 to ≈ 200 MPa) in which stress strain hysteric behavior due to reversible dislocation flow in the soft grains; (c) Region III (FG: from ≈ 350 to ≈ 1100 MPa; CG from ≈200 to ≈650 MPa) accumulation of dislocation walls (DWs) results in cyclic hardening and contribute to larger hysteretic loops and thus a larger energy dissipation per loading cycle than in Region II; (d) Region IV (FG: from ≈ 1100 MPa to failure, CG from ≈ 600 MPa to failure) characterized by the occurrence of microcracking that, in addition to the other aforementioned deformation mechanisms, contributes to the energy dissipated in each loading cycle. Effect of grains sizes on all transitions stresses is discussed in more detils in this paper.

2:40 PM

(ICACC-S12-037-2016) The stability of V_2AlC with Al in the 800 to 1000 °C temperature range and the *in situ* synthesis of V_2AlC/Al composites

M. T. Agne*[1]; M. Radovic[2]; M. Barsoum[1]; 1. Drexel University, USA; 2. Texas A&M University, USA

The unique properties of the MAX phases make them a desirable reinforcement material in metal matrix composites. The promising results of MAX reinforced Mg matrix composites have spurred interest in developing Al-MAX composites with comparable or better properties. Herein, two-phase Al-V_2AlC composites were synthesized from elemental powders. The nominal compositions were chosen so that *in situ* reaction would produce a 75/25 vol. % Al/V_2AlC and a 50/50 vol. % Al/V_2AlC composites. The powders were heated to 1000 °C and reacted for 0.5, 2.5 or 10 h under flowing Ar. Water quenched samples produced two-phase Al-V_2AlC composites, but furnace cooled samples did not. X-ray diffraction, scanning electron microscopy and differential scanning calorimetry were used to investigate the stability of V_2AlC with Al in the 800 to 1000 °C range. The Al-V-C phase diagram was defined in the Al-rich corner; at 800 °C, the Al and V_2AlC phases were found to be in equilibrium with both Al_3V and Al_4C_3, but not with each other. This study is a requisite step for the development of Al-V_2AlC composites and advanced composites in the Al-V-C system.

Novel Processing Methods II

Room: Tomoka B

Session Chair: Konstantina Lambrinou, SCK-CEN

3:20 PM

(ICACC-S12-038-2016) Densification and Phase Evolution of SHS Derived Ti_2AlN Active Precurssor Powders During Hot Pressing Processes

L. Chlubny*[1]; J. Lis[1]; C. Kapusta[1]; K. Chabior[1]; P. Chachlowska[1]; K. Zielenska[1]; 1. AGH University of Science and Technology, Poland

Ti_2AlN belongs to the interesting group of ternary nanolaminate materials called MAX phases. These compounds are characterised by heterodesmic chemical bonding and thanks to this fact they posses unique set of properties situating them between metals and ceramics. One of the best methods of synthesizing fine active precursors powders of these materials is Self-propagating High-temperature Synthesis (SHS). This method utilizes exothermal effect of the chemical reaction in adiabatic conditions and allows obtaining many compounds such as nitrides, carbides, composites, intermetallics, etc. at low energy consumption and with high efficiency and in relatively short time. In this paper authors would like to present results of studies on densification and phase evolution phenomenon during hot pressing of various SHS derived Ti_2AlN active precursor powders. Powders were synthesized by SHS method with local ignition system in filtration combustion regime using different nitrogen pressure and various chemical reactions. The selected powders were hot-pressed at temperatures range from 1250 to 1400°C. The phase evolution and apparent densities of obtained samples were examined in order to establish the optimal conditions for manufacturing of near single phase Ti_2AlN material.

3:40 PM

(ICACC-S12-039-2016) MAX phases thin films synthesis by thermal annealing of multi layers deposition at RT

D. Magne*[1]; V. Mauchamp[1]; P. Guerin[1]; T. Cabioch[1]; 1. Institut PPRIME, France

MAX phases thin film synthesis is generally achieved by direct high temperature deposition, mainly by magnetron sputtering. One of the main problems with this approach is the high temperature needed, for example 800°C for Ti_2AlC. In this context, an alternative approach, which consists in room temperature (RT) thin film deposition followed by an annealing under vacuum, could be of interest since it reduces the synthesis cost and can be appropriate for industrial applications. In the present work, the synthesis of various MAX phases (Ti_2AlC, Ti_2AlN and V_2AlC) was achieved on Al_2O_3 (0001) by using such a thermal annealing technique. Several couples of bilayers systems were annealed: (MX/MA); (2M/AX) and $(M+A_{(x)})/(A_{(1-x)}X)$, the last system giving the most promising results for the synthesis of single phased thin films. The mechanisms involved in the formation of the MAX phase during thermal annealing will be discussed on the basis of X-Ray diffraction experiments and cross-sectional Transmission Electron Microscopy observations after RT deposition and for various annealing temperatures (up to 750°C). Finally, the possibility to achieve the synthesis of epitaxial MAX phases thin films by using such a thermal annealing technique will be discussed.

4:00 PM

(ICACC-S12-040-2016) Ceramics at high temperature modelled through elastoplasticity

D. Bigoni*[1]; F. Dal Corso[1]; M. Penasa[1]; S. Gregoire[2]; S. Romero Baivier[2]; 1. University of Trento, Italy; 2. Vesuvius Group S.A., Belgium

Although ceramics are usually considered brittle materials characterized by only small traces of inelastic deformations at failure, their mechanical behaviour can be strongly affected by inelasticity under specific working conditions. For instance, this is the case of the liquid steel technology where a refractory material is exposed to a high temperature environment so that non-negligible inelastic deformations are developed. A thermoelastoplastic constitutive model, consistent with thermodynamics principles, is proposed to predict the mechanical response of ceramics subject to high-temperature conditions. This model is calibrated on a specifically designed experimental protocol revealing the yield and failure conditions at varying the temperature. Through implementation of the model in external subroutine to commercial finite element codes, numerical simulations are performed to optimize the design of ceramic structural elements to be employed in the liquid steel industry

S13: Advanced Materials for Sustainable Nuclear Fission and Fusion Energy

Accident Tolerant Fuels IV

Room: St. John

Session Chairs: Christina Back; Anne Campbell, Oak Ridge National Laboratory

1:30 PM

(ICACC-S13-034-2016) Development of Caulked Joint between Zircaloy and SiC/SiC Composite Tubes By Using Diode Laser (Invited)

H. Serizawa*[1]; Y. Asakura[2]; H. Motoki[3]; J. Park[2]; H. Kishimoto[4]; A. Kohyama[2]; 1. Osaka University, Japan; 2. OASIS, Muroran Institute of Technology, Japan; 3. School of Engineering, Osaka University, Japan; 4. College of Design and Manufacturing Technology, Muroran Institute of Technology, Japan

As for the fuel cladding in the light-water reactor, silicon carbide fiber reinforced silicon carbide composite (SiC/SiC composite) is one of the promising candidates as a replacement of Zircaloy due to many superiorities, where it is necessary to develop the end-cap seal of SiC/SiC composite cladding. In this research, as one possible design, the applicability of diode laser irradiation for joining between SiC/SiC composite and Zircaloy tubes was examined based on the caulking method. As the method for fitting two tubes, a screw cutting was conducted for the inner face of Zircaloy tube and the outer surface of SiC/SiC composite according to our previous study. The diode laser beam irradiation was circumferentially applied to the outer surface of Zircaloy tube. In addition, in order to improve the weldability of SiC/SiC composite and Zircaloy, the nano-powder of titanium was inserted into a gap between SiC/SiC composite and Zircaloy. Although only the surface of Zircaloy tube was melted by the diode laser irradiation, all proportional solid solution of zirconium and titanium was produced at the inner face of Zircaloy tube and then SiC/SiC composite and Zircaloy was partially well joined. The microstructural observations will be discussed in order to examine an airtightness of this joint.

2:00 PM

(ICACC-S13-035-2016) Fabrication and Hydrothermal Corrosion of NITE-SiC with Various Sintering Additives

K. Terrani*[1]; Y. Katoh[1]; C. Parish[1]; Y. Kim[2]; 1. Oak Ridge National Laboratory, USA; 2. GE, USA

Among the various additives employed to reduce the sintering temperature of SiC, the oxides involve a mixture of alumina and rare earth oxides. Alumina effectively reduces the sintering temperature by forming a eutectic with the rare earth oxides to facilitate liquid-phase sintering of SiC. However, its presence can prove detrimental to the material under certain applications such as hydrothermal environments where it can be selectively leached from the grain boundaries. This exposes the surface of SiC grains to corrosion by high-temperature water and leaves a porous material with reduced mechanical integrity. The viability of alumina-free oxide-based sintering systems or ones with significantly reduced alumina content to produce dense SiC at temperatures below 1900°C has been examined. Also a limited set of hydrothermal corrosion data from these materials with reduced alumina content is discussed.

2:20 PM

(ICACC-S13-037-2016) Hydrothermal corrosion behavior of silicon carbide joints

T. Koyanagi*[1]; K. Terrani[1]; J. Kiggans[1]; Y. Kim[2]; T. Hinoki[3]; Y. Katoh[1]; 1. Oak Ridge National Laboratory, USA; 2. GE Global Research Center, USA; 3. Kyoto University, Japan

Development of environmental resistant silicon carbide (SiC) joints in reactor service conditions is a critical requirement for SiC based accident tolerant fuels and core structures for light water reactor applications. Hydrothermal corrosion is one of the most important phenomena considered under the normal operation. This paper discusses hydrothermal corrosion behavior of 4 types of SiC joints in PWR and BWR relevant chemical conditions. The experiments were conducted in an autoclave system at GE Global Research Center. High-purity CVD SiC bonded specimens were prepared by diffusion bonding with titanium and molybdenum inserts, slurry bonding using Ti-Si-C system, and liquid phase sintering SiC nano-powder. Most of the joints withstood the corrosion tests for 5 weeks. Differential corrosion rates between the SiC substrate and the bonding layers were evaluated from a step-height at the substrate/bonding-layer interface using a 3D display optical microscope. The details of corrosion behavior will be presented based on the step-height measurement and microstructural characterizations. This work was sponsored by the U.S. Department of Energy, Office of Nuclear Energy, for the Fuel Cycle Research & Development program under contact DE-AC05-00OR22725 with Oak Ridge National Laboratories managed by UT-Battelle, LLC

2:40 PM

(ICACC-S13-038-2016) SiC Composite for BWR Channel Applications

K. Yueh*[1]; P. Cantonwine[5]; D. Carpenter[2]; S. Johnson[4]; Y. Katoh[3]; G. Kohse[2]; K. Terrani[3]; 1. Electric Power Research Institute, USA; 2. Massachusetts Institute of Technology, USA; 3. Oak Ridge National Laboratory, USA; 4. Westinghouse Electric Company, USA; 5. Global nuclear fuel, USA

A number of evaluations and tests have been performed as part of a feasibility study to gauge viability of the BWR channel concept. The feasibility study included fragmentation resistance, volumetric swelling differential, neutron induced swelling, economic benefit, thermal shock resistance, mechanical properties, seismic, and corrosion under BWR-like conditions. The results, with the exception of the corrosion test, indicate SiC composite could meet the BWR channel mechanical design requirements. In the current study test materials were exposed to BWR-like oxidizing conditions in the MIT research reactor. Test samples experienced up to 17% mass loss over a period of 2.5 months. The accelerated corrosion has been verified to be caused by the oxidizing BWR-like test condition. SiC is not in the lowest thermodynamic state and thus susceptible to oxidation. Unlike most other materials SiO_2 reaction product does not form a protective layer. A strategy to mitigate the corrosion is to modify the surface by introducing an additive. Initial efforts have been focused on additions of zirconium and titanium in a co-CVD process since both $ZrSiO_4$ and $TiSiO_4$ are insoluble in water. Test coupons coated with ZrSiC were subjected corrosion test in an oxygenated autoclave and preliminary evaluation indicate the formation of a new surface, possibly ZrSiO4. Further examination is needed to verify it's crystallographic structure and if it is protective.

3:20 PM

(ICACC-S13-039-2016) SiC Composite Claddings with Metallic Seal Coatings for Improved LOCA Tolerance

J. S. O'Dell*[1]; L. L. Snead[2]; 1. Plasma Processes, LLC, USA; 2. Nuclear Materials Consulting, USA

The unfortunate events at the Fukushima Daiichi nuclear power plants highlight the need for enhancing the accident tolerance of nuclear fuel. Of particular concern is the potential overheating of standard zirconium alloy claddings in a loss of coolant accident (LOCA). One of the leading, high-risk/high-reward candidates for future claddings is a silicon carbide (SiC) composite. However, the inherent open porosity present in the majority of fibrous based composites and the unavoidable propagation of a fine network of cracks under modest load has raised hermeticity as a fundamental design issue. Some SiC claddings seek to overcome this issue through one or more ceramic coatings, though such coatings are intrinsically brittle; thus, raising the question as to the ability to withhold fission products. While fission product retention is still an

open question, recently published work suggests that a fully-ceramic design has serious issues. Therefore, exploring alternative design solutions is prudent. One such configuration is the hybrid design, which employs a thin ductile coating on the SiC composite. This paper will demonstrate the use of advanced Vacuum Plasma Spray (VPS) processing to produce dense metallic seal coatings on SiC composite claddings. Promising overcoatings of zircaloy have been demonstrated, while other "accident tolerant" coatings such as chromium and steels are also being pursued.

3:40 PM

(ICACC-S13-040-2016) Electrochemical chromium-based environmental barrier coatings for SiC composites in LWR systems

C. Ang*[1]; J. Kiggans[1]; B. Jolly[1]; C. Kemery[3]; J. Thomson[1]; K. Terrani[2]; Y. Katoh[2]; 1. Oak Ridge National Lab, USA; 2. Oak Ridge National Laboratory, USA; 3. NEO Industries, USA

SiC composites are continuing to undergo evaluation with the Advanced Fuels Campaign as an Accident Tolerant Fuel cladding. One feasibility issue is the corrosion response of SiC in all three LWR chemistries, which indicate a need for Environmental Barrier Coatings (EBCs) to prevent recession of SiC cladding before completing fuel burn. Chromium-based (Cr) EBCs are being investigated in order to overcome the challenges of deposition, high cost and surface adhesion. The industry partner for this project is NEO Industries, LLC (Marysville, TN). Three options based on nickel offer an interphase compatibility coating between chromium and SiC. Thus far, industrial-type hypophosphite and laboratory hydrazine-based nickel are respectively the first and second generation compatibility coatings for Cr; a third system based on carbon has overcome all processing hurdles. In nickel compatibility coatings, phosphorous was controlled by citrate content, or can be eliminated via hydrazine-based nickel. At minimum, adhesion requires control of surface oxide growth, phosphorous compounds, an interphase between Ni-SiC and a closed connection during electrolytic deposition. Thermal tests simulating fuel exchange up to 400°C (673K) are discussed. Control of the composition of the interphase between Cr and SiC becomes critical for minimizing coefficient of thermal expansion mismatches and microcracking.

4:00 PM

(ICACC-S13-041-2016) Discussion of potential fuel cladding chemical interactions in LWR designs utilizing SiC/SiC cladding

T. J. Gerczak*[1]; 1. Oak Ridge National Lab, USA

SiC/SiC composite fuel cladding is being considered for application in accident tolerant fuel designs for light water reactor (LWR) applications. Technical knowledge gaps currently exist concerning the expected performance of SiC/SiC composite cladding under LWR operating conditions, namely potential fuel cladding chemical interactions (FCCI). A review of potential issues regarding FCCI will be discussed based on expected fuel behavior under LWR normal operating conditions and accident scenarios. Specifically, a focus on the interaction of noble metal fission products with SiC will be reviewed as well as interactions of other fission products and radionuclides with SiC that are present in the fuel/cladding systems. The discussion on interactions of fission products will leverage lessons learned from the role of SiC as a metallic fission product barrier in TRISO fuel applications. Based on this discussion, the feasibility of SiC/SiC composite cladding in terms of tolerance to FCCI will be addressed.

4:20 PM

(ICACC-S13-042-2016) Design and Manufacturing of SiC Wrapped Zircaloy Hybrid Cladding for Accident Tolerant Fuels

P. Xu*[1]; J. Choi[1]; E. J. Lahoda[1]; K. Sridharan[2]; B. Maier[2]; A. Yacout[3]; M. Pellin[3]; G. Markham[4]; D. E. Wolfe[5]; 1. Westinghouse Electric Company, USA; 2. University of Wisconsin, USA; 3. Argonne National Laboratory, USA; 4. Ceramic Tubular Products, LLC, USA; 5. Pennsylvania State University, USA

SiC is being extensively investigated as the accident tolerant fuel cladding for LWR applications due to its excellent irradiation stability and high temperature strength. Nevertheless, development of SiC cladding has experienced significant technical challenges mainly due to microcracking under tensile loads. Substantial microcracking may lead to an unacceptable loss of hermeticity and fuel leakers. To overcome this challenge, a hybrid concept is being pursued by using thin wall zircaloy cladding as the inner hermetic layer and SiC ceramic composite matrix as the outer accident tolerant layer. To improve the water and chemical resistance of zircaloy cladding during high temperature processing and reactor operations, a corrosion resistant coating is applied to the outer surface of the zircaloy. A preliminary design was performed using finite element models to determine the geometry of the cladding and temperatures of the fuel and the cladding during normal operation and power transients. The outer SiC CMC layer is made by wrapping SiC fibers onto the zircaloy tube using winding machine followed by matrix infiltration using the Atomic Layer Deposition (ALD) technique. Autoclave tests will be performed for the fabricated tubes in 360°C water for extended period of time. In-reactor irradiation testing will be performed for the samples that show promise in the high temperature water tests.

S14: Crystalline Materials for Electrical, Optical and Medical Applications

Optical Material III

Room: Tomoka C

Session Chairs: Gisele Maxwell, Shasta Crystals Inc; James Harrington, Rutgers University

1:30 PM

(ICACC-S14-029-2016) Crystal Growth of Novel Scintillators (Invited)

E. Bourret*[1]; 1. Lawrence Berkeley National Laboratory, USA

There is a strong demand for application-driven novel scintillators, mainly due to the needs for domestic and international security. The pace of discovery of new scintillators has increased dramatically in the last few years after the discovery at LBNL of efficient scintillation in mixed and ternary halides. We will present the crystal growth challenges encountered to grow several new scintillators, halides and oxides. The structure and growth habit will be presented. The properties and engineering of the new scintillator crystals will be discussed as they related to applications.

2:00 PM

(ICACC-S14-030-2016) Halide Elpasolite Structure Crystal Materials (Invited)

J. M. Frank*[1]; P. Menge[1]; V. Ouspenski[2]; J. Lejay[2]; 1. Saint-Gobain Crystals, USA; 2. Saint-Gobain Recherche, France

Ce3+ activated elpasolite structured crystals such as Cs_2LiYCl_6:Ce (CLYC) and $Cs_2LiLaBr_6$:Ce (CLLB) have been shown to be excellent scintillators. These materials are of interest to the radiation detection community due to the fact that they have excellent energy resolution for gamma radiation, and as Li containing materials, also can be used for neutron detection. While these elpasolite materials are excellent scintillators, they are challenging to process as they are both hygroscopic and melt incongruently. This presents a great challenge to

the crystal growth community. Efforts to commercialize these materials requires high yield crystal growth greater than 1 metric ton per year, necessitating several problems to be solved. Advancements and results from working on these problems for CLLB at sizes up to 2.5" in diameter will be presented.

2:30 PM

(ICACC-S14-031-2016) Sintering and Optical Performance of Eu:$BaCl_2$ Transparent Ceramic Scintillators

T. Shoulders*[2]; C. Piriou[3]; E. Bourret[1]; G. Bizarri[1]; R. Gaume[2]; 1. Lawrence Berkeley National Laboratory, USA; 2. University of Central Florida, USA; 3. University of Limoges, France

The rare earth doped alkaline earth halides are an interesting class of materials, which have demonstrated high energy resolution as gamma scintillators in the single crystalline form. This study focuses on a low-cost, low-temperature (< 0.5 T_m), and high-pressure (200 – 400 MPa) sintering method to produce transparent ceramic $BaCl_2$. The challenges in sintering to high visible transparency are discussed within the framework of the high sensitivity of Eu:$BaCl_2$ to the ambient atmosphere as well as the volatility of chlorides at high sintering temperatures. Furthermore, the presence of a plastic deformation sintering mechanism is shown to impart a strong dependence of the final density on the average size and size distribution of powders. Scanning electron microscopy and x-ray diffraction measurements are used to quantify the scattering centers, pores and mis-aligned grain boundaries (texture) respectively. It has been found that large particle sizes, above 100 μm, favor the formation of ceramics having the lowest population of pores in the hundreds of nanometer size range. Porosity, along with the texture induced by the high-pressure sintering method, is related to the optical transmission, measured by ultraviolet-visible spectrophotometry.

3:10 PM

(ICACC-S14-032-2016) Morphology control of ceramic materials by novel soft chemical synthesis methods (Invited)

K. Toda*[1]; 1. Niigat University, Japan

Progress of the solid state reaction required to fulfill two conditions; Thermodynamics (Is a reaction favoured?) and Kinetics (How fast is a reaction?). If the reaction speed based on defect thermodynamics is extremely slow, we cannot observe final products at room temperature. Many researchers claimed that the ionic-diffusion in ionic crystal is very slow at room temperature. Therefore, the ceramic materials are generally synthesized at high temperature. Since final product layer spatially separates the raw materials at the interface, mass transport of raw materials occurs through the product layer. Observed data of ionic-diffusion in the course of the solid state reactions are not true diffusion rate. On the other hand, we recently proposed the novel low-temperature solid state synthesis methods, such as water assisted room temperature solid state reaction (WASSR) method and solid hydratethermal (hydrothermal) reaction (SHR) method, to synthesize the ceramic materials in a single phase form at low temperature. In this study, we present the practicability of our original novel solid state reaction methods on an industrial application in the ceramic oxide materials synthesis processing.

3:40 PM

(ICACC-S14-033-2016) Discovery of New Phosphor Hosts via Unit Replacement Strategies (Invited)

Z. Xia*[1]; 1. University of Science and Technology Beijing, China

Our recent work concentrates on the discovery of new phosphor materials based on the iso-structural solid-solution evolution and host modification. We have proposed the Unit Replacement strategy in order to fabricate the new phosphor hosts, which is typically represented by the double substitution of [Mg^{2+}–Si^{4+}] for [Al^{3+}-Al^{3+}] in Al-based garnet ($Y_3Al_5O_{12}$), and we propose that the [Mg^{2+}–Si^{4+}] or [Al^{3+}-Al^{3+}] couple as the "Unit". Other example on the unit replacement include the design of Sr_3AlO_5 phase from Sr_3SiO_5 via the double substitution of [Al^{3+}–F^-] for [Si^{4+}-O^{2-}], also including our similar design of $Ca_2Al_3O_6F$ phase from $Ca_2Al_2SiO_7$. We also design the $La_5Si_3O_{12}N$ phase from $La_5Si_2BO_{13}$ via the [B^{3+}–O^{2-}] by the [Si^{4+}–N^{3-}] substitution,[1] and the $NaScSi_2O_6$-based phosphor from $CaMgSi_2O_6$-based phosphor from the unit replacement of [Na^+–Sc^{3+}] for [Ca^{2+}-Mg^{2+}] unit.[2] Our recent study on the M_2SiO_4-based silicate phosphor also demonstrated the importance of such a general strategy for the fabrication of th new phosphor hosts. Accordingly, we have also made a smart design via the crystallographci sites engineering in order to change the crystal field enviroment and bulid up the energy transfer process, thus the luminesence tuning behavior can be found in my systems. Some typical examples and representative work are included in my talk.

4:10 PM

(ICACC-S14-034-2016) Fabrication of transparent and luminescent SiAlON bulk ceramics (Invited)

J. Tatami*[1]; T. Takahashi[2]; 1. Yokohama National University, Japan; 2. Kanagawa Academy of Science and Technology, Japan

One of the typical systems of the current white LEDs is composed of blue or UV LEDs and ceramic phosphor particles which were dispersed in a resin. One of the problems to be solved in high power application is the thermal degradation of the resin because the operation temperature increases as applied power. In this study, we prepared the transparent and luminescent SiAlON ceramics by controlling powder processing. As a result, the developed Ce doped Y-α SiAlON ceramics showed over 60% transparency at 600 nm in wavelength and blue or blue-green emission excited by UV light. The maximum excitation and emission were obtained at 370 and 480 nm, respectively. Transparent Eu doped Ca-α SiAlON ceramics was also developed, of which emission was yellow color by blue light excitation. The wavelength of excitation and emission and quantum efficiency of the Ca-α SiAlON ceramics is almost the same as that of the powders reported in the previous study. Eu^{2+}doped $CaAlSiN_3$ ceramics developed by spark plasma sintering technique showed high relative density. SEM observation showed that the grain size was less than 1 μm and there was no pore. The emission and excitation peaks of photoluminescence were about 471 and 633 nm, respectively, which is almost the same as the previous study. Furthermore, luminescence of red color was confirmed by radiation of the UV or blue light behind the sample.

4:40 PM

(ICACC-S14-035-2016) Lanthanide-doped $LaSi_3N_5$ based phosphors: Ab initio study of electronic structures, band gaps and energy level locations

Z. Lences*[1]; I. Ibrahim[1]; P. Sajgalik[1]; 1. Institute of Inorganoc Chemistry, Slovak Academy of Sciences, Slovakia

Lanthanide (Ln) doped $LaSi_3N_5$ based phosphors were prepared experimentally and their electronic structure and band gaps were calculated using the screened Coulomb hybrid HSE06 functional. The synthesized $LaSi_3N_5$:Ce phosphor emits violet-blue light, $LaSi_3N_5$:Eu – green-yellow, $LaSi_3N_5$:Sm red light. The calculations showed that with increasing atomic number the band gap of Ln^{3+}-doped $LaSi_3N_5$ smoothly decreases from 4.6 eV (Ce) to 0.5 eV (Eu). The band gap of Ln^{2+}-doped $LaSi_3N_5$ increases from ~0.80 eV (Ce, Pr) to 0.95 eV (Nd, Pm), 1.43 eV (Sm), and to 3.28 eV (Eu). The electronic transition in Ln^{2+}-doped LaSi3N5 has 4f -> 5d character. Because the Ln dopants are experimentally added in a form of oxides, also the influence of N/O substitution on the band gap of LaSi3N5 was calculated. The results showed that with increasing oxygen content in the cell of $LaSi_3N_5$ the band gaps decreased by 0.2 – 0.6 eV. The energy level locations were constructed from the ab initio calculated electronic structures and compared with the empirical energy level diagram. There is a good agreement between calculated and experimental data and the method can be used for phosphor material design.

FS1: Geopolymers, Chemically Bonded Ceramics, Eco-friendly and Sustainable Materials

Synthesis, Processing and Microstructure

Room: Coquina Salon E

Session Chair: Waltraud Kriven, University of Illinois at Urbana-Champaign

1:30 PM

(ICACC-FS1-001-2016) Rheological properties of zeolite-seeded geopolymers (Invited)

M. Pernechele*[1]; T. Troczynski[1]; M. Pawlik[1]; 1. University of British Columbia, Canada

The effects of zeolite seeds and other inorganic seeds on the early stages of metakaolin-based geopolymers formation are studied in terms of rheological properties of the pastes. The rheology of geopolymers has often been neglected, though the understanding of the flow behavior is essential for further advancement of geopolymer technologies and it can give insights on the geopolymerization reactions mechanisms. The rheological properties of the fresh pastes were characterized using a HAAKE Viscotester 550 rotational viscometer equipped with a temperature control vessel. The values of viscosity over time provide valuable information on the kinetics of seeds-assisted geopolymerization. The flow curves of the geopolymeric pastes were analysed using the Herschel-Bulkley model, allowing the determination of yield stress, consistency and shear dependence of the system. The variations over time of the viscoelastic parameters G′, G″ and tanδ were studied using oscillation frequency sweep tests at different temperatures. The activation energies of the geopolymerization reactions were obtained from the maximum values of the loss tangent, tanδ, as a function of temperature. The effects of the inorganic seeds were evaluated both in terms of variation in viscosity over time and in terms of the activation energy of the reaction.

2:00 PM

(ICACC-FS1-002-2016) Geopolymer based from brick clays: effect of the alkali cations on the geopolymerization reaction and on the alkaline earth releasing (Invited)

J. Peyne*[1]; S. Rossignol[1]; E. Joussein[2]; J. Gautron[3]; 1. Laboratoire SPCTS, France; 2. GRESE, France; 3. Bouyer Leroux, France

From the late 1970s, the alkali activated aluminosilicate binders, also named geopolymers have demonstrated a great interest for several applications due to their outstanding properties, such as mechanical, chemical and thermal properties. Recent researches have investigated the use of low quality clay, by-products sourced from various industries instead of a pure metakaolin, which is one the most aluminosilicate materials used for geopolymer. The aim of this work is to produce geopolymers from clays which are used initially in the brick production. This work is based in the utilization of several Na-K alkaline solutions in the geopolymer mixtures based from raw and calcined brick clay. First, physical and chemical characterizations of the clays were studied by particle size distribution, wettability, and specific surface area measurements. Moreover, the mineralogy was obtained by X rays diffraction and FTIR spectroscopy. From these data, it was possible to establish a feasibility parameter to evaluate the clay reactivity. Then, several geopolymer (Na- and K-based) mixtures were studied by FTIR monitoring and mechanical tests. The results evidence the effect of alkali cations on the geopolymerization reaction as well as the alkaline earth releasing from the clay.

2:30 PM

(ICACC-FS1-003-2016) Metakaolin-based geopolymer cements from commercial sodium waterglass and sodium waterglass from rice husk ash: A comparative study

H. Tchakoute Kouamo*[1]; C. H. Rüscher[2]; 1. Unuiversité of Yaoundé I/ Leibniz University, Hannover, Germany; 2. Leibniz Universität Hannover, Germany

Three different sodium waterglass (NWG) such as commercial NWG (S1), NWG from pure rice husk ash (S2) and NWG from raw rice husk ash (S3) were applied for producing geopolymer cements using metakaolin (MK) as aluminosilicate source. Geopolymer cements (Geo1, Geo2 and Geo3) were prepare using each NWG with the molar ratios SiO_2/Na_2O and H_2O/Na_2O kept constant at 1.5 and 12 respectively and the mass ratio NWG/MK = 0.83. It could be observed that the water absorption of Geo1, Geo2 and Geo3 after 28 days at room temperature are 17%, 19% and 23.2% and the mass loss using TG measurement are 15.80%, 14.70% and 12.36% respectively. Their compressive strength at 20 days (37.5/34.3/29.6 MPa) and 28 days (43.3/40.3/33.2 MPa) staying at room temperature increases with increasing the ageing and decreases in the course Geo1/Geo2/Geo3. It is discussed that the presence of phosphate (3.81%) known as corrosion inhibitors in raw rice husk ash hinders the dissolution of SiO_2. This entails the formation of condensed silica in S3 and induces the higher unreacted MK content in Geo3, promotes more pores and voids suggesting thus higher water absorption, lower mass loss and compressive strength compare to Geo1 and Geo2.

3:20 PM

(ICACC-FS1-005-2016) Influence of Mix Design Parameters on Geopolymer Mechanical Properties and Microstructure

M. Lahoti*[1]; E. Yang[1]; K. Tan[1]; 1. Nanyang Technological University, Singapore

This paper reports on the influence of four mix design parameters (Si/Al, w/solids, Al/Na and H_2O/Na_2O) on mechanical properties and microstructure of metakaolin geopolymers. A series of test specimens measuring 50mm cubes were prepared by adding different concentration and amounts of sodium silicate solution to metakaolin. From the compressive strengths results of the hardened geopolymers, on surface Si/Al appears most significant but actually the contributions of w/solids and Al/Na cannot be segregated from that of Si/Al. Also, H_2O/Na_2O doesn't seem to have a significant impact on the compressive strengths. W/solids ratio has been found to influence the density, porosity and microstructure of the geopolymers. However, it has been suggested that it's not the chief factor affecting these properties. Observations under SEM suggest that Si/Al most significantly influences the microstructure but the other three factors indeed have certain minor influence. In order to quantify the impact of mix design parameters on compressive strengths, a statistical analysis was performed on large set of experimental data as well as data collected from previous works. The plots suggest that Si/Al is the most critical parameter. In a nutshell, all four mix design parameters have a certain influence on the microstructure and mechanical properties of geopolymers though Si/Al appears to be most significant.

Mechanical Properties

Room: Coquina Salon E
Session Chair: Yiannis Pontikes, KULeuven

3:40 PM

(ICACC-FS1-006-2016) Thermal performance of Metakaolin-Based Geopolymers: Volume Stability and Residual Mechanical Properties

M. Lahoti*[1]; E. Yang[1]; K. Tan[1]; 1. Nanyang Technological University, Singapore

For any structure to perform well under fire scenario, the structural material should exhibit thermal stability at micro, meso and macro levels. Excellent thermal stability for geopolymers has been reported at micro level. But to apply this novel material for structures, a step forward is to better understand performance at meso-level by studying the volume stability and residual mechanical properties. Thus, a series of 50mm cube geopolymer specimens with different Si/Al ratios were prepared and exposed to different heating profiles. Volumetric shrinkage and crack patterns (which are an indication of volume stability) and residual strengths and densities were measured and performance was compared. Volume instability at meso-level was linked to the changes taking place at micro-level through SEM images. The performance of Si/Al 1.75 geopolymer appeared most promising. Performance of geopolymers was also compared with OPC paste. A vital observation that helps to appreciate the merit of geopolymers for high temperature applications is the crumbling of OPC paste at 900°C while geopolymers still retaining significant strengths even though suffering shrinkage and cracks. This point towards potential of geopolymers to perform soundly as a fire resistant material and also the need to impart sufficient volume stability and mechanical properties when subject to high temperatures.

4:00 PM

(ICACC-FS1-007-2016) IR-spectroscopic investigation of geopolymer-binder and CSH-phase stability on heating temperature in post-fired cements (Invited)

C. Rüscher*[1]; K. Unterderweide[2]; E. Rigo[2]; 1. Leibniz University Hannover, Germany; 2. Materialpruefanstalt fuer das Bauwesen, Germany

The mechanical (compressive) strength of concretes based on geopolymer and CSH-type binders depend on heating temperatures. For concretes using geopolymer binder the strength could even increase on heating between 300 and 800°C. For concretes based on ordinary Portland cements the strength decrease with increasing temperature to 800°C to less than 30% of its 300°C value. The origin of this decrease in strength could be related to a destruction of the cement related CSH-phases formed during hardening of the concrete. In order to investigate this possibility, we investigated in a first step the temperature behavior of some hydrated Portland cements (CEM I 42.5 R) using infrared absorption spectroscopy (ATR- and KBr-technique). It could be observed that the position peak maximum (PM) of the asymmetric Si-O-stretching mode is a function of the temperature. In the ATR-spectra the effective PM decreases linearly with increasing temperature between 300 and 800°C. This correlation is independent from the time the sample was exposed to temperature. The decrease of the PM is explained by a destruction of Si-O-Si-chains of the CSH phases into monosilicate ß-C2S. We discuss that an effective temperature profiling of post fired concretes could be achieved using a micro-ATR technique. Some new results on post heated geopolymer cements will be discussed, too.

FS4: Additive Manufacturing and 3D Printing Technologies

Ink Jet Printing

Room: Coquina Salon C
Session Chairs: Soshu Kirihara, Osaka University; Elizabeth Kupp, The Pennsylvania State University

1:30 PM

(ICACC-FS4-001-2016) Enabling Direct Digital Manufacturing using 3D Printing for next generation complex heterogeneous devices (Invited)

K. Church*[1]; 1. nScrypt, USA

3D Printing has been dubbed the future of manufacturing but for this to be true several pieces of the manufacturing puzzle must fall into place. The performance of 3D Printed devices must match or exceed existing devices. The throughput must significantly increase for 3D Printing to compete in mainstream manufacturing. Devices that are unique in 3D shape but made of just one material will be limited in use. Devices of value are complex, uniquely shaped and comprised a many materials with specific yet diverse material properties. Transitioning from plastics to metals or metals to ceramics is challenging, but 3D printing affords new possibilities to mix materials in a gradient manner to allow for a more consistent transition. This talk will demonstrate true heterogeneous printing of plastics, metals and composites and provide unique shapes with digital control and electrical function within one structure or device. The digital approach allows the user to print and place specific materials and components without touching or the need for post assembly. The shape may add value to the device, but the rough surface may degrade the performance such as RF or optical devices and therefore the same tool that prints can also pick and place and mill and polish; a factory in a tool. Throughput can be demonstrated using parallel, factory line printing; true Digital Manufacturing.

2:00 PM

(ICACC-FS4-002-2016) Additive Manufacturing with an Inorganic Binder

P. Colombo*[1]; G. Franchin[1]; H. Elsayed[1]; A. Conte[1]; P. Scanferla[1]; A. De Marzi[1]; A. Beretta[2]; A. Italiano[2]; 1. University of Padova, Italy; 2. Desamanera srl, Italy

We used, for the first time, a mixture based on an inorganic binder for direct and indirect 3D printing of components for different applications. The printed components can then be used at room temperature or at high temperature, as they can easily withstand heating up to 1200°C. For direct ink writing (DIW), mixtures of suitable rheology were developed, enabling the fabrication of highly porous scaffolds with large overhangs. For indirect powder-based 3D-printing (P-3DP), a binder mixture of suitable reactivity and rheology was sprayed on a bed of ceramic powders, resulting in large scale parts. Details on the fabrication procedures, as well as the characterization of the printed components will be presented.

2:20 PM

(ICACC-FS4-003-2016) Additive Manufacturing of Ceramics Using Polymer Jetting

E. R. Kupp*[1]; G. L. Messing[1]; 1. The Pennsylvania State University, USA

Additive manufacturing of metal parts using a powder bed and inkjet binder jetting has been accomplished. The source materials utilized in this printing process are dense metal beads with diameters of ≤ 100 μm which have excellent flow properties and pack with a relative density of ≈ 55%. A ceramic analog to these dense beads is difficult to produce, and would not be sinterable due to low surface/interfacial energy, while submicron ceramic powders do not have the necessary flow properties to achieve acceptable green densities using additive manufacturing processes. We have developed a process to

utilize powder bed printing technology with granulated (i.e., spray dried) submicron alumina powder. The porous granules of this material have the requisite size and flow properties to be utilized for powder bed printing, but they present unique challenges that must be overcome in order to successfully build parts using this method. For example, the granule and printing binders must be compatible, but not necessarily the same. Also, capillary forces draw binder jetted during additive manufacturing into the granules and reduce the amount available for intergranular binding. Changes in printing parameters are required to produce robust, high green density parts using porous granules in place of dense beads in powder bed additive manufacturing processed.

2:40 PM

(ICACC-FS4-004-2016) Fabrication of titania nano layer by inexpensive inkjet printing via sol-gel route

C. Gadea*[1]; D. Marani[1]; S. Ramousse[1]; V. Esposito[1]; 1. Technical University of Denmark, Denmark

Inkjet printing of inorganic materials has in the past years been spreading in several key technologies, especially using the colloidal suspension-based inks. However, particle size distribution of these suspensions limits the possibility of using such type of processing technique. A way to overcome this challenge is to use particle-free solutions such as sol-gel inks, in which particles are formed by hydrolysis/condensation of a metallic precursor with water during the heat treatment. The challenge using this type of reactive inks is to inhibit the hydrolysis/condensation between the solvent (water) and the precursor in order to process the ink, while keeping the printability of the ink stable over time. In this study, a TiO_2 nano layer has been successfully deposited by inexpensive inkjet printing of stable aqueous titanium based sol-gel on a functional ITO-coated glass substrate. Formulation optimization and long term stability of the sol have been studied, and crystallinity and microstructure of the film have been characterized.

Fused Deposition Modeling

Room: Coquina Salon C
Session Chair: Michael Halbig, NASA Glenn Research Center

3:20 PM

(ICACC-FS4-005-2016) Additive Manufacturing and Characterization of Polylactic Acid (PLA) Composites Containing Metallic Reinforcements

L. Kuentz*[1]; A. Salem[2]; M. Singh[3]; M. C. Halbig[4]; J. Salem[4]; 1. Lake Ridge Academy, USA; 2. Hawken School, USA; 3. Ohio Aerospace Institute, USA; 4. NASA Glenn Research Center, USA

Additive manufacturing of polymeric systems using 3D printing has become quite popular recently due to rapid growth and availability of low cost and open source 3D printers. Two widely used 3D printing filaments are based on polylactic acid (PLA) and acrylonitrile butadiene styrene (ABS) systems. PLA is much more environmentally friendly since it is made from renewable resources. Recently, polylactic acid-based metal powder containing composite filaments have emerged which could be utilized for multifunctional applications. In order to utilize functionalities of composite filaments, printing behavior and properties of 3-D printed composites need to be characterized and compared with the pure PLA materials. In this study, pure PLA and composite specimens with different metallic reinforcements (Copper, Bronze, Tungsten, Iron, etc) were 3D printed at various layer heights and resulting microstructures and properties were characterized. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) behavior the filaments were studied. The microscopy results show an increase in porosity between 3-D printed regular PLA and the metal composite PLA samples, which could produce weaker mechanical properties in the metal composite materials. Tensile strength and fracture toughness behavior of specimens as a function of print layer height will be presented.

3:40 PM

(ICACC-FS4-006-2016) Additive Manufacturing of Light Weight, High Strength Polymer Composite Materials and Structures

A. Salem*[1]; B. Hausmann[2]; L. Kuentz[3]; M. Singh[4]; M. C. Halbig[5]; B. A. Lerch[5]; 1. Hawken School, USA; 2. Case Western Reserve University, USA; 3. Lake Ridge Academy, USA; 4. Ohio Aerospace Institute, USA; 5. NASA Glenn Research Center, USA

Additive manufacturing (AM) has rapidly become a salient feature in today's society. It allows excellent control of material placement over length scale such that complex geometry, function, and composition can be widely tailored. This unique control over geometry allows for the creation of high-performance structural materials suitable for high-strength, lightweight applications. In recent years, countless parts have been printed across the globe, but only a small fraction of these parts have been tested and characterized. As a result, very little is known about the materials including parameters such as mechanical properties, microstructure, and print effects. Recently, there has been a rapid growth in the development of filaments used for AM technologies. Materials such as carbon nanotube, carbon fiber, and metals have been added to the polymer based filaments in order to better suit 3-D printing for industries such as the aerospace, medical, and automotive. This research focuses on the effects of second phase materials within Acrylonitrile Butadiene Styrene (ABS) filaments. In an attempt to further characterize these filaments and 3-D printed materials, thermogravimetric analysis, differential scanning calorimetry, microstructural analysis, fracture toughness tests, tensile tests, as well as tribological tests have been performed.

4:00 PM

(ICACC-FS4-007-2016) Additive Manufacturing of Optically Transparent Glass

G. Franchin*[1]; J. Klein[2]; M. Stern[2]; M. Kayser[2]; C. Inamura[2]; S. Dave[2]; J. Weaver[3]; P. Houk[2]; P. Colombo[1]; M. C. Yang[2]; N. Oxman[2]; 1. University of Padova, Italy; 2. Massachusetts Institute of Technology, USA; 3. Harvard University, USA

We present a fully functional extrusion-based printer for optically transparent glass. The platform is comprised of modular elements, able to operate at the high temperatures required to process glass from a molten state to an annealed product. Automated extrusion through a 10 mm diameter nozzle with a build rate of approximately 460 mm^3/s enabled the creation of three dimensional (3D) parts as described by Computer Aided Design (CAD) models with a build volume of 250x250x300 mm^3. Processing parameters such as temperature and glass viscosity, layer height and feed rate, were calibrated to 3D-print components with controlled shapes and properties. Geometric constraints, coiling patterns and the integration of color were explored, contributing to a new design and manufacturing space. Characterization of printed components was performed in order to determine their morphological, mechanical and optical properties. Printed parts demonstrated strong adhesion between layers and good optical clarity; complex caustic patterns were created when objects were illuminated. Fabricated parts were highly repeatable and resembled the visual and mechanical properties of conventionally produced glass objects. This research lies at the intersection of design, engineering, science and art. 3D printed objects can be extended beyond art to implementations across scales and functional domains such as product design and architectural design.

4:20 PM

(ICACC-FS4-008-2016) Rapid Manufacturing of Ceramic Parts

W. Xiufeng*[1]; W. Jia[1]; Y. Chenglong[1]; F. Xiaopu[1]; J. Hongtao[1]; Y. Yang[1]; L. Hui[1]; 1. Shaanxi University of Science and Technology, China

Common ceramic rapid manufacturing technology are Laminated Object Manufacturing, Stereo Lithography, Selective Laser Curing, Three-Dimensional Printing et al. In order to break through the traditional ceramic parts manufacturing technology and promote ceramic pats rapid manufacturing technology, a new ceramic parts rapid manufacturing process is designed to build complex ceramic parts and fine ceramic parts. A special fiber material is used to be the support material for ceramic parts manufacturing. By this way, ceramic parts with arbitrary shapes can be made fast and subtly. The nozzle of the printer will extrude ceramic slurry to pile up each layer of the three dimensional model formed by the computer. After printing each layer, the special material will be placed on the former layer. And the special fiber supporting material will be removed in the furnace. This special material has a unique structure which can help the layers bond together and enhance the performance of parts. This rapid manufacturing method induce a new method of the ceramic parts by three dimensional printing technology and solved the supporting material problem. It provides a new research and application direction for a wide range ceramic materials rapid manufacturing technology.

Posters

Poster Session B

Room: Ocean Center Arena

(ICACC-EMERG-P001-2016) X-ray Photoelectron Spectroscopy Analysis of Select Two-dimensional Transition Metal Carbides (MXenes)

J. Halim*[1]; K. M. Cook[3]; M. Naguib[4]; P. Eklund[2]; Y. Gogotsi[1]; J. Rosen[2]; M. Barsoum[1]; 1. Drexel University, USA; 2. Linkoping University, Sweden; 3. Naval Air Systems Command, USA; 4. Oak Ridge National Lab, USA

Among 2D materials, MXenes are the newest and fastest growing. MXenes are two-dimensional transition metal carbides and carbonitrides with a general formula of $M_{n+1}X_nT_x$, where M is the transition metal, X is C and/or O, and T stands for O, OH and/or F surface terminations. Given the importance of surface chemistry on the properties of MXenes, the surface chemistry of five different MXenes, $Ti_3C_2T_x$, Ti_2CT_x, Ti_3CNT_x, Nb_2CT_x, and $Nb_4C_3T_x$, were studied by X-ray Photoemission Spectroscopy (XPS). We were able to identify and quantify the surface groups present before, and after Ar^+ sputtering for freshly prepared and aged samples (1 month to 12 months old). In all the cases, the presence of the three surface terminations species was confirmed. The formulas for freshly prepared $Ti_3C_2T_x$ before and after sputtering were determined to be $Ti_3C_2O_{0.3}(OH)_{0.3}F_{1.2}$ and $Ti_3C_{1.8}O_{0.6}(OH)_{0.4}F_{0.8}$ respectively. The overall formulas for the other aged MXenes, measured after sputtering, were determined to be $Ti_3C_{1.8}O_{0.6}(OH)_{0.9}(F)_{0.3}$, $Ti_2C_{0.8}O_{0.4}(OH)_{0.9}(F)_{0.3}$, $Ti_3C_{0.6}N_{0.8}O_{0.4}(OH)_{1.2}(F)_{0.25}$, $Nb_2C_{0.9}O_{1.2}(OH)_{0.6}F_{0.3}$ and $Nb_4C_{2.3}O_{0.7}(OH)_{0.8}F_{0.7}$. We also focused on studying the effect of the number of layers and changing the M and X elements on the distribution of the terminations. This information can, in turn, be used to better design and tailor these novel 2D materials for various applications.

(ICACC-EMERG-P002-2016) Graphene as a heat sink of ultrasound probe

Y. Kim*[1]; W. Seo[1]; B. Choi[2]; 1. Hanbat National University, The Republic of Korea; 2. FC Ultrasound, The Republic of Korea

Ultrasound imaging system using the ultrasonic probe should be harmless to the human body. However the temperature of acoustic lens surface of the ultrasonic probe was raised because ultrasonic wave oscillator was heated up in the diagnostic process. It can lead to damage the physical body. Therefore, it is necessary to ensure the safety of the patient to diagnose and to lower the surface temperature of the probe through the rapid removal of heat generated during the ultrasonic diagnosis. In this study, we tried to restrict increasing temperature of the acoustic lens surface using graphene sheet as a heat sink. We will investigate the effects of thickness of graphene sheets formed between polyimide thin films on the properties of heat removal. The relationship between structure of graphene sheet and characteristic of heat removal will be discussed.

(ICACC-EMERG-P003-2016) Thermal analysis and calorimetry applied to the studies of 2D carbon-based nanomaterials

K. Lilova*[1]; L. Brown[1]; 1. Setaram Inc., USA

Graphene, single-walled (SWCNTs) and multi-walled nanotubes (MWCNTs), onion-like carbons (OLCs) and nanodiamonds are attractive materials due to their two-dimensional structure, unique properties, and potential applications in many fields as electronics, catalysts, photonics, robotics, mechanics, energy storage, and orthopedics. All those new developments require a thorough study of the mechanical, physical and chemical properties of the nanocarbons and the corresponding composites. The density and the thermal expansion coefficients of MWCNTs-containing composites can be investigated using thermomechanical techniques. Thermogravimetry combined with differential scanning calorimetry (TG-DSC), is a powerful method to determine the amount of the impurities, the effect of the thermal treatment, and the thermal stability of CNTs and graphene composites. The isothermal immersion and oxidative calorimetry are commonly used to study the surface properties and thermodynamic stability of CNTs and OLCs, which are critical for their applications as catalysts and energy storage materials. These techniques will be introduced and illustrated by several examples on 2D nanomaterials.

(ICACC-FS1-P004-2016) Effect of phyllosilicate type on the microstructure and properties of kaolin-based ceramic tapes

G. Lecomte*[1]; K. Lebdioua[1]; M. Laffort[1]; N. Houta[1]; N. Tessier-Doyen[1]; Y. Abouliatim[2]; C. Peyratout[1]; 1. ENSCI, France; 2. ENSA, Morocco

The purpose of this work was to highlight the effective influence of the nature and shape of clay minerals on the texture, sintering behavior and the final characteristics of kaolin-based ceramics shaped by tape casting. Palygorskite (P) and talc (T), which are respectively 2:1 and fibrous-like clay minerals, were added into aqueous slurries of kaolin in various amounts: 10,20,30,40 and 50 mass % (with respect to kaolin + added clay). The increase of talc content into kaolin-based slurries from 10 to 50 mass % does not significantly affect the rheological behavior according to the tape casting process. For palygorskite, the binder and plasticizer content were modified accordingly. Both kaolin-P and kaolin-T tapes exhibit a highly textured microstructure within the thickness. The increasing amount of the palygorskite content up to 20 mass% tends to significantly decrease the open porosity while preserving the difference in roughness between the top and bottom surfaces of the tapes sintered at 1100°C. With talc, 10 mass% appeared as a threshold content above which the addition of talc is detrimental both for the porosity and the flexural bi-axial strength. The optimal properties of use were obtained for the tapes containing 50 mass% of talc (sintering at 900°C); 20 mass% of palygorskite or 10 mass% of talc (sintering at 1100°C).

(ICACC-FS1-P005-2016) Geopolymers as Adsorbent for Heavy Metals Removal From Wastewaters

I. Kara*[1]; D. YILMAZER[2]; S. T. Akar[2]; 1. Anadolu University, Turkey; 2. Eskisehir Osmangazi University, Turkey

With the increase of industrialisation, heavy metal pollution in wastewaters is becoming a major concern for the environment. Therefore, removal of heavy metal ions from wastewaters effectively by low cost methods is of importance. Porous materials

function as adsorbents and geopolymers, as being porous materials with few tens of nanometers pore size, could be low cost adsorbents for this purpose. In this study, meta-kaolin based geopolymers were produced by using Na-silicate and tested for removal of Ni^{2+} and Zn^{2+} ions from aqueous solutions. The effect of amount of teh geopolymer adsorbent, initial pH of solution, initial ion concentration, temperature and contact time on adsorption behaviour were studied. It was revealed for the first time the meta-kaloin based geopolymers can be a viable and effective adsorbents for the removal of Ni^{2+} and Zn^{2+} ions with over 99% efficency.

(ICACC-FS5-P064-2016) Combining Flash Sintering / Sinterforging with Hybrid FAST/SPS Technology for Oxide and Non-Oxide Materials

J. Hennicke*[1]; T. Kessel[1]; J. Raethel[2]; 1. FCT Systeme GmbH, Germany; 2. Fraunhofer IKTS, Germany

Sintering assisted by an electric field of high field strength ("flash sintering") allows essential progress in the development of innovative materials due to an extremely high densification rate, if a certain threshold of field strength is exceeded. Unfortunately typical FAST/SPS sintering systems are not able to provide the required field strength. Moreover it is not possible to heat the powder compact independent on the electric field strength. To overcome these limitations, a versatile Hybrid-FAST/SPS sintering system with additional flash sintering / sinterforging capability was developed, which allows a virtually arbitrary combination of classical field assisted sintering, hybrid sintering, conventional hot pressing and flash sintering / sinterforging in reducing as well as in oxidizing atmosphere. By means of examples the poster will demonstrate various applications of the different options. Also first results in the development of new oxide and non-oxide materials will be shown.

(ICACC-FS6-P006-2016) FEM crystal plasticity simulation analysis for a microcompressed single crystal

J. Jung[1]; C. Kyung Mox*[1]; I. Park[1]; Y. Choi[1]; 1. Pusan National University, The Republic of Korea

Microcompressed deformation behavior of a single crystal with the variation of the inclination angle of a primary slip plane was evaluated by utilizing the crystal plasticity finite element method (FEM) simulation. We considered the occurrence of single slip keeping the operation of only a primary slip system. The range of inclination angle was 36.3 to 48.7 degrees. From the result of simulation, two types of definite global deformation behavior were revealed in terms of the inclination angles, namely the global deformation along the primary slip direction and along the opposite diagonal direction to the primary slip direction. It was also shown that flow curve, lattice rotation and primary slip system evolution varied with the inclination angles in the present study.

(ICACC-FS6-P007-2016) First principles study of thermal stability of $LiNiO_2$ materials coated with ultrathin amorphous Al_2O_3 layers

J. Kang*[1]; B. Han[2]; 1. DGIST, The Republic of Korea; 2. Yonsei University, The Republic of Korea

Development of materials with outstanding energy capacity and structural durability is especially of paramount importance in Li-ion batteries. The bi-functional properties have been serious challenged to high Ni cathodes via unfavorable electrochemical and thermal instability when exposed to liquid organic-phase electrolytes or under ambient environment above room temperature. Conformal ultrathin Al_2O_3 coating by atomic layer deposition (ALD) has been mostly employed to enhance the electrochemical stability of the cathodes. However, atomistic understanding of thermal stability issue still remains. In this presentation, we extensively utilize density functional theory (DFT) calculations to identify the thermal stabilities of Al_2O_3 coated $LiNiO_2$ (LNO) (012) surface. First, the interface structures between LNO and varying Al_2O_3 coating layers increased from 0.20 nm ~ 0.88 nm were calculated. We identify that phase transformation of Al_2O_3 from ordered into amorphous structure as the thickness reach about 0.88 nm. Second, thermal stability of LNO (012) facet with and without Al_2O_3 coating layer are predicted at higher than ambient temperature using ab-initio molecular dynamics. Finally, by calculating electron density distributions we characterize chemical bonding natures of Li-O and Al-O to understand underlying mechanism providing such high thermal stability.

(ICACC-S3-P008-2016) Production of Li_2O-doped-GDC dense electrolyte at 950°C by water based tape casting

V. De Marco*[1]; V. M. Sglavo[1]; A. Grazioli[1]; N. Zampini[1]; 1. University of Trento, Italy

The addition of small amount of metal oxides can increase the sinterability of gadolinia-doped ceria, suitable electrolyte material for LT-SOFC, thus reducing the temperature necessary for its densification. The aim of the present work was to produce Li2O-doped GDC gas tight electrolyte by water-based tape with no interconnected porosity at temperature compatible for coupling with a copper (II) oxide (CuO) containing anode. Initially, the effect of lithium oxide as sintering aid was studies by dilatometry carried out on samples produced by uniaxial pressing. Then, the aqueous slurry for tape casting was optimized: the correct dispersant concentration was identified by analyzing the viscosity of slurries. Finally, the solid load and the additives (binder-plasticizer) amount were varied to obtain the optimal viscosity. The cast samples sintered at 950°C (more than 500°C below the typical sintering temperature of GDC) showed an almost fully dense microstructure.

(ICACC-S3-P010-2016) Current collection apparatus to improve the electrochemical measurement reliability for the solid oxide fuel cell

J. Chang[1]; M. Lee[1]; R. Yang[1]; T. Lin*[1]; Y. Chang[1]; W. Kao[1]; L. Lee[1]; R. Lee[1]; 1. Institute of Nuclear Energy Research, Taiwan

A current collection apparatus to improve the electrochemical measurement reliability for a solid oxide fuel cell has been proposed in this article. The tested cell consists of a Ni-YSZ anode as the cell substrate, an 8 μm thick YSZ electrolyte, a screen-printed LSM cathode, and a Pt current collector. The cathode and anode layers are well adherent to the YSZ electrolyte as a typical cell structure. The effects to influence on the cell performance are investigated, including the current collector setup, temperature, and flow rates of air and hydrogen fuel. The experimental results demonstrate that the modification of a current collector setup can efficiently provide good wire bonding strength between the current collector and the cell electrode, therefore eliminate the wire resistance related to the contact problem. It can enhance the measured output power density consequently. The cell performance can also be enhanced by the increase of operation temperature. According to the results of the electrochemical test and electrochemical impedance spectroscopy (EIS) of cell-I, the maximum power density, electrolyte ASR (R_0), and electrode ASR (R_1+R_2) at operation temperature of 800 C° are 180 mW cm^{-2}, 2.7 Ω cm^{-2} and 3.29 Ω cm^{-2}, respectively.

(ICACC-S3-P011-2016) Densification and Electrical Conductivity of Gadolinia-Doped Ceria Solid Electrolyte

R. M. Batista[1]; E. N. Muccillo*[1]; 1. Energy and Nuclear Research Institute, Brazil

Bulk specimens of ceria 10 mol% gadolinia solid solutions were sintered in oxidizing, inert and reducing atmospheres. The main purpose of this work was to evaluate the effects of the sintering procedure on densification and on the grain and grain boundary conductivities of the solid electrolyte. The sintering process was conducted at a fixed temperature (1250°C) for 2 h. High density (≤ 95%) was achieved for specimens sintered in both oxidant and inert atmospheres. The microstructure of sintered specimens consists of polygonal grains and low porosity. The specimens sintered under reducing atmosphere display relatively large grains and grain and grain boundary conductivities remarkably lower than those of

specimens sintered in oxidant and inert atmospheres. Activation energy values for total electrical conductivity amounts 0.90 eV for all studied specimens, evidencing no changes in the main mechanism of electric conduction.

(ICACC-S3-P012-2016) Development of SOFC Stack Materials with NH_3 as Fuel

H. Iwai*[1]; M. Saito[1]; Y. Yamamoto[1]; K. Inaoka[1]; S. Suzuki[1]; Y. Takahashi[1]; 1. Noritake Co., Ltd, Japan

Solid oxide fuel cells (SOFCs) have received a lot of attention as promising electrochemical power generation devices due to their high electrical efficiency and adaptability to a variety of fuels such as hydrocarbons, ammonia, and hydrogen. Ammonia is expected as CO_2-free hydrogen energy carriers of high hydrogen density. By supplying ammonia directly to the SOFC stack, to achieve the power generation used ammonia as fuel. The aim of the this study is the development of SOFC with ammonia as fuel.With the development of ammonia utilization technology, application of hydrogen to expand. We will introduce degradation behavior of SOFC stack materials (electrode, sealing glass and metal interconnector) with ammonia gas and the results of materials development.

(ICACC-S3-P013-2016) La-doped $BaSnO_3$ as Anode Material for Low Temperature-Solid Oxide Fuel cells

M. Abdul Jabbar*[1]; K. Pan[1]; A. Jaiswal[1]; I. Robinson[1]; E. D. Wachsman[1]; 1. University of Maryland, USA

Barium stannate doped with 2 at.% of lanthanum has been synthesized and investigated as a potential anode material for low temperature solid oxide fuel cells (LT-SOFCs). $Ba_{0.98}La_{0.02}SnO_{3-\delta}$ceramichas been calcined at 1200-1300°C in air to obtain the cubic perovskite phase and then sintered at 1550°C for 12h.The sintered sample has shown approx. 7% shrinkage and 70% density. For the 30% porous sample,electrical conductivity values of 8.7 S/cm and 9.3 S/cm, respectively had been achieved, at 600°C and 400°C, respectively in 10% H_2/3%H_2O/N_2.The preliminary results has shown a decent redox stability, approx. 7 % loss in conductivity at 600°Cwhen cycled 3 times between air and reducing conditionsovera period of 60 h. Post-test XRD analysis on $Ba_{0.98}La_{0.02}SnO_{3-\delta}$samples shows structural stability by retaining the cubic perovskite phase.The material is also stable in dry and humidified H_2. Interestingly, the material has shown semi-conductor like behavior in the presence of methane. The conductivity values of the materials in 97%CH_4/3%H_2O gas were 6.4 and 2.2 S/cm at 600 and 500°C, respectively. This material has promising performance for integration into an LT-SOFC anode, but processing challenges remain.

(ICACC-S3-P014-2016) Ceria coatings for the hydrogen side of the interconnects for SOFC/SOEC applications

D. Szymczewska[2]; P. Z. Jasinski[2]; M. Chen[1]; S. Molin*[1]; P. Hendriksen[1]; 1. Technical University of Denmark, Denmark; 2. Gdansk University of Technology, Poland

High temperature corrosion of steel interconnects is considered an important degradation issue of the fuel/electrolysis cell stacks. Much effort has been made to mitigate the oxygen side corrosion issues, whereas limited research has been performed for the hydrogen side. For the standard SOFC/SOEC uncoated alloys, corrosion rate for the oxygen and the hydrogen/steam sides are similar. Therefore, a robust coating for the hydrogen side should be sought to ensure long lifetime with low degradation. In this study, an undoped ceria (CeO_2) is evaluated as a protective coating for the Crofer 22 APU interconnect. Layers with different thicknesses are produced by a low cost, low temperature spray pyrolysis technique. Additionally, a Gadolinum Doped Ceria coated sample produced by a commercial PVD process is included for study. Samples with coatings are evaluated for corrosion properties in the atmosphere of humidified (4 vol.% steam) hydrogen at 800°C for 1000 hours and its properties are compared to the uncoated samples. This project is financed at Gdansk University of Technology by NCN grant 2012/05/B/ST7/02153 "Functional layers for solid oxide fuel cells " and at Technical University of Denmark by a grant from the ForskEL project 2015-1-12276 "Towards solid oxide electrolysis plants in 2020" funded by Energinet.dk. D. Sz. wants to acknowledge an internship stipend by the InterPhD programme at GUT.

(ICACC-S3-P015-2016) Synthesis of $Sr_2MgMoO_{6-\delta}$ by Atmosphere-Controlled Calcination method and Characterization for Solid Oxide Fuel Cells

M. Kinoshita[1]; K. Hara[1]; T. Onozawa[1]; K. Shin-mura[1]; Y. Otani[1]; S. Ogawa*[1]; E. Niwa[2]; T. Hashimoto[2]; K. Sasaki[1]; 1. Tokai University, Japan; 2. Nihon University, Japan

$Sr_2MgMoO_{6-\delta}$ is a B-site ordered double-perovskite, a mixed ionic and electronic conductor in the reducing atmosphere at the anode for solid oxide fuel cells (SOFCs), and has been under investigation as a promising anode material for hydrocarbon-fueled SOFCs, because of its high tolerance to carbon deposition and sulfur poisoning. The synthesis process of the powder reported by the previous studies is confusing and requests expensive chemicals. In this study, a simple solid state reaction method by conventional chemicals is investigated in order to synthesize a high purity powder of $Sr_2MgMoO_{6-\delta}$ $SrCO_3$ or $SrNO_3$, MgO, and MoO_3 are used as starting materials. Atmosphere-controlled calcinations using the flow gases of 5%H_2/Ar and O_2 are alternatively performed at proper sintering temperature. The successfully synthesized powder is a high purity phase of $Sr_2MgMoO_{6-\delta}$. The reaction process is determined based on the high temperature X-ray diffraction data. Conductivity property under a reducing atmosphere is also evaluated.

(ICACC-S5-P016-2016) Effect of CNTs as fillers on the mechanical properties of kenaf-polypropylene composites

R. Paskaramoorthy*[1]; 1. University of the Witwatersrand, South Africa

In this study, the effects of carbon nanotubes (CNT) in improving the interfacial bonding in, and consequently the mechanical properties of, kenaf reinforced polypropylene composite are presented. Fibers were treated with NaOH solution of 6% concentration followed bya silane treatment using 5% by fibre weight of 3-aminopropyltriethoxysilane. Composite laminates were then made by compression moulding. The first set of composite laminates was made with kenaf fiber content of 20-35% by mass. No CNTs were included. Tensile and flexural strength were found to increase with fibre content until the latter reached 30%. Both properties, however, decreased when the fiber content was further increased to 35%. SEM examination of fractured surface of composite laminates made with 35% fibre content showed poor wetting and a few instances of fiber pull-out. The second set of laminates were made using 30% by mass of kenaf fiber and 0.25%, 0.50%, 0.75% and 1.0% by mass of functionalized CNT. Both mechanical properties showed improvement of varying degrees. SEM examinations of fractured surface indicated comparably fewer instances of fiber pull-out, indicating improvement of fiber-matrix interfacial bonding. Closer examination also revealed the presence of CNTs in the interfacial region which possibly acted as a bridge between the fibers and matrix and contributed to improved mechanical properties.

(ICACC-S5-P017-2016) Pulse electric current sintering of hydroxyapatite/β-tricalcium phosphate composites

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Hydroxyapatite (HA) / β-tricalcium phosphate (β-TCP) composites attracts attentions as bone implant materials. As one of the fabrication method of HA/β-TCP is mixing of HA and β-TCP powder in advance of sintering. This method enables the control the ratio of content of β-TCP easier. However, it is difficult to obtain dense composites. In this study, we focused on pulse electric current sintering (PECS) to obtain dense HA/β-TCP composites. The sinterability is evaluated with relative density and grain size measurements. Composition of sintered body was also characterized by X-ray diffraction. In comparison with pressure-less sintering,

PECS increased relative density of the composites without grain growth. In HA/β-TCP sintered by PECS, the phase transformation from β-TCP to α-TCP was promoted. This is due to higher thermal energy by spark discharge during PECS. In HA/β-TCP with MgO as a sintering additive sintered by PECS, stabilization of β-TCP phase, which was observed in pressureless sintering, was not occurred, because shorter sintering time during PECS process is not enough for the diffusion of Mg ion.

(ICACC-S5-P065-2016) Chromatic silica sol-gel/ polydiacetylene composites for biological and medical applications

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In this study, we have developed new methods of synthesis two or three dimensional silica sol-gels comprising polydiacetylene (PDA) molecules. Polydiacetylene is a conjugated ene–yne polymer assembly produced upon ultraviolet irradiation of ordered diacetylene monomers has unique chromatic properties. PDA matrixes were shown to undergo dramatic visible colorimetric and fluorescence transformations induced by diverse biological and chemical molecules and environmental stimuli, thus making PDA a powerful constituent in sensing platforms. A transparent silica-gel matrix containing individual PDA or lipid/PDA assemblies can be a novel array-based diagnostic platform. We demonstrated ability to use new silica sol-gel/PDA systems in biological and medical research. In particular this formulation can be used: Detection of bacterial proliferation; *In situ* analysis of bacterial biofilms; Diseases Diagnostic; Sensors of membrane active compounds etc.

(ICACC-S6-P018-2016) New Rock Salt type Structure from Chemical or Electrochemical insertion

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Regarding the field of energy storage, the design of new materials that provide high energy densities and long cycle life together with being economic and environmental benign is crucial. Therefore, the soft chemistry used to prepare the original frameworks, new structures is in perfect appropriateness with such a target. Moreover, one of the primordial properties needed for the new materials to be a good candidate for such a challenge is the property of good ionic conduction. Our research is focused on the synthesis by soft chemistry of new "metastable" frameworks with large tunnels or layered structures at low temperature. We will discuss on our strategies to generate original framework showing ionic conductivity. The first approach is based on topotactic reactions starting from existing ionic conductors with a compact anionic framework. In the case of vanadium oxide, starting from $NaVO_3$, we will show that the lithium/sodium insertion leads to new nanoscale rock salt type structure Na_2VO_3. Such material show a reversible capacity of 200mAh/g. Others examples based on manganese oxides will be discuss.

(ICACC-S6-P019-2016) Thermoelectric Properties of *n* - type $Bi_2Te_{3-x}Se_x$ Prepared by Hot Extrusion

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Thermoelectric materials enable energy conversion from thermal to electricity and vice versa. Among the various thermoelectric materials, Bi-Te based materials have the highest thermoelectric figure-of-merit (ZT) around room temperature. Recently, it was reported that the nanostructured poly-crystalline p-type Bi-Te alloys exhibit better thermoelectric and mechanical properties over the conventional single-crystalline materials. In case of *n*-type materials, however, owing to the strong anisotropy, random orientation of grains in polycrystals lead to a serious degradation of thermoelectric performance. Thus, texturing of basal planes to a particular direction is one of the most promising ways to enhance thermoelectric performance of *n*-type materials. Here, we show the orientation of basal planes and enhancement of thermoelectric properties using hot extrusion technique. The material of *n*-type $BiTe_3$-xSe_x was used as a model system. The microstructure is characterized by X-ray diffraction. Electron back-scatter diffraction was used to analyze the grain size and orientation in a real space. Harman method was used to measure ZT. In this presentation, the correlation between hot extrusion conditions, microstructure, and thermoelectric properties will be discussed.

(ICACC-S6-P020-2016) Structural and Microwave Dielectric Properties of $(1-x)Li_2TiO_3$ + xMgO Ceramics Prepared by Solid State Reaction Method

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In this study, (1- x) Li_2TiO_3 + xMgO (x= 0, 0.1, 0.3, and 0.5) ceramic samples were prepared by the solid-state reaction method and those were characterized by using X-ray diffraction spectra and FTIR Spectroscopy. The samples sintered in air at 1000 ^{0}C have shown a good crystallinity situation from its XRD peaks and they have a cubic pyrochlore structure. According to the assignment of the FTIR spectra of Li_2TiO_3 band in the region700–500cm^{-1} should be assigned to Ti–O stretching vibrations in TiO6 octahedra and bands in the region 500– 400 cm^{-1} to Li–O stretching vibrations and O–Li–O bending vibrations. Another peak located at 2345 cm^{-1} is due to the Ti–O vibrations. The electrical and dielectric properties of the (1- x) Li_2TiO_3 + xMgO (x= 0, 0.1, 0.3, and 0.5) ceramics were studied using Impedance analyzer. The results show that the dielectric constant in the samples decrease from 23.2 to 10.6 with increasing Mg content from x= 0 to 0.5. In addition, the Q×f value was greatly improved by small level of MgO addition.

(ICACC-S6-P021-2016) Dielectric, Structural and Spectroscopic Properties of Mg- doped $CaCu_3Ti_4O_{12}$ Ceramics by Solid State Reaction Method

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Since the discovery of gigantic dielectric constant in CCTO supercapacitor in 2000, development of its practical application to energy storage has been of great interest .In this study, the $CaCu_3Ti_4O_{12}$ (CCTO) and Mg doped CCTO ceramic samples ($Ca_{1-x}Mg_xCu_3Ti_4O_{12}$) were synthesized by the traditional solid state reaction method using $CaC0_3$, CuO, MgO, and TiO_2. shorter time compared with conventional ceramic methods. The precursors were calcined at 950 °C in air for 12 h to obtain nanocrystalline powders of CCTO and Mg doped CCTO samples and then the samples were sintered at 1000 °C in air for 12h . The sintered CCTO and Mg doped CCTO samples were characterized by XRD, FTIR, and Raman spectroscopy. The XRD results indicated that all sintered samples have a typical perovskite $CaCu_3Ti_4O_{12}$ structure and a small amount of CuO and Rutile. From the FTIR spectra the modes observed at 606, 525 and 463 cm^{-1} was assigned to vibration modes of Ca–O, Cu–O and Ti–O–Ti, respectively. The dielectric constant of x=0 at 1 kHz is about ~ 12734 and increases to ~18381 at higher Mg^{+2} (x=0.4) content. However, the dielectric constant for x=0.8 sample shows different behavior leading to decrease in the dielectric constant. The dielectric loss of CCTO samples can be reduced with the addition of Mg dopant.

(ICACC-S6-P022-2016) Solid state synthesis of geikielite and karrooite

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$MgTiO_3$ (Synthetic Geikielite) and $MgTi_2O_5$ (Synthetic Karrooite) are the important microwave electronic dielectric ceramic materials with wide application such as in resonators, filters, and antennas for communication, radar and global positioning systems operating at microwave frequencies. In this study, Synthetic geikielite and karrooite were synthesized via the conventional solid-state reaction method using stoichiometric amounts of high-purity MgCO3 and TiO_2 and were characterized by XRD, FTIR, and Raman spectroscopy. The phases of $MgTi_2O_5$ and $MgTiO_3$ are identified by the XRD

pattern. In the FTIR spectrum, the bands at 416, 440, and 461 cm^{-1} are characteristic for $MgTiO_3$ mineral. In addition, a very broad absorption band from 500- 700 cm^{-1} was observed, which was due to the bending vibration of Ti- O- Ti bonds. The weak at 251 and 207 cm^{-1} are due to the additional phase $MgTi_2O_5$. Lattice vibrations are observed as weak to medium intense bands below 200 cm^{-1}. In the Raman spectrum, all ten bends corresponding to $MgTiO_3$ were observed at 224, 279, 302, 352, 395, 643, and 708 cm-1. On the other hand, only two modes of Mg_2TiO_4 are present at 328 and 481 cm^{-1}. The bands at 455, 336, 455, and 359 cm^{-1} is assigned to the O- Ti- O bending modes of $MgTiO_3$ phase.

(ICACC-S6-P023-2016) Thermal conductivity changes in WO_3 films caused by hydrogen intercalation/deintercalation

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We are developing "thermal switching materials", of which the thermal conductivity varies over a wide range. WO_3 is expected as a thermal switching material. The electrical conductivity of WO_3 can change owing to the metal-insulator transition caused by hydrogen intercalation/deintercalation quickly and reversibly. Since the electrical conductivity changes cause the electron thermal conductivity changes, the thermal conductivity is expected to change. Here, we report the thermal conductivity changes of WO_3 films associated with hydrogen intercalation/deintercalation. Amorphous WO_3 films were deposited by an rf magnetron sputtering method with flowing Ar/O_2 mixed gas. Hydrogen intercalation/deintercalation was carried out by using electrochemical reaction. The as-deposited film was insulator and the thermal conductivity was 1.06 W/mK. After intercalating hydrogen to the film, the electrical conductivity changed to 9.17×10^3 $\Omega^{-1}m^{-1}$ owing to metal-insulator transition. The thermal conductivity increased to 1.20 W/mK. Then, by hydrogen deintercalation, the film became an insulator again and the thermal conductivity decreased to 0.875 W/mK. The electron thermal conductivity of the hydrogen-intercalated film was estimated to be 6.77×10^{-2} W/mK. These results indicate that the thermal conductivity changes were caused by the electron thermal conductivity changes due to metal-insulator transition.

(ICACC-S6-P024-2016) Temperature-dependent density of states (DOS) effective mass and related thermoelectric properties of $Bi_{2-x}Sb_xTe_3$ compounds

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Temperature-dependent density of states (DOS) effective mass and related thermoelectric properties of $Bi_{2-x}Sb_xTe_3$ compounds were investigated. The compounds were prepared by the consolidation of spex-milled powder using spark plasma sintering. The electrical conductivity of the compound was enhanced significantly by Sb-alloying due to the hole generation through the formation of anti-site defect, and it exhibited the temperature dependence of $\mu \propto T^{-3/2}$, indicating that the charge transport in the compounds is dominantly governed by hole-acoustic phonon scattering. The increase in DOS effective mass by Sb-alloying and temperature-dependent DOS effective mass were discussed in terms of Pisarenko's relation. Lorentz numbers were calculated for better understanding of the effects of Sb-alloying on the thermal conductivity, and the ZT of up to 1.17 was achieved at 370K in $Bi_{0.42}Sb_{1.58}Te_3$.

(ICACC-S6-P025-2016) Anisotropic properties of higher manganese silicide prepared via arc melting and hot press

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Higher Manganese Silicide is a thermoelectric material with promising applications due to its low price and high abundance. While HMS is anisotropic, it is mostly used as randomly oriented polycrystalline material. This is done mainly due to the difficulty of production of anisotropic samples and the poor mechanical properties of single crystals. However this prevents the use of the higher ZT direction in the material. HMS samples were prepared between by arc melting and crushed to 150 - 250 Mesh and hot pressed. The samples were cut in different directions and their thermoelectric properties were investigated. 10% degree of texture was determined from XRD analysis and shown to effect the thermoelectric properties of HMS in different diractions. The dagree of anisotropy was modeled using the general effective media to show the differences in the thermoelectric propreties.

(ICACC-S7-P026-2016) Applications of Cu_2O Particles with Modulated Size and Morphology in Sensing 4-Nitrophenol

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This study proposed to apply cuprous oxide (Cu_2O) particles with different dimension and shape for the applications in sensing 4-nitrophenol. Mainly, two types of surfactants were used as templates to modulate the size of prepared Cu_2O particles. In addition, ammonia water was used for adjusting the pH environment and to control the shape of particles including cubic, sphere, octahedral and star-like Cu_2O. The physical characteristics of Cu_2O particles were studied by Scanning Electron Microscope (SEM), Transmission Electron Microscopy (TEM), X-Ray Diffraction (XRD), UV/VIS spectrophotometer and Zeta Potential Meter and Particle Size Analyzer. For applying Cu_2O particles for sensing 4-nitrophenol, both cyclic voltammetry and amperometry methods were investigated. The optimized biosensor was prepared by modifying the electrode with octahedral Cu_2O particles, which showed two detection linear ranges from 10 to 100 μM, and from 100 to 400 μM with the sensitivity of 0.393 and 0.173 μA μM^{-1} cm^{-2}, respectively. The detection limit obtained for the resultant sensor is about 0.5 μM. On the other hand, the electrode using spherical Cu_2O particles for the surface modification showed the detection linear range from 10 to 400 μM with a slightly higher sensitivity of 0.408 μA μM^{-1} cm^{-2} with lower detection limit of 0.005 μM.

(ICACC-S7-P027-2016) Surface enhancement of 3D printed thermoplasts via plasma assisted vapor deposition approaches for unmanned areal vehicles

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With increased availability of microelectronic components and additive manufacturing techniques, such as fused deposition modeling (FDM) the construction and fabrication of unmanned areal vehicles (UAV) became possible for everybody. FDM or fused filament fabrication (FFF) is a 3D-printing technique where a molten material is deposited layer-by-layer to build complex structures. Commercially available thermoplasts used in common FDM 3D-printers often lack either chemical and/or mechanical stability and durability. Subsequent surface modification allows to overcome these drawbacks by adding additional protective layers, thus for example reducing the UV damage and long term degradation. Furthermore, treatment of the surface reduces the porosity in 3D- printed materials, making it dense and thereby decreases the drag resistance of the UAV. Especially plasma assisted chemical vapor deposition (PECVD) and physical vapor deposition (PVD) techniques allow the functionalization of temperature sensitive materials and conformal coverage of construction elements of complex shapes and surfaces.

A quadrotor helicopter was designed and fabricated using PLA, ABS and carbon fibre reinforced ABS. Metals (Ti, Al) and metal oxides (SiO2, TiO2) were deposited using PECVD methods as either single layer or multi layer to provide environmental protective coatings.

(ICACC-S7-P028-2016) Thin Film silicon solar cells on graphite substrates

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Cell performance of silicon thin film layers deposited by plasma enhanced chemical vapour deposition (PECVD) on graphite substrates has been investigated. To enhance the performance of solar cells, the surface morphologies of the back reflectors were modified by changing the barrier layer on graphite. The surface roughness of graphite substrate with the barrier layer reduced from ~2um to ~80nm. As compared with an amorphous silicon solar cell, a crystalline silicon solar cell exhibited the improved cell conversion efficiency by ~ 0.6% absolute. In addition, we fabricated thin film silicon solar cells on many kinds of graphite substrate including carbon fiber. We achieved ~ 9% cell efficiency for a crystalline silicon thin film solar cell on graphite substrate. We also disuss the effect of transparent-conductive-oxide thickness with barrier layer on cell efficiency and quntum efficiency.

(ICACC-S7-P029-2016) The synthesis of metal(Ti/Cr/Mo/B) alloying DLC coating for the application on bipolar plates in fuel cell

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Diamond-like carbon (DLC) film is considered to be a potential coating for several varieties of tribological applications because of its high hardness, good thermal conductivity, low friction coefficient, excellent wear resistance and chemical inertness. However, the lack of thermal stability and poor adhesion to ferrous substrates has limited its widespread use. Furthermore, DLC films are insulating; therefore, applications in electronics have yet to be developed. So, there have been developed the modified DLC coatings by doping or alloying of different elements to improve the properties in respect to pure DLC coatings. In this study, the effect of Ti, Cr, Mo, B addition has been studied on the properties of DLC coatings. Especially, the improvement of the electrical conductivity of DLC coatings without losing the chemical properties has been examined to find out the usefulness of DLC coatings for the application in fuel cell. In this study, DLC coatings were deposited by PECVD equipped with sputter gun and Ti, Cr, Mo, B were added to DLC coatings with increasing DC pulsed power on sputter gun. As a result, metal content in DLC coatings could be controlled by varying DC pulsed power and process pressure for metal targets.

(ICACC-S7-P030-2016) Characterization and structure-properties studies of metal oxide nanomaterials using thermal analysis and calorimetry

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Nanomaterials have become extremely important as catalysts, batteries, and sensors because of the high surface-to-volume ratio, which makes them more reactive than the macroscopic analogues. The particle size decrease may result in a stabilization of different structures and phases and subsequently to affect the synthesis and the functions of the materials. Creating new surface or interface in solids results in an excess free energy with a largest contribution coming from the surface energy (enthalpy). The experimental surface energetics study of nanoparticles involves a combination of techniques. The total amount of the adsorbed on the surface molecules can be measured by TG-DSC. A coupled manometric-calorimetric technique can be used to obtain the heat of the adsorption of the surface molecules. The high temperature calorimetry measurements give the difference in the thermodynamic stability between the macroscopic and nanoparticles. The change in the thermodynamic stability fields and in the phase equilibria of several nanoparticles containing Co, Zn, Fe, Mn, and Sn will be shown as examples. SnO2 and Sn-Ti solid solutions are excellent gas sensors. Co oxides are used as catalysts for CO oxidation and water splitting. ZnO with various morphology have been studied for gas sensor and photodetectors, while the Mn and Ca-Mn oxides are water oxidation catalysts.

(ICACC-S7-P031-2016) Relationship between surface excess and changes in the nanoparticles' macroscopic properties

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In this work, samples with Zn-doped concentration were synthesized by Pechini's method and calcined at 500°C. The powders were also investigated by X-Ray diffraction, FT-IR spectroscopy, surface area by S_{BET} and ESA. The results showed variations in the specifics surface areas and changes in the surface chemistry. The isoelectric point changed from 4.7 (Zn-SnO2 0%) to 6.4 (Zn-SnO2 10%) suggesting that the ion added in the samples formed a surface excess. This surface excess was analyzed through concentrated nitric acid wash in ultrasonic bath. The acid solutions generated from that wash were analyzed and quantified the Zn^{2+} present in the surface excess. The results showed that the sample Zn-SnO2 10% presented 90.06% of ion Zn^{2+} in the surface excess. Therefore, can be concluded that the changes in the macroscopic properties is associated with this surface excess.

(ICACC-S7-P032-2016) Structure and Bonding in Polyiodide Ions in f-Element Crown-Ether Complexes

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A large number of polyiodide anions have been observed in solids and one has the impression that their design depends upon size and shape of the counter-cation. The vast majority among polyiodides are triiodides. These can easily be made deliberately by the addition of elemental iodine to solutions which contain iodide anions and an appropriate cation. The triiodide anion, I_3^-, is a linear 22 electron species with three-centre-four-electron bonding obeying the Gillespie-Nyholm VSEPR concept. Higher polyiodide assemblies are loose connections between iodide, di-iodine and triiodide and may be put together, on paper, in a construction-kit manner. However, their distinction is not always beyond arbitrariness, often a matter of taste and follows selfmade rules, mostly based on distances.This work on polyiodides has focused on lanthanide ions in combination with various crown ethers as cations. The number of respective reports in the literature is rather limited; all but four contain triiodide as the polyiodide anion. Surprisingly, the exceptions are $[Pr(b15c5)_2]I_{21}$, $[Y(H_2O)_8(db24c8)_3]_2(I_3)_3(I_5)_3$, and $[Lu(db18c6)(H_2O)_3(THF)_6]_4(I_3)_2(I_5)_6(I_8)(I_{12})$ [4] having less frequent higher anionic aggregates. Their structures will be presented together with new results, for example $[Gd(OH)(H_2O)(b18c6)]I(I_3)CH_3CN$, $[Eu_2(OH)_2(CH_3CN)_2(b18c6)_2](I_3)_4$, $[La_2(OH)_2(thf)_2(b18c6)_2](I_3)_4(thf)_4$, and $[La_2(I)_2(OH)_2(db18c6)_2]I(I_3)_2$.

(ICACC-S7-P033-2016) Al/V-doped TiO_2 Nanotube Array as Wide-range Hydrogen Sensor

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The present study proposes the use of an Al/V-doped TiO_2 nanotube array sensor for wide-range detection of both dilute and high-concentration hydrogen atmospheres ranging from 50 ppm to 2% H_2. Highly ordered doped TiO_2 nanotubes were fabricated through DC pulse anodization of a Ti6Al4V alloy substrate and further annealing at 600 °C. The nanotube arrays were characterized through examination of morphology (FESEM), elemental composition (EDX and XPS) and crystalline structure (XRD and Raman). The response of nanotube sensor toward hydrogen atmospheres at temperatures ranging from 25 to 200 °C was investigated. Experimental results revealed that the Al/V-doped TiO_2 nanotube sensor presented

remarkable reversibility and repeatability as well as a quick response to the hydrogen atmospheres. The nanotube sensor shows great potential for use as a robust semiconducting hydrogen sensor working at temperatures up to 200 °C.

(ICACC-S7-P034-2016) Magnetic Heating of Iron Oxide and Strontium Ferriet Nanoparticles Embedded in Agar

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Synthesis and coating of superparamagnetic monodispersed iron oxide and strontium ferrite nanoparticles (NP) will be carried out by co-precipitation method at room temperature. The obtained Fe_3O_4 and $SrFe_{12}O_{19}$ nanoparticles were coated with oleic acid and silica since stober process used in silica coating. FTIR and VSM measurement methods will be used for materials characterization. In addition the NPs will be embedded into agar matrix to simulate the biologic conditions and then magnetic heating experiments will be carried out to evaluate their performance in terms of maximal temperature T_{max} and heating rate ($\Delta T/\Delta t$) in different processing conditions.

(ICACC-S7-P035-2016) Abundant Metal Oxide Photocatalysts for Solar Hydrogen Production

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A sustainable hydrogen supply is of key importance for the ongoing energy transition from fossil fuels to renewable energies, and efficient methods of hydrogen production, powered my renewable power sources, need to be evaluated. In contrast to electrolysis powdered by renewable energy sources (PV, wind, etc.), photoelectrochemical (PEC) water splitting technology enables the direct conversion of solar to chemical energy by water splitting using photocatalytic electrodes. The main drawback of this technology, which prevented a widespread commercialization till now, were missing photo catalysts, which combine a broad absorption of solar irradiation with high catalytic efficiency and sufficient long term stability to be used in commercial applications. The European research project SOLAROGENIX (http://www.solarogenix.eu) investigates the feasibility of abundant, stable metal oxide photoanodes for application in PEC water splitting modules. In addition to fundamental research on photocatalyst composition, morphology and electronic structure, the scaled up synthesis and module sized fabrication allows an assessment of the "Levelized Cost of Energy" (LCOE), which is crucial for the evaluation against competing technologies. This presentation will focus on recent results of photocatalyst design and fabrication in large area photo anodes for PEC water splitting applications.

(ICACC-S7-P066-2016) An Integrated Approach Towards in-situ Diagnostics of On-Surface and Gas Phase Reactions: Direct On-Chip Fabrication of Gas Sensing Materials via Chemical Vapor Deposition

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The commercial application of fuctional metal oxides in general, and specifically nanostructures thereof, depend on the availability of reproducible synthesis protocols, to tune the final properties of the resulting material. The chemical vapor deposition (CVD), a general vacuum technique for surface coatings, where metal organic precursors are decomposed at high temperatures. The correct choice of suitable precursor molecules therefore allows to produce metal oxide materials in a closed process, without the need of external reactants (e.g. O2, H2), in high purity and crystallinity, which is necessary for example for chemoresistive gas sensors to achieve a high selectivity, sensitivity and stability of the final device. A major concern of current CVD techniques for (micro-)electronic applications is the missing capability to control the materials properties during the synthesis process and to integrate the active material directly on microelectronic platforms during growth, as well as to analyze the evolving gas phase species during the deposition process and link their appearance to the resulting film property.

(ICACC-S7-P036-2016) Nanoindentation and SEM study of Silicon Carbide Systems

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In this study, scanning electron microscopy (SEM) and nanoindentation techniques were used to evaluate a silicon carbide system. Statistical sets of nanoindentations were done on 135 um X 135 um areas, focusing mainly on larger grids incorporating different microstructural phases. The histogram and contour maps of hardness and elastic modulus, H/E (GPa) and the volumetric fractions of the microstructural phases revealed the correlation between the mechanical properties and the microstructure. The experimental hardness values drop over 20% with high temperature heat treatment. The heat treatment has greater influences on the mechanical behaviors of the matrix than the large grains within the system based on the nanoindentation data. The microstructures were analyzed using a Phenom ProX desktop SEM and the results were combined with data the from iNano nanoindenter to correlate the mechanical properties of individual grains to the indents.

(ICACC-S7-P037-2016) High Efficient Photocatalytic Hydrogen Evolution on Decorated Graphene Nanohybrid

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For enhancing the efficiency of photocatalytic hydrogen evolution, cocatalyst is a challenging issue and has got extensive attentions because it offers the low activation potential active sites for H_2 evolution. So far, noble metals, sulfides of transition metals and transition metal-based molecular complexes are excellent cocatalyst for hydrogen evolution. However, scarcity of noble metals and instability of molecular complexes are still main obstacles. Recently, cobalt tin composite oxide has been extensively studied as a promising candidate. In the present talk, we reported the synthesis of amorphous cobalt tin composite oxides ($CoSn_xO_y$) decorated graphene composite ($CoSn_xO_y$/G) by in-situ chemical deposition in graphene oxide. After sensitized by dye EY, this noble-metal-free photocatalyst exhibits excellent photocatalytic hydrogen production activity under visible light irradiation (λ420 nm). The amount of H_2 evolution was 974.6 μmol over the EY-sensitized $CoSn_xO_y$/G photocatalyst in 3 h. The highest apparent quantum efficiencies (AQEs) of EY-CoS_x/G was 20.1% at 430nm.

(ICACC-S7-P038-2016) Deposition and Characterization of Nanostructure ZnO:Sb Films

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In this work, nanostructure Sb doped ZnO films were deposited by the sol gel dip coating method. Sb content was increased from 0.6% to 1% in increments of 0.1. The variations of the structural, optical and morphological properties with the antimony incorporation were investigated. X-ray diffraction data showed that the films were polycrystalline. XRD results were evaluated to understand the effect of Sb content on the crystalline structure and orientation of the films. The elemental analysis and surface morphology of the deposited thin films were investigated by EDX and Scanning electron micrograph (SEM), respectively. These SEM images reveal that the surface morphologies of the films are significantly affected by the concentration of Sb. The electrical properties of ZnO films were investigated by Hall effect measurements system using the Van der Pauw configuration under 0.55T magnetic field at room temperature. Through these measurements, some electrical parameters such as the conduction type, resistivity (ρ), carrier concentration (*n*) and mobility (μ) were easily determined. Acknowledgement: This work

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(ICACC-S7-P039-2016) XRD studies and microstructure of hexagonal nanotube Mg doped ZnO films deposited by MW-CBD

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Magnesium (Mg) doped ZnO films have attracted considerable attentions due to their characteristics which can effectively affect the electronic and optical properties. Microwave assisted chemical bath deposition (MW-CBD) method was used to prepare nanotube Mg doped ZnO (1%, 5% and 10%) films onto p-Si substrates. Zinc nitrate hexahydrate, Magnesium nitrate and an equal molar concentration of hexamethylenetetramine were dissolved in DI water. The solution was stirred 2 h at 90 °C. After, solution was irradiated using a temperature-controlled microwave synthesis system at 600 W and 10 min irradiation time. The films were washed with DI water to remove the remaining salt. Finally, the films were dried at 60°C for 1 h. The effect of Mg content on the structural and morphological properties of ZnO films was investigated. To investigate the crystalline structure and the orientation of the films, XRD patterns were used. The lattice parameters and texture coefficient values of the films were determined. Field emission scanning electron microscope (FESEM) was used to analyze the surface morphology of the nanotube Mg doped ZnO. Acknowledgements: This work was supported by Anadolu University Commission of Scientific Research Projects under Grant No. 1402F055 and 1305F082.

(ICACC-S7-P040-2016) Synthesis of ZnO:Ni Nanopowders by Microwave Assisted Hydrothermal Method

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A number of methods have been used for synthesizing ZnO nanopowders by both physical and chemical processes, including sonochemical and microwave-assisted synthesis, refluxing method, hydrothermal method and vapor transport process. These synthesis methods involve complex procedures and complicated equipment. Among these, microwave synthesis is a synthesis method which entirely different from the other method. In the microwave method, a microwave diffuses to the material being heated volumetrically. Doping is a widely used method to improve electrical, optical and magnetic properties of semiconductor materials. In transition metal ions, Nickel ion is an important in different transparent materials. In this work, Ni doped ZnO nanorods were synthesized using a microwave assisted hydrothermal synthesis method. Ni doped ZnO nanopowders were produced using zinc acetate dihydrate as the zinc cation precursor, sodium hydroxide as the hydroxide anion source and nickel acetate as doping source. The synthesized Ni doped ZnO nanopowders were characterized by X ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR) and Field Emission Scanning Electron Microscopy (FESEM). Acknowledgements: This work was supported by Anadolu University Commission of Scientific Research Projects under Grant No. 1402F055 and 1305F082.

(ICACC-S7-P041-2016) Polymer/SiO_2 Bilayer Dielectrics for CuPc-based OFETs and their Electrical Characteristics

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Organic field effect transistors (OFETs) have been extensively studied due to their potential toward driving circuits for display or low-cost logic applications. For a good OFET unit device, a considerable amount of research work has focused on dielectrics, organic semiconductor active channels, and source/drain electrodes because these are important components for operating the transistor. In this study, Copper (II) Phthalocyanine (CuPc) based OFET with top contacts bottom gate configurations were fabricated. To obtain bilayer gate dielectric, we spin-coated Polyvinyl alcohol with 150nm layer on SiO_2 dielectric layer. As an active layer CuPc thin-film with 50 nm thickness was evaporated on PVA dielectric layer by using thermal evaporation method. Finally the source and drain electrodes were prepared by evaporating a Au layer through a shadow mask. The electrical measurements of CuPc based-OFET were performed using a semiconductor characterization system with connected Probe Station at room temperature under dark condition. The field emission scanning electron microscopy (FE-SEM) was used to investigate the morphology of CuPc active layer. Acknowledgement: Anadolu University Commission of Research Projects supported this work under Grant no. 1501F030.

(ICACC-S7-P066-2016) Gas sensing characteristics and mechanisms of lyophilized TiO_2 quantum dots

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The gas sensing properties of TiO_2 nanoparticles synthesized by lyophilisation technique are reported for typical gases of CO, CH_4, NO_2 and NH_3 in comparison with the reference TiO_2 material from Degussa™. The two typical TiO_2 nanomaterials (TiO_2-LT-pH11 and TiO_2-LT300) are lyophilized at a pH of 11 and lyophilized and annealed at 200°C and 300°C respectively. It is found that TiO_2-LT-pH11, Degussa™ TiO_2, and TiO_2-LT300 have responses of 14%, 6% and 4% to NO_2 respectively whereas the responses to CO are 6.5%, 14% and 6% respectively. TiO_2-LT300 outperforms both Degissa™ TiO_2 and TiO_2-LT-pH11 on NH_3 response with a value of 3.5% where both of the competitors show negligible response. The synthesis parameters and proposed phase diagram are presented and the sensing characteristics as well as the selective detection in TiO-LT-pH11 are discussed in terms of the surface area as well as the impurities in this material.

(ICACC-S7-P067-2016) Investigation of Gas Sensing Properties of a-Fe2O3 Thin Films Prepared by Plasma Enhanced Chemical Vapour Deposition

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The development of highly sensitive, selective, reliable and compact sensing devices to flammable, toxic chemical and biological agents is of major importance. Over the last decades, bulk and thin film metal oxides have been widely studied and used for sensing species such as CO, CO_2, CH_4, C_2H_5OH, C_3H_8, acetone, humidity, etc. As an environment friendly n-type semiconductor, a-Fe_2O_3, has been proven to be a good gas sensitive material for detection of toxic, combustible, explosive and harmful gases in both domestic and industrial applications, extensive studies have been carried out to improve the gas sensing performances of the a-Fe2O3 based sensor [1, 2]. Iron was deposited on silicon and alumina substrates by plasma enhance chemical vapour deposition (PECVD), $Fe(CO)_5$ was used a precursor. The samples were then annealed at 700°C in air for the formation of the a-Fe_2O_3 phase. XRD results confirmed the crystallinity of the films and were indexed to a-Fe_2O_3 phase. In this study, we report on the gas sensing properties of a-Fe_2O_3 thin films. The optimum operating temperature of the sensor was discovered to be at 350°C for all tested gases. The sensors also showed good sensitivity towards humidity at room temperature.

(ICACC-S8-P042-2016) Ceramic Nitride powders - specialized development for high purity AlN and Si_3N_4

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Due to their unique properties nitride ceramics have found their place in many technical applications and became high tech materials in the Engineered Ceramics industry; AlN is known for excellent thermal conductivity and good chemical resistance whereas Si_3N_4 qualifies by good thermal shock resistance and high fracture toughness. Today's powder manufacturers face a multitude of challenges to satisfy their customers' needs for higher quality at reasonable prices. H.C. Starck – Germany, a renowned producer of non-oxide ceramic powders, has recently introduced a full set of highly pure

AlN powders. The distinct grades are varying by their fineness, hence qualified for tape casting and other ceramic process technologies. Preferred applications are power management and heat sinks in electronics. The Si_3N_4 portfolio has been expanded, now offering a complete portfolio with numerous grades of dedicated fineness and/or purity as required by current innovative applications. Preferred applications are looking for high strength and excellent corrosion resistance, typically in HT environment. Recently new industries showed remarkably interest for higher purity powders, e.g. PV and LED industry, which required new powder developments. We will discuss the results of chemical and physical powder characterization, with emphasis on the improvements achieved and their potential impact for the use of the powders.

(ICACC-S8-P043-2016) Near net shape processing of ZnS materials by slip casting and sintering

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High-performance ZnS transparent ceramics are promising candidate materials for utilizations in optical windows and domes for infrared imaging. The practical applications require ZnS ceramics to be prepared in a large scale and with complex shapes, and therefore advanced wet-forming techniques have attracted increasing attentions. In our present study, slip casting was applied to process ZnS green bodies. The starting powders were self-synthesized nanometer ZnS particles with a high sinterability. Cold isostatic pressing was further adopted in order to homogenize the microstructures of casted green bodies. Dense ZnS ceramics were fabricated via a pressureless sintering followed by a hot isostatic pressing. The processing parameters were studied to tailor the microstructures as well as the optical properties.

(ICACC-S8-P044-2016) Novel Particulate Reinforced Multifunctional Composites

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In this poster, as a part of undergraduate research, we will present recent developments on the research and development of novel vibration sensitive composites which can perform multifunctional functions like energy harvesting, energy storage, and solid lubrication, among others. Green design is integral component of research for the 21st century. Scientists and researchers are being continuously challenged on a variety of global issues, including population growth, rapid urbanization, infrastructure decline, climate change, and water scarcity. There is a potential to deliver game-changing solutions by designing sustainable materials.

(ICACC-S8-P045-2016) Heywang model and corrected impedance relations based on doped BaTiO3-ceramics fractal nature

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The BaTiO3-ceramics doped with additives is important from the point of view of curious resistivity behavior (PTCR), multilayer ceramic capacitors (MLCC), thermal sensors etc. Here, the influence of Er2O3,Yb2O3 and Ho2O3 on microstructure development and dielectric properties of BaTiO3-ceramics is studied. BaTiO3-ceramics, doped with 0.01 up to 0.5 wt % of Er2O3,Yb2O3 and Ho2O3, prepared by conventional solid state procedure is sintered up to 1400oC for 2 hours. Microstructure investigations of doped BaTiO3 was performed using the scanning electron microscopy (SEM) as well as energy dispersive spectrometer (EDS). Dielectric measurements were carried out as a function of temperature up to 180°C at different frequencies. With novel issue, the fractal correction coefficient α that encounters BaTiO3-ceramics fractal morphology coming separately from grains and pores plus dynamics complexity caused by the flux of different micro particles (electronic gas, ions). These intrinsic parameters affect temperature loss which in turn influences the Heywang model resulting in modified Heywang model, showing the augmentation of dielectric constant as a direct consequence. This causes the overall microelectronic properties of doped ceramics. The behavior if two-grain intergranular equivalent impedance is considered upon varying fractal correction parameter α and frequency.

(ICACC-S8-P046-2016) Thermal Fatigue of Cu Metallized Ceramic Substrates for Power Modules under Severe Thermal Cycling Condition

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Heat dissipating board for the power modules usually consists of a ceramic substrate such as aluminum nitrides or silicon nitrides sandwiched by copper plates. Mechanical reliability of the substrate after sever heat cycles is important since thermal stress due to thermal expansion mismatch between Cu and ceramic plates damages both ceramic substrate and Cu layers and eventually detachment of Cu layers occurs. Then, a severe thermal fatigue test of the metallized substrate is necessary to ensure the reliability of the modules. In this study, thermal fatigue of four kinds of metallized ceramic substrates made of Si_3N_4 or AlN was investigated under thermal cycling conditions from -40 to 250°C for up to 1000 cycles. The AlN substrates exhibited detachment of Cu layer after ca.10 cycles when the thickness of Cu layer was 0.30 mm, whereas no detachment of the Cu layer was observed for the Si_3N_4 substrate even after 1000 cycles. The different fatigue behaviors were discussed in conjunction with the mechanical properties of ceramic substrates and the residual thermal stress estimated using FEM analysis. This work was supported by Council for Science, Technology and Innovation (CSTI), Cross-ministerial Strategic Innovation Promotion Program (SIP), "Next-generation power electronics/Consistent R&D of next-generation SiC power electronics" (funding agency: NEDO).

(ICACC-S8-P047-2016) Round-Robin Test on Fracture Toughness of Ceramic Thin Plate Performed Through Single-Edge Precracked Plate method

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Ceramic substrates such as aluminum nitrides or silicon nitrides are used widely as heat dissipating board for the power modules and they are usually sandwiched by copper plates. Thermal expansion mismatch between Cu and ceramic plates causes cyclic thermal stress when the modules are exposed to sever heat cycles and eventually detachment of Cu plate occurs. Then, high fracture toughness of the thin ceramic plate is necessary to prevent such a damage of the heat dissipating board. In our previous study, fracture toughness of such a thin ceramic plate with a thickness of ~0.32 mm was measured using single-edge precracked plate method, which was modified from single-edge precracked beam (SEPB) technique. In our new approach, a small, thin single-edge notched plate is glued on one side of a brass beam with wax. The assembly is deformed in three-points bending to introduce the precrack. The flexural strength of the precracked specimen is measured using a special fixture for the thin plates. In this study, round-robin test was conducted using silicon nitrides, aluminum nitrides and alumina to test both feasibility of the new technique and reproducibility of K_{IC}. It was found that the scatters in K_{IC} among the participating laboratories were moderate, indicating the new approach is easy to perform and can give reliable values.

(ICACC-S8-P048-2016) Pulverization of Y_2O_3 nanoparticles through nanocomposite particles prepared by mechanical treatment

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Although nanoparticles are being increasingly investigated in industry and academic research due to their widespread applications in all the scientific and production fields, they are easy to form agglomerates. Ball milling or beads milling is usually utilized by dispersion of the aggregates of nanoparticles. However, contamination possibly results from wear of grinding media in these processes. In our previous research, nanocomposite particles were prepared by mechanical treatment to obtain uniform dispersion of nanoparticles in ceramics. If the core particle is removed from the nanocompsite particles, nanoparticles should be dispersed without any media. In this study, we focused on using nanocomposite particles prepared by the mechanical treatment to pulverize Y_2O_3 nanoparticles. $CaCl_2$ and aggregate Y_2O_3 nanoparticles were mechanically treated to make nanocomposite particles, in which high shear force and compressive stress is applied to the particles. It was observed that Y_2O_3 nanoparticles are uniformly dispersed on the surface of the $CaCl_2$ particles. The powder mixtures were put into distilled water and rinsed by centrifugation and decantation. Specific surface area of the treated Y_2O_3 nanoparticles was higher than as-received powder because aggregates were successfully dispersed.

(ICACC-S8-P049-2016) Effect of cold rolling on structure and properties of cast Ti-7.5Mo alloy

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The present study evaluates the cold-workability and mechanical performance of a fast-cooled and cold-rolled Ti–7.5Mo alloy. The effects of cold rolling on the morphology, crystal structure and tensile properties of the alloy are investigated. The as-cast alloy has an acicular morphology comprising fine, α″ platelets/needles uniformly distributed throughout the alloy. During rolling, a stress-assisted α″-to-α′ phase transformation accompanied with a strong preferred orientation toward α′ (002) plane occurs. EBSD-IPFs indicate that the as-cast alloy sample has several different preferred orientations. When the alloy was cold-rolled by 20% reduction in thickness, a texture toward [10–10] orientation was observed. With increased reduction in thickness, the preferred orientation gradually shifted from [10–10] toward [2–1–10]. TEM examination confirms that α″ and α′ phases co-exist in all cold-rolled samples, and the phase transformation appears more extensive in more severely cold-rolled samples. When heavily cold-rolled, distortion and fracture of the martensitic platelets/needles as well as boundary kinks/curls are frequently observed. The research is supported by MOST102-2622-E-006-041-CC2 (Taiwan, Republic of China).

(ICACC-S9-P050-2016) 3D mapping of density and crack propagation through sintering of catalysis pellets by X-ray tomography

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For the electro-chemical performance catalyst pellets are desired to have a high hierarchical porous network, to allow for the desired mass transport, as well as a high surface area to increase the reactive area. For mass manufacturing these can, with great advantage, be produced by powder pressing. The pressing itself introduces unavoidable inhomogeneity, due to shaping and powder pressing is performed simultaneously at a very high rate. The sintering of the ceramic pellets is critical in the production of the catalyst support; because the inhomogeneity across the pellet will result in different densification rates and internal stresses as a consequence. If the energy release rate of creating an internal crack is higher than the surface energy minimization during sintering, cracks may appear internally in the sintering structure. In this study, sintering of pressed catalyst pellets is studied by X-ray tomography, resulting in time and spatially (3D) resolved imaging. By X-ray tomography, the density and densification in the entire sample in 3D can be measured non-destructively. The fine resolution of roughly 10 μm allows for a detailed and precise mapping of density, but cracks has also been successfully mapped. This can be utilized to analyze the conditions for the crack propagation, and as a guide for restrictions on the allowable inhomogeneity to avoid significant cracks.

(ICACC-S9-P051-2016) Ceramic Nanofibers and Porous Nanofibrous Structures by Electrospinning

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Electrospinning has been widely used for the manufacturing of nanofibers and nanofibrous materials (NFMs). Inorganic nanofibers form the second largest group in NFMs after polymers, and research on inorganic nanofibers, especially oxide ceramic nanofibers, has reached an unprecedented level. However, production of sizeable quantities of ceramic nanofibers is still limited by a generally slow electrospinning process, and ceramic NFMs are fragile and tend to break into small pieces. In this work we introduce alternating current electrospinning as a potential candidate for high-rate production of both short and extended nanofibrous porous ceramic structures from the ceramic precursor fibers. Several types of ceramic nanofibers (Al_2O_3, WO_3, ZrO_2, WC) in the form of loose fibers, bundles, porous sheets and yarns have been successfully prepared by this uncommon method at the rates up to 1 - 2 orders of magnitude faster when compared with traditional electrospinning. We discuss the results of ac-electrospun ceramic fiber characterization and process/fiber structure and property relationships.

(ICACC-S9-P052-2016) The Development of Melting Gels Toward Porous Materials

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Conventional melting gels, mainly made of Methytriethoxysiloxane (MTES) and Dimethyldiethoxysiloxane (DMDES) in composition, are solid form at low temperature (e.g. ambient temperature) but liquid (viscous) at high temperature (e.g. around 110°C) and surprisingly reversible between these two states upon temperature cycling as long as it is below a consolidate temperature. In this study, it is my preliminary interest to explore the feasibility of melting gels toward porous materials by modified current synthesis process of melting gel. That is to say investigating the porous properties of melting gel, including pore shape, pore volume, pore size, surface area and strength, as function of methyl group substitution in starting monomers (MTES and DMDES) with larger (ethyl, phenyl), hydrophilic (-OH), and hydrophobic (-R) groups. In conjunction, various process parameters such as High-Low H2O/Si, pH, and/or thermal treatment temperature and duration are also studied. The porous property of the modified melting gels as function of (1) aforementioned starting materials and (2) H_2O/Si, pH, and/or thermal treatment temperature and duration will be presented. Then the potential of the modified melting gels for porous application will be discussed.

(ICACC-S9-P053-2016) Porosity control of porous alumina prepared by alumina and aluminum

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Macroporous ceramics have great attention in the engineering field such as metallurgy, automobile, water conservation, environmental purification or petrochemistry, production of energy, medical science, as well as waste management. Porous alumina could be prepared by mixing alumina powders, aluminum powder and polysiloxanes. During sintering, oxidation of aluminum powder and the reaction with polysiloxane have been observed, without any volume change. This phenomenon means that it can make a possible to modulate wide range of porosity of porous alumina by varied initial

particle diameter of raw powders, the ratio of mixture and sintering condition, in which alumina powders with various average diameters ranging from 0.1 to 50 μm and aluminum powders with average diameter of 3 μm have been employed to make porous alumina. Microstructure, phase evolution and specific surface area of samples obtained will be also discussed.

(ICACC-S9-P054-2016) Open Cell Geopolymer foam

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Metakaolin-based geopolymer foams were synthesized by gelcasting using H_2O_2 or H_2O_2 plus canola oil as foaming agent. Pre-oxidized SiC or SiC powders were added as supplementary materials in a low amount (< 5 wt%). The results show that add the addition of pre-oxidized improves the strength of the foams produced by the peroxide route because of the reaction between the SiO_2 layer on the SiC particles and the Al_2O_3 in the matrix, forming a geopolymeric network. The addition of the SiC powders enhanced the strength of the foams obtained by the combined route (peroxide and saponification). The in situ formation of surfactant molecules (saponification route) led to a much larger amount of total porosity in the foams. In addition, some of the foams were subjected to a hydrothermal treatment (100°C for 6 to 24h), leading to the development of a thick zeolite layer on the surface of the cell walls.

(ICACC-S9-P055-2016) Light ceramic proppants: Effect of addition of selected waste materials on the mechanical properties and pores distribution evaluation

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Proppants, also known as backfilling material is a collection of chemically inert, non-combustible and mono dimensional solid granules that supplied by a liquid during hydraulic fracturing to a gas or oil deposits. Proppants settle and thicken in the shale to form a mechanical support which is permeable to gas and oil. Their main task is to keep shale open for the entire time of extraction from the rock gas and / or oil. Thanks to the high strength parameters specified porosity and adequate spherical ensure better flow of the hydrocarbons in the extraction shale. The presented results show the effect of addition of the selected waste materials (fly ashes from the combustion of biomass) and firing parameters on the densification, mechanical properties and the pore distribution of light proppants.

(ICACC-S9-P056-2016) Superhydrophobic porous carbon nanoparticle materials with potential use in water-oil separation

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Superhydrophobic and oleophilic porous carbon nanoparticle (CNP) network materials were synthesized by glow discharge deposition using CF_4 and C_2H_2 as the precursor. The growth morphology, microstructure, porosity, composition, and wetting behavior of the F-porous CNP materials were characterized using SEM, BET analysis, XPS and contact angle (CA) test. The results show that the porous carbon materials were composed of agglomerated amorphous CNPs with diameters of approximately 30~50 nm, and had a superhydrophobic property with a CA of approximately 150°. The incorporation of fluorine could significantly change the wettability and repellency of the porous CNP materials. By varying the fluorine content, the porous CNP networks exhibited tunable repellence against liquids with various degrees of surface tension. Accordingly, these F-porous CNP networks could be applied for the separation of water-oil mixtures or oil-spill cleanup.

(ICACC-S9-P057-2016) Porous Titanium Carbide Ceramics Prepared by Pore Forming Agent Process

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Titanium carbide is a typically transition metal carbide. Due to coexistence of the ionic bond, covalent bond and metal bond, titanium carbide possesses characteristics of high hardness, high melting point, high wear resistance and electrical conductivity simultaneously. As a result, porous titanium carbide ceramics, which contain high volume fractions of porosity, will have wide potential applications in industrial and engineering fields. Porous titanium carbide ceramics were fabricated by pore forming agent method with titanium carbide powder as the raw material, nickel powder as the binder and urea as the pore forming agent. The pore quantity and size were decided by the pore forming agent, while the pore uniformly distributed was achieved by using the layer-layout method when the green was prepared. Urea were evaporated at vicinity of 150°C under vacuum, and then the porous titanium carbide ceramics came into being at different temperature between 1400 and 1600°C for various time in the same atmosphere. Microstructure and fracture morphology of porous titanium carbide ceramics were characterized by optical and scanning electron microscopy. The results show that a large number of macro and micro pores coexist in the prepared porous titanium carbide. Moreover, pore size, fraction and distribution in porous titanium carbide ceramics can be controlled on the demand.

(ICACC-S9-P058-2016) First-Principles Calculation on Degradation of Pt-Co/C Nano-Particle Catalyst in Polymer Electrolyte Fuel Cell

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Pt/C catalyst is used in an anode of polymer electrolyte fuel cell (PEFC). CO in the fuel degrades the catalytic activity of the Pt/C electrode. Here, the types of porous supports and alloy element affect the properties of the catalyst. To solve the problem of the degradation, we focused on alloy element. Some experiments show that Pt-Co/C has higher tolerance for degradation than Pt/C. However, it is unclear how Co alloying affects the CO tolerance. To reveal the effect of Co alloying, we studied the adsorption processes of CO on Pt and Pt-Co/C nanoparticles by first-principles calculation. We investigated the stable adsorption site of CO on the Pt_{55} cluster. The adsorption energy on the on-top site shows the largest value of -41.75 kcal/mol. Thus, CO tends to adsorb on the on-top site of the Pt nano-particle. To reveal the effect of Co alloying on the adsorption energy, we substituted a Co atom for a Pt atom and calculated the adsorption energy on the on-top site of Pt. When the outermost Pt atom next to the on-top site is replaced with Co, the adsorption energy is -42.51 kcal/mol. When the Pt atom under the on-top site is replaced with Co, the adsorption energy is -38.00 kcal/mol. Then, the adsorption energy by replacing Pt atoms under the on-top site with Co atoms takes a smaller value. Thus, we suggest that Co alloying is effective to increase CO tolerance.

(ICACC-S11-P059-2016) Corrosion behavior of AlN and secondary phase grains in AlN ceramics by CF_4/O_2 plasma

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Aluminum nitride (AlN) ceramics have been applied to structural components for semiconductor production equipment. In the semiconductor process, corrosion of AlN ceramics results from repeated exposure to halogen plasma. Thus, it is important to improve and understand the corrosion resistance of AlN components for semiconductor process. Although the corrosion behavior of AlN and secondary phase grains ceramics is needed in order to improve the corrosion resistance of AlN ceramics, such information has not been reported, yet. In this study, corrosion behavior of AlN and secondary phase grains in AlN ceramics by CF_4/O_2 plasma was investigated. AlN ceramics were prepared by adding Y_2O_3 as sintering aids. AlN and yttrium aluminate as secondary phase were identified by XRD. The corrosion test was carried out using polished sample in CF_4/O_2 plasma for 0 – 4 hours. The corroded surface was observed by SEM and SPM. Corrosion depth of AlN ceramics was also estimated quantitatively from surface profiles taken by SPM. As a result, it was found that corroded depth of AlN grains were larger than that of secondary phase grains. Both of them increased in the proportion to

the soaking time. Difference in the corrosion behavior was explained by the sublimation pressure of fluorides generated by reaction with CF_4/O_2 plasma.

(ICACC-S11-P060-2016) Preform design for Improving the Coefficient of Utilization of Light-Weight Material with High strength

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This paper deals with the study on the preform design for improving the coefficient of utilization of light-weight material with high strength for structural part. In this paper the coefficient of utilization of a material is a value of final product weight over billet weight. Therefore the material loss decreases as the coefficient increases. Generally the products including many structural parts are used at highly stressed sections and are well accepted at a wide range of industry such as automobile, aerospace, electric appliance and et cetera. Accordingly, recent R&D activities have been emphasized on improvement of the coefficient and near net shaping technology for cost effectiveness, better performance and especially saving material. At the experiment for forming structural part with about W150mm×L240mm, preform design is one of the most important factor for the decrease of material loss. Finally the material loss of the part through the forming experiment were minimized. Additionally the part with defect were deleted using the FE analysis and doing additional experiment. As a result the proposed and developed part with optimized preform design was found; the loss of material would be reduced. This work represents the improvement of the coefficient of utilization of a material (CUM) for forming structural part using near net shaping technology.

(ICACC-S11-P061-2016) The Influence of Different Pt Substrates on Crystallization Behavior of Lead Zirconate Titanate (PZT) Thin Films

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Crystallographic properties of the thin films prepared by chemical solution deposition (CSD) depend on the crystallization behavior during processing, which is determined by different parameters such as underlying substrates, thermal profile and etc. For synthesis of solution-deposited PZT thin films, various intermediate phases are produced by the reaction between platinized substrates and thin films during thermal treatment for crystallization, which is suggested to provide the thin films with crystallographic texture. However, it is difficult to characterize the crystallographic relationship between intermediate phases and thin films because transient and intermediate phases are formed for very short times during crystallization. In the present work, phase and texture evolution of the PZT thin films on two different Pt substrates is characterized during thermal treatment; (1) Pt coating on a Ti adhesion layer and (2) a Pt coating on a TiO_2 adhesion layer. Phase and texture evolution of the thin films were monitored during crystallization using *in situ* X-ray diffraction at a synchrotron source. Based on the observation, the crystallographic relationship between intermediate phases and thin films are discussed. Also, the degree of texture in platinized Si substrate is suggested to be one of the critical factors to determine the degree of texture in PZT thin films.

(ICACC-S11-P062-2016) The properties of ternary Mo-Cu-X-N, (X= Ni, Cr, B) coating synthesized by magnetron sputtering process with single alloying targets

H. Lee*[1]; P. Shin[2]; S. Shin[1]; K. Moon[1]; 1. KITECH, The Republic of Korea; 2. Inha University, The Republic of Korea

In this study, we tried to deposit Mo-Cu-X-N(X= Ni, Cr, B) thin coatings showing high hardness and low friction at low and high temperatures to reduce energy consumption and wear problems in engine parts. In general, this kind of nano-composite coating is made by various processes using multiple targets such as Mo, Cu and X(X= Ni, Cr, B). However, it is difficult to control the exact composition, homogeneous deposition of large scale specimens during the deposition with multiple targets. We wanted to create the single Mo-Cu-X(X= Ni, Cr, B) alloying targets with the composition showing the best friction coefficient and surface hardness. Single alloying targets with the composition showing the best properties were prepared by powder metallurgy methods, such as mechanical alloying and spark plasma sintering. Mo-Cu-X(X= Ni, Cr, B) targets were prepared subsequently. The nano-composite Mo-Cu-X(X= Ni, Cr, B) coatings prepared using the alloying targets will be eventually compared with the films from the multiple targets.

(ICACC-S11-P063-2016) Chemical interactions between SiAlON and Inconel 718 superalloy

F. Kara*[1]; A. Celik[2]; M. Sert Alagac[3]; S. Turan[1]; 1. Anadolu University, Turkey; 2. MDA Advanced Ceramics Ltd., Turkey; 3. Alp Havacilik AS, Turkey

SiAlON ceramics are among the ceramic materials used as cutting tools for machining of Ni-based superalloys. There have been a number of SiAlON ceramics in the market, used particularly for scale turning of wrought Inconel materials. There are also new developments regarding the use of SiAlON ceramics as solid milling cutters in aerospace industry. For such applications, chemical interactions between SiAlON and the metal part is important for the wear performance of the cutting tool. In this investigation, chemical interactions between Inconel 718 and various SiAlON ceramics with different z value and dopant type and with TiN reinforcement were investigated. It was observed that as z value of β-SiAlON decreases, the chemical interaction increases, as expected. The presence of TiN particles in SiAlON as a reinforcement decreases substantially the interaction. The interfacial morphology between the Inconel and the SiAlONs, which may be important for cutting performance, is affected by TiN presence and SiAlON grain size.

Thursday, January 28, 2016

S1: Mechanical Behavior and Performance of Ceramics & Composites

Ceramic Matrix Composites I

Room: Coquina Salon D

Session Chairs: Marina Ruggles-Wrenn, Air Force Institute of Technology; Rajesh Kumar, United Technologies Research Center

8:30 AM

(ICACC-S1-050-2016) Progress and Plans for CMC Research at NASA Glenn in 2016 (Invited)

J. E. Grady*[1]; 1. NASA Glenn Research Center, USA

As part of NASA's Aeronautics research mission, Glenn Research Center has developed advanced constituents for a 2700°F CMC for turbine engine applications. In this presentation, fiber and matrix development and characterization for SiC/SiC composites will be reviewed and resulting improvements in CMC mechanical properties and durability will be summarized. Progress toward the development and validation of models predicting the effects of the engine environment on durability of CMC and Environmental Barrier Coatings will be summarized and progress toward the development of CMC joining technology for 2400F joint applications will be reviewed. Research plans for 2016 and opportunities for collaboration will be summarized.

9:00 AM

(ICACC-S1-051-2016) Investigation of the statistical distributions of fracture strengths for various fibers using the tow testing approach

J. L. Lamon*[1]; M. R'Mili[2]; 1. CNRS, France; 2. CNRS/Institut National des Sciences Appliquées, France

The fracture of CMCs is dictated by the fibers and the tows. The determination of sound mechanical and statistical characteristics is a prerequisite to the development of a sound multiscale approach to failure prediction and design of composites. The present paper investigates the flaw strength distributions for a wide variety of fibers (ceramic, carbon, glass, basalt and natural fibers). Tensile testing of tows is very powerful because a single test is able to provide a huge amount of filament strength data (several hundreds/thousands, depending on the number of filaments in a tow test specimen). The paper discusses the tow testing-based procedure to produce reliable statistical distributions of filament strength data and reproducible statistical parameters. The statistical distributions are determined by fitting the theoretical equation of tow tensile behavior to the results of experiments. This approach allows the bias and uncertainties introduced when using conventional methods to be alleviated. It is shown that the inherent scatter in fracture data is described by both the Weibull and the Normal distributions. The influence of various factors including sample size, specimen selection and probability estimator is discussed.

9:20 AM

(ICACC-S1-052-2016) Quantifying Amorphous Content in Commercially Available SiC Fibers

I. Wolford*[1]; T. Key[2]; M. O'Malley[1]; M. Cinibulk[1]; 1. Air Force Research Lab, USA; 2. UES, Inc, USA

SiC/SiC ceramic matrix composites (CMCs) with potential applications at ≥2700°F (1482°C) are of significant interest to the Air Force. The high temperature performance of SiC fibers used within these composites is greatly affected by the presence of amorphous SiOC and free carbon. Therefore quantification of this material within commercially available SiC fibers is extremely important. In this work Hi-Nicalon, Hi-Nicalon Type S, Tyranno SA3, Cef-NITE, and Sylramic SiC fibers were studied. Changes in mass, composition, grain size, and amorphous content were measured as a function of processing temperature and time. The amorphous SiOC and free carbon in each fiber was quantified using the spike-in method in conjunction with Rietveld refinement. Transmission electron microscopy (TEM) was used to confirm changes in fiber microstructure.

9:40 AM

(ICACC-S1-053-2016) Formation of Boron Nitride Interphase on SiC Fibers for SiC_f/SiC Composites by Electrophoretic Deposition Method and Their Mechanical Properties

K. Yoshida[1]; N. Mizuta[1]; T. Yano[1]; M. Kotani[2]; T. Aoki*[2]; T. Ogasawara[2]; 1. Tokyo Institute of Technology, Japan; 2. Japan Aerospace Exploration Agency (JAXA), Japan

Continuous silicon carbide fiber-reinforced silicon carbide matrix (SiC_f/SiC) composites have been recognized as key materials for aerospace industries, high-temperature gas turbines and future nuclear and fusion applications because they show a pseudo-ductile fracture behavior and excellent fracture tolerance. Fiber/matrix interfaces act as an important role for toughening and strengthening SiC_f/SiC composites. Currently, carbon or hexagonal-boron nitride (BN) has been formed on SiC fibers as the interphases, and these interphases have been generally formed by chemical vapor infiltration (CVI), chemical vapor deposition (CVD) or solution-coating/pyrolysis process. Present authors paid attention to electrophoretic deposition (EPD) process to form interphases on SiC fibers for SiC_f/SiC composites and demonstrated that EPD process was effective to form homogeneous C-interphase on SiC fibers. In this study, BN interphase on SiC fibers for SiC_f/SiC composites was formed by EPD, and unidirectional SiC_f/SiC composites were fabricated using the SiC fibers with BN interphases, and their mechanical properties were discussed. It was observed that plate-like BN particles were deposited well on the SiC fibers, and the homogeneous BN interphases were successfully formed on the SiC fibers.

10:20 AM

(ICACC-S1-054-2016) Model for Strength of Hi-Nicalon™-S SiC Fiber after Oxidation in Dry and Wet Air

R. Hay*[1]; P. Mogilevsky[1]; R. Krishnamurthy[1]; 1. Air Force Research Laboratory, USA

Hi-Nicalon™-S SiC fiber strengths were measured after oxidation between 700° and 1400°C in wet and dry air. Fiber strengths were modeled using oxidation and scale crystallization kinetics, change in load-bearing area, residual stress, and the method of superimposition for crack tip stress intensity factors. Growth stress from volume expansion in scales during oxidation, thermal stress, and stress from phase transformations in crystalline scales contribute to stress intensity factors. Compressive residual stress in scales increases strength. Tensile stress does the opposite. Methods for modeling strengths of fibers with partially crystallized scales are developed. Maps of predicted fiber strength as a function of oxidation temperature, time, and scale thickness are constructed and compared to experimental measurements of oxidized fiber strength. The model predicts the small strength increases that accompany glass scale formation and decreases that accompany crystallization at larger thickness, and explains some of the strength differences between fibers oxidized in dry and wet air. Modeling assumptions and strength degradation and enhancement mechanisms, including effects of impurities on crystallization, are discussed.

10:40 AM

(ICACC-S1-055-2016) Thermal and Mechanical Stability and Performance of SiC Fibers for SiC-SiC CMC's

E. B. Callaway*[1]; F. W. Zok[1]; 1. University of California, Santa Barbara, USA

The thermochemical history of fibers during composite processing can significantly affect fiber properties. The effects can include phase evolution, grain growth, surface roughening, and surface oxidation. The current study aims to investigate the mechanical stability of Hi-Nicalon-S SiC fibers during polymer impregnation and pyrolsis (PIP) processing. The stress-strain characteristics and Weibull statistics of fiber failure are obtained through fiber bundle uniaxial tension tests. These tests are performed on: (i) pristine (uncoated) tows, (ii) coated tows without a matrix, and (iii) coated tows (without a matrix) after each step in the heat treatments that simulate the PIP cycle. Fiber fracture surfaces are examined by SEM and TEM to ascertain the nature of microstructure evolution and fiber degradation during the processing cycle. The results will be compared to mini-composites tested during the various stages of processing with the aim of forming a processing space that produces satisfactory post-processing fiber properties.

11:00 AM

(ICACC-S1-056-2016) BN Interphase Oxidation in SiC/SiC CMCs

M. Wilson*[1]; E. Opila[1]; 1. University of Virginia, USA

The oxidation of Ceramic Matrix Composites (CMC) is a complex process due to the combined oxidation of ceramic fibers, matrix, and an interphase. Previously, the oxidation of free-standing Hi-Nicalon SiC fibers was studied. The fiber oxidation in a CMC, however, is affected by the addition of an interphase. In this study, the oxidation of SiC/BN/SiC CMCs was conducted in dry (O_2) and wet (50 v% H_2O/50 v% O_2) environments to examine the oxidation of a BN interphase. The CMC oxidation experiments were investigated using thermogravimetric analysis at temperatures of 800, 1200, and 1300°C. Scanning Electron Microscopy (SEM) was

used to characterize the morphology and extent of oxidation of the BN interphase as a function of temperature and environment. Volatility and relevant oxidation reactions also varied as a function of temperature, and were explored with SEM and Energy-Dispersive Spectroscopy (EDS). Extent of fiber oxidation in CMCs will be compared to the oxidation of free-standing fibers in both the dry and wet environments.

11:20 AM

(ICACC-S1-057-2016) Enhanced oxidation resistance of SiC/SiC minicomposites via slurry infiltration

J. Zhou*[2]; A. S. Almansour[1]; G. G. Chase[2]; G. Morscher[1]; 1. The University of Akron, USA; 2. University of Akron, USA

Environmental barrier coatings (EBCs) are required for SiC fiber reinforced SiC matrix composites (SiC/SiC) in application of turbine engine in order to provide elevated temperature chemical and environmental stability. For example, SiC-based composites will be degraded elevated temperatures due to the reaction of the protective silica layer with water to form volatile silicon hydroxide ($Si(OH)_4$). Oxide based coatings are required to protect the SiC material from these kinds of reactions. One approach could be to hybridize the matrix so that part of the matrix is the EBC material. A slurry-based approach is one way to achieve this. In this study, slurries were developed analyzed and optimized by changing slurry recipes, surface properties, infiltration process, and air sintering temperatures. Moreover, mullite-based slurry-derived EBC matrix/coating layers with different compositions were infiltrated into porous SiC/SiC minicomposites as a way to optimize slurry composition for infiltration and coating integrity. The best composition was determined by examining the longitudinal and cross-section of minicomposites using SEM. Afterwards, coated minicomposites were precracked in air at room temperature during tensile test then tested in tensile creep in air at 1200 C in order to study the type of protection that EBC provided at high temperatures.

11:40 AM

(ICACC-S1-058-2016) Tension-compression fatigue of an oxide/oxide ceramic composite at 1200°C in air and in steam

R. Lanser[1]; M. Ruggles-Wrenn*[1]; 1. Air Force Institute of Technology, USA

Tension-compression fatigue behavior of an oxide-oxide ceramic matrix composite was investigated at 1200°C in air and in steam. The composite is comprised of an alumina matrix reinforced with Nextel™720 alumina-mullite fibers woven in an eight harness satin weave (8HSW). The composite has no interface between the fiber and matrix, and relies on the porous matrix for flaw tolerance. Tension-compression fatigue behavior was studied for fatigue stresses ranging from 60 to 120 MPa at a frequency of 1.0 Hz. The R ratio (minimum stress to maximum stress) was -1.0. Fatigue run-out was defined as 10^5 cycles and was achieved at 80 MPa in air and at 70 MPa in steam. Steam reduced fatigue lives by an order of magnitude. Specimens that achieved fatigue run-out were subjected to tensile tests to failure to characterize the retained tensile properties. Specimens subjected to prior fatigue in air retained 100% of their tensile strength. The steam environment severely degraded tensile properties. Tension-compression fatigue was considerably more damaging than tension-tension fatigue. Composite microstructure, as well as damage and failure mechanisms were investigated.

S3: 13th International Symposium on Solid Oxide Fuel Cells (SOFC): Materials, Science and Technology

Degradation and Lifetime Prediction / Surface and Interfacial Interactions

Room: Crystal

Session Chairs: Vincenzo Esposito, Technical University of Denmark; Anil Virkar, University of Utah

8:30 AM

(ICACC-S3-042-2016) Factors limiting performance and lifetime of SOFCs (Invited)

N. H. Menzler*[2]; D. Roehrens[2]; J. Szasz[3]; T. Keuter[2]; A. Beez[2]; Q. Fang[2]; M. Bram[2]; E. Ivers-Tiffee[3]; O. Guillon[1]; 1. Forschungszentrum Juelich, Germany; 2. Forschungszentrum Juelich GmbH, Germany; 3. Karlsruhe Institute of Technology, Germany

Costs of SOFC (systems) are still the main hurdle for market entry. They can be directly minimized by reducing material and manufacturing costs but also indirectly by enhancing layer performance and by reducing degradation. The higher the cell performance, the less layers are needed to obtain the gross system power, while at the same time a low degradation rate is necessary to sustain the performance. The lower the voltage loss, the more power is available during operation. Several factors influence either the performance or the degradation rate. This presentation highlights some influencing factors, e.g. microstructures, powder characteristics and sintering parameters of the cathodic barrier layer which inhibits the interdiffusion of cathode elements to the electrolyte. Recent results have shown that this interaction drastically influences the power. Additionally, in stacks losses from contacting and interfaces have to be taken into account. And, on the other hand, during operation interactions happen: Cr containing species from the metallic interconnects interact with cathode materials. Furthermore, oxygen diffusion into the fuel side compartment caused by back diffusion from outside air during system shut down or free burning of the external reformer can lead to Ni re-oxidation. This leads to volume expansion, creation of stress and can finally result in electrolyte cracking and thus catastrophic cell and layer failure.

9:00 AM

(ICACC-S3-043-2016) Ageing of ceramic materials during solid oxide cells operation (Invited)

D. Montinaro*[1]; 1. SOLIDpower SpA, Italy

The recent interest in the fabrication of energy systems based on solid oxide devices suitable to operate in SOFC-, SOE- and reversible SOFC/SOE-mode leads to the development of new advanced ceramic materials which allow to operate at intermediate temperatures maintaining durable electrochemical performances. In the present work the ageing behaviours of specific stack materials and interfaces were simulated by exposing single components to severe SOFC operation environment and operating conditions.These tests include Area Specific Resistance Measurements performed on $MnCo_2O_4$-coated ferritic stainless steels and sealing glass samples applied on steel and YSZ. The ageing behaviour of single cells was also accelerated by increasing the current density. The effect of long term operation on stack materials under real operative conditions was also investigated by microstructural analyses on short stacks after 5000h operation in SOFC-mode in natural gas steam reforming conditions and after ca. 10000h in SOE conditions.

9:30 AM

(ICACC-S3-044-2016) Fundamental Study on Degradation of SOFC materials in AIST (Invited)

K. Yamaji*[1]; 1. AIST, Japan

NEDO project "Technology Development for promoting SOFC commercialization" (FY 2013- 2017) focuses on a life time of 90,000 h with a degradation rate of 0.1 % / 1,000 h. In this project, AIST is carrying out three main topics; evaluation of stacks durability, elucidation of degradation mechanism using thermodynamic analysis, and research and development of rapid evaluation method of durability. For the thermodynamic analysis, fundamental data on degradation are acquired and test methods on accelerating degradation due to impurities are investigated. Our recent research activities on degradation of SOFC materials is going to be introduced in this paper.

10:20 AM

(ICACC-S3-045-2016) Structure Optimization of Ni/YSZ Electrodes for Durable Solid Oxide Electrolysis Cells (Invited)

A. Hauch*[1]; K. Brodersen[1]; M. Chen[1]; A. Hagen[1]; K. Hansen[1]; P. Hendriksen[1]; J. Hjelm[1]; P. Jørgensen[1]; M. Mogensen[1]; T. Ramos[1]; 1. Technical University of Denmark, Denmark

Studies show that Ni/YSZ electrodes tested at high electrolysis currents suffer performance loss due to Ni migration away from the anode/electrolyte interface. The purpose of this work was therefore to optimize the Ni/YSZ electrode structures to hinder Ni migration. Optimization was done by varying Ni/YSZ ratios and particle size distributions (PSDs) for tape cast electrodes. Full Ni/YSZ-YSZ-CGO-LSC based SOEC were produced. Long-term steam electrolysis stability (1-2 kh) was tested and the SOEC were characterized via impedance spectroscopy and scanning electron microscopy. It was found that: 1) the polarization resistance increased during the first few hundred hours for all cells after which it stabilized, 2) a linear increase in ohmic resistance occurred for some SOEC, 3) the cells that experienced large ohmic resistance increase had significant loss of Ni in the active Ni/YSZ electrodes while the YSZ network seemed intact for all cells and 4) for cells having same Ni/YSZ ratios the densest Ni/YSZ electrodes showed the smallest ohmic resistance increase. We conclude that stable performance at high current density was achieved through structural optimization during ceramic processing. Degradation rate less than 0.4 %/kh was obtained at -1 A/cm^2 and 800 °C. Optimization of Ni/YSZ electrodes should aim at: 1) fine and size-matched PSDs, 2) high density and 3) well-dispersed/ mixed phases.

10:50 AM

(ICACC-S3-046-2016) Mitigation of Chromium Poisoning in SOFC

C. Liang[1]; B. Hu[1]; M. Mahapatra[1]; P. Singh*[1]; 1. University of Connecticut, USA

Chromium evaporation from iron and nickel base alloys, commonly used in the active electrochemical stacks and balance of plant has been extensively studied in our laboratory under nominal systems operating conditions. This presentation aims at gas phase chromium species poisoning of cathode and mitigation of chromium poisoning in intermediate to high temperature electrochemical systems operating in 600-1000C temperature range. Approaches for reducing the overall chromium flux ingested into the electrochemically active cell and stack will be outlined and experimental results will be presented. Thermochemical models for the gas-solid reactions and associated chromium capture mechanism will be discussed.

11:10 AM

(ICACC-S3-047-2016) Contribution of grain boundary segregation of impurity and oxygen vacancy to local grain boundary diffusion in aliovalent cation doped ZrO_2

T. Yokoi*[1]; M. Yoshiya[1]; 1. Osaka University, Japan

Grain boundary (GB) and GB segregation (GBSG) of point defects can have significant effects on GB diffusion of oxygen ions of nanocrystalline materials as well as polycrystalline materials for aliovalent cation doped ZrO_2, which is known as an ionic conductor. To control oxygen diffusion, it is critical to clarify atomic-level contributions of GB and GBSG to the GB diffusion since changes caused by GBs are usually confined to a few nanometers from GBs. However, it is still difficult to determine atomic arrangements at GBs and therefore the effects of GBs and GBSG on GB diffusion are still unclear. For this issue, we perform atomistic simulations to determine the preferred distribution of point defects at GBs in several bicrystal models. In addition, molecular dynamics (MD) simulations are performed to reveal the contribution of a point defects' arrangement to GB diffusion. Our results indicate that the point defects' arrangement is obviously nonrandom; the point defects occupy the specific sites at the GB. The trend is observed in all bicrystal models studied, and thus may occur in practical materials. In addition, our MD simulations indicate that the nonrandom point defects' distribution substantially affects GB diffusion. The results suggest that point defects' distribution is a critical parameter to control ionic conductivity.

11:30 AM

(ICACC-S3-048-2016) 1000+ h In-Operando XRD Tests of LSM/YSZ SOFC Cathodes in Combined H_2O and CO_2

J. S. Hardy*[1]; C. A. Coyle[1]; N. Canfield[1]; J. W. Stevenson[1]; 1. Pacific Northwest National Laboratory, USA

X-ray diffraction of the LSM/YSZ cathode on anode-supported SOFCs was performed during 1000 hour cell tests. A cell was operated at 775°C under constant current conditions at ~0.8 V while simultaneously exposed to 3% H_2O and 12% CO_2 contaminants in the cathode air. The resulting XRD patterns from the cathode were inspected visually and analyzed using Rietveld refinement to evaluate time-dependent changes. A gradual expansion of the LSM lattice was detected during exposure to the contaminants. Summation of the XRD patterns accumulated over the entire 1000+ hours of testing resulted in cumulative count times that made it possible to identify phases present in the cathode in quantities as low as one tenth of a percent. The minor phases included Mn-oxides, La-oxide, and La-zirconate pyrochlore. The performance, Rietveld refinement, and phase composition results will be compared to those of similar tests performed while the cathode air contained no contaminants or H_2O only. A summary of compositional changes in LSM that have the potential to cause the measured lattice expansion are discussed.

11:50 AM

(ICACC-S3-049-2016) Stability and performance issues of BSCF as oxygen electrode material for intermediate temperature proton-conducting SOEC/SOFC

S. Sun*[1]; Z. Cheng[1]; 1. Florida International University, USA

Intermediate temperature (400-700°C) solid oxide electrolysis cells/solid electrolyte oxide fuel cells (IT-SOEC/SOFC) have attracted great attention recently. The realization of IT-SOEC/SOFC is helped by adopting proper proton-conducting electrolyte materials, which offer better ionic conductivity compared to conventional oxide ion conducting electrolytes in intermediate temperature range. Besides that, oxygen electrode is often considered to be the main factor limiting the overall cell performance. One of the most promising cathode materials studied recently is $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$(BSCF) perovskite oxide, which offers low formation energy of oxygen vacancy and low polarization resistance. However, the performance, in particular, stability of BSCF electrode for proton conducting

SOFC at intermediate temperature has not been well addressed yet. This study aims to understand the mechanism of performance degradation during operation of BSCF/$BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$(BZCYYb)/NiO-BZCYYb anode-support proton-conducting SOEC/SOFC under various conditions. The focus is on revealing the impacts of CO_2 (>400ppm), water vapor, and other potential chemical reactions (e.g., between the BSCF and electrolyte) on cell performance and degradation, and the directions for future research to improve proton conducting IT-SOEC/SOFC will be pointed out.

S5: Next Generation Bioceramics and Biocomposites

Bioceramics III

Room: Coquina Salon F

Session Chairs: Thierry Azaïs, University Paris 6; Stephan Wolf, Friedrich-Alexander-University Erlangen-Neurnberg; Laurie Gower, University of Florida

8:30 AM

(ICACC-S5-017-2016) A Biomimetic Approach to Remineralization of Dental Caries (Invited)

N. Saxena*[1]; L. Gower[1]; G. Marshall[2]; S. Habelitz[2]; 1. University of Florida, USA; 2. University of California, San Fransisco, USA

Dental caries remains the most prevalent chronic disease in the United States. In this work, collagen mineralization approaches will be explored in order to restore dentin after demineralization. In the polymer-induced liquid-precursor (PILP) process developed by our group, anionic polymers are used to sequester ion clusters, mimicking the role of non-collagenous proteins found in mineralized tissues. This results in liquid-liquid phase separation, forming droplets that infiltrate collagen fibrils and lead to intrafibrillar mineralization. Our group has had success in mineralizing collagen scaffolds to the levels found in dentin as well as restoring 50% of the mechanical properties of dentin after remineralization via the PILP process. While previous work in our group has utilized just an anionic polymer, polyaspartic acid, this work explores the efficacy of PILP mineralization with the addition of other molecules, with the goal to further enhance mechanical properties and restore the dentin back to its native structure and properties.

8:50 AM

(ICACC-S5-018-2016) Solid state NMR characterization of surface species from biominerals (Invited)

T. Azaïs*[1]; 1. University Paris 6, France

In this communication, we show how solid state nuclear magnetic resonance (ssNMR) can allow the structural characterization of surfaces from natural biominerals including bone apatite and aragonite from nacre. Bone mineral consists of nanoplatelets compositionally close to hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$. It has been proposed since the late 50's that the crystalline apatitic core of bone mineral is covered by an independent mineral domain. We show that the use of a combination of highly advanced ssNMR techniques applied to fresh and intact bone samples leads to an unprecedented structural characterization of that outer domain: in particular, we demonstrate that the surface layer of bone mineral is amorphous, highly hydrophilic and composed of divalent ions: Ca^{2+}, HPO_4^{2-}, CO_3^{2-}. Moreover, we demonstrate that aragonite (polymorph of $CaCO_3$) platelets from nacre are also surrounded by an amorphous layer that can be selectively studied through ^{13}C ssNMR. Finally, we will discuss the benefit of using dynamic nuclear polarization (DNP) combined to ssNMR to selectively enhanced signals from surface species from mineral particles. Indeed, DNP is a recently developed technique that allows the magnetization transfer from radicals unpaired electrons to nuclei inducing a huge enhancement of the NMR signal (up to 150 !).

9:10 AM

(ICACC-S5-019-2016) Textural Clues about the Formation Mechanism of Nacreous-Type Biominerals (Invited)

L. Gower*[1]; 1. University of Florida, USA

The nacreous layer of mollusk shells has been a well-studied biomineral because of its remarkable combination of strength and fracture toughness. Nacre consists of thin tablets of aragonite that are organized into a brick-n-mortar structure, with organic matrix serving as the mortar as well as a modulator of the biomineralization reaction that forms it. There are two main types of nacre, sheet and columnar, which appear to form by somewhat different cellular mechanisms, but ultimately form in a similar nanolaminated architecture. There is also a calcitic analogue to nacre found in the seminacre of bryozoan. These organisms are from an entirely different phylum, yet form a similar tabular morphology, but with more random organization. Our *in vitro* model system, which uses a polymer-induced liquid-precursor (PILP) process to mimic the tabular and sheet-like morphology found in nacre, also creates a variety of crystallographic features that emulate biominerals, including nanogranular or mesocrystalline texture, laminated subtexture of tablets, triaxial strain, anisotropic occlusion of polymer, and unusual macrostepped screw dislocations that could be responsible for nacre's tessellated structure. This talk will review the literature and discuss a variety of mineralogical signatures that may be providing clues to the formation mechanism of nacreous structures.

9:40 AM

(ICACC-S5-021-2016) Mineralization by Colloid Attachment and Transformation allows for Simple Generation of Nanogranular Composite Materials with Complex Crystallinity (Invited)

S. E. Wolf*[1]; 1. Friedrich-Alexander-University Erlangen-Nürnberg, Germany

Biominerals, such as nacre, typically form *in vivo* by a nonclassical since colloid-mediated mineralization process. A similar mineralization by colloid attachment and transformation (MCAT) can be easily triggered *in vitro* by the employment of polyelectrolytes in the so-called polymer-induced liquid-precursor (PILP) process. The polymeric additive, imitating the action of unusually acidic proteins *in vivo*, suppresses classical nucleation of a solid crystalline phase and promotes the formation of a transient and highly hydrated liquid-condensed mineral precursor phase. This unusual phase becomes the crucial mineralization agent changing fundamentally the character of the mineralization reaction. The PILP process counts therefore among the ambassadors of nonclassical crystallization processes which currently shake our traditional perception of crystallization processes. In this contribution, we will give an overview of the current state of knowledge concerning the PILP process, its connection to nonclassical crystallization processes, and its morphosynthetic potency. We will finally demonstrate that the pseudomorphicity of the PILP process enable us to generate complex crystallographic properties such as crystal lattice tilting, twisting and crystal branching similar to those which toughen biominerals *in vivo*.

10:20 AM

(ICACC-S5-022-2016) An in-vitro model system to study the role of acidic biopolymers in idiopathic stone formation (Invited)

A. Lovett*[1]; D. Rodriguez[1]; S. Khan[1]; L. Gower[1]; 1. University of Florida, USA

Randall's plaques (RP) are consistent among the most common type of kidney stone formers, idiopathic calcium oxalate stone formers. This group forms renal stones without any systemic symptoms, which adds to the difficulty of understanding this painful disease. One theory of RP formation is that calcium phosphate deposits initially form in the thin loops of Henle, which then spread into the interstitium, and ultimately make their way across the urothelium, where upon exposure to urine, serve as a nidus for overgrowth with calcium oxalate into a stone. Many of the unusual morphologies in

RP and stones can be reproduced using a polymer-induced liquid precursor process where acidic polypeptides induce a liquid phase amorphous precursor to the mineral, yielding non-equilibrium crystal morphologies. Since there are many acidic molecules present in renal tissue and urine, this system may be involved. Thus, our goal is to develop an in vitro model system of the two stages of stone formation to study the role of various molecules. The development of "biomimetic" RP using decellularized kidney tissue is investigated, which will serve as a nidus for calcium oxalate overgrowth studies. The papilla are mineralized and then characterized to determine if the morphologies match that of native plaque. The goal is to develop strategies to avoid RP and its detrimental consequences in stone formation.

10:40 AM

(ICACC-S5-023-2016) Preceramic Polymer-derived Sphene bioceramic coating on cpTi Substrates for Orthopaedic Implants

H. Elsayed[1]; L. Biasetto[2]; F. Bonollo[2]; P. Colombo[1]; E. Bernardo*[1]; 1. University of Padova, Italy; 2. Università di Padova, Italy

We coated cpTi substrates with a bioceramic layer using a novel process involving a preceramic polymer containing active fillers, and the coatings were deposited using a commercially available airbrush. The sphene ($CaTiSiO_5$) bioceramic coating was obtained from a silicone powder containing $CaCO_3$ and TiO_2 particles as active fillers. Different analyses were conducted on the samples, including X-ray diffraction, FE-SEM coupled with EDS, surface roughness and adhesion tests (scratch test). The presence of residual stresses deriving from the different CTE of the coating and substrate was evaluated by placing Knoop hardness indents along the coating interface. The analysis proved that we were able to produce a calcium titanate/titanium bioceramic composite in which the bioactive ceramic coating had a strong adhesion to the underlying metal substrate, making it a good candidate for orthopedic and dental implants.

11:00 AM

(ICACC-S5-024-2016) Biomimetic Bone: Reproducing Nature's Hierarchical Composite (Invited)

B. Wingender*[1]; P. Bradley[2]; J. Ruberti[2]; L. Gower[1]; 1. University of Florida, USA; 2. Northeastern University, USA

We propose that the next generation of bone substitutes could be load-bearing if they are engineered as a bioactive material which emulates the hierarchical organization of the interpenetrating protein and mineral phases and is capable of maintaining the mechanical properties throughout bioresorption. The polymer-induced liquid-precursor (PILP) process has been previously shown to result in the intrafibrillar mineralization of a variety of type I collagen substrates, which has reproduced the fundamental nanostructural of native mineralized tissues. In order to achieve bone-like mechanical properties, we are now targeting the lamellar microstructure of bone by preparing films of dense, collagen scaffolds that are assembled with cholesteric order. These liquid-crystalline (LC) collagen scaffolds are made by concentrating acidic collagen solutions, and then stabilizing the assembly through fibrillogenesis brought on by neutralization. We then mineralized these dense, LC collagen constructs via the PILP process to create a bioresorbable material with a high degree of mineral loading, mimicking bone's hierarchical organization from the nanoscale to the microscale. It is hypothesized that this biomimetic material will enable us to emulate the high strength and toughness of bone, while also providing a bone-like matrix that can stimulate cellular activity to regenerate natural bone tissue.

S6: Advanced Materials and Technologies for Direct Thermal Energy Conversion and Rechargeable Energy Storage

Lithium Batteries and Beyond

Room: Tomoka A

Session Chairs: Valerie Pralong, CNRS ENSICAEN; Kisuk Kang, Seoul National Univeristy

8:30 AM

(ICACC-S6-036-2016) Composite Cathodes with LiF/NaF for Li/Na-ion Batteries (Invited)

S. Okada*[1]; A. Kitajou[1]; H. Hori[1]; N. Dimov[1]; T. Yamashita[1]; D. Tsunoe[1]; P. Barpanda[2]; 1. Kyushu University, Japan; 2. Indian Institute of Science, India

As the example of composite cathode with LiF, the synthesis and cathode performances of the composite cathode of LiF and FeO are introduced. Rutile-type LiFeOF is simply obtained by the ball milling method and the rechargeable capacity was much better than that of the iron-based cathodes such as LiFePO4. Rocksalt-type LiFeOF was obtained from LiF and FeO by the dry ball-milling method under ambient pressure. The reversible capacity was 290 mAh/g with an average voltage of 2.5 V. The energy density over 720 mWh/g is the highest energy density among iron-based insertion-type cathode materials. In addition, the electrochemical activity of Li in LiFeOF was confirmed by the charge and discharge reactions in the full cell with LiFeOF cathode and Li4Ti5O12 anode. In the presentation, the other examples of the composite cathodes with LiF/NaF such as LiF-VPO4 and NaF-FeSO4 will be also introduced.

9:00 AM

(ICACC-S6-037-2016) Olivine with zero anti-site defect and three dimensional lithium diffusion paths (Invited)

K. Kang*[1]; K. Park[1]; 1. Seoul National Univeristy, The Republic of Korea

Lithium iron phosphate (LFP) has attracted tremendous attention as a next-generation electrode material in lithium rechargeable batteries for large scale energy storage systems due to the use of low-cost iron and chemical/electrochemical stability. While the lithium diffusion in LFP, the essential property in battery operation, is relatively fast due to the one-dimensional tunnel present in the olivine crystal, the tunnel is inherently susceptible to immobile anti-site defects which, if any, block the lithium diffusion and lead to the inferior performance. Herein, we demonstrate that the kinetic issue arising from the defects in LFP can be completely eliminated in a new olivine LFP, which we successfully synthesized for the first time. The doping in the olivine structure reduces the concentration of defects in the tunnel by 7 orders of magnitude. Moreover, it opens up a new lithium diffusion path along the [101] direction making the olivine LFP as a three-dimensional lithium diffuser. We also find that the intrinsic energy barrier for phase transition gets notably lower in the lithium excess olivine LFP. The fundamentally different nature of the new olivine than normal LFP additionally induces faster charging capability, lowering thermal solid-solution temperature and less memory effect.

9:30 AM

(ICACC-S6-038-2016) Silicon anodes and electrolyte interactions (Invited)

K. Edstrom*[1]; C. Xu[1]; F. Lindgren[1]; M. Yue[1]; T. Gustafsson[1]; F. Bjorefors[1]; 1. Uppsala University, Sweden

Silicon electrodes are extensively studied due to their possibility to increase the total capacity of a lithium battery. The studies are focused on different ways to handle large particle expansion during lithium reactions by studying: binder formulations for electrode preparation, mixing with suitable amounts of carbon, influencing

the surface chemistry, include different additives in the electrolyte, using different lithium salts, etc. In this presentation we will give examples of how we have used different techniques to understand the interactions between different electrolytes or binders and silicon electrodes. We will show new results on electrodes where the silicon particles are embedded into grafén and binder to prevent direct exposure to electrolyte and where the cycling efficiency is considerable improved. We will discuss our results in the light of careful interface characterisation using HAXPES (high kinetic XPS) and ambient pressure XPS.

10:20 AM

(ICACC-S6-039-2016) Design of metal oxide nanoparticles to the control the electrochemical properties (Invited)

S. Cassaignon*[1]; 1. UPMC, France

Emergence of nanotechnology increasingly shows examples of the material potentiality which has, at least one dimension less than 100 nm. The preparation of nano-objects by soft chemistry in aqueous with crystal structure, size and morphology perfectly controlled is based on the use of molecular precursors and adjustment of the physico-chemical parameters (acidity, ionic strength, temperature) during the precipitation of the solid. The growth of nano-crystals can be limited or favored in some crystallographic directions. It is also possible to involve redox processes in addition to the acido-basic reactions. That can significantly enhance the potentiality of this chemistry in the design of particles. Furthermore, the synthesis of hierarchical materials with multiple scales of organization and often formed from the assembly of nanoparticles, raises a growing interest, mainly thanks to their ability to combine the functions of the various elementary units . This allows to consider interesting applications of these systems in various fields and especially in the field of Energy.

10:50 AM

(ICACC-S6-040-2016) Challenges in magnesium ion batteries (Invited)

M. Matsui*[1]; 1. Japan Science and Technology Agency, Japan

Rechargeable magnesium batteries are expected as a potential post lithium-ion system, because the magnesium metal anode has 1.9 times higher capacity density compared with lithium metal. Furthermore the magnesium metal anode typically does not form dendrite during the charging process. Despite of these advantages of the magnesium metal anode, there still remain a lot of challenges in the rechargeable magnesium batteries. Firstly, the electrolyte solutions compatible with magnesium metal anode are very limited, because conventional ionic electrolyte solutions easily form passivation layer at the surface of the magnesium metal. In order to realize the reversible magnesium deposition / dissolution, the electrolyte solutions need to contain halides, which causes corrosion of positive electrodes. Therefore, finding a novel electrolyte solution which shows reversible magnesium deposition / dissolution and does not contain any corrosive species, is very crucial for the development of the rechargeable magnesium batteries. Another approach for the anode is using intermetallic compounds such as Mg_3Bi_2 or Mg_2Sn, because these intermetallic compound anodes are compatible with the conventional ionic electrolyte solutions. In the conference, several analytical study results for the anode / electrolyte interphase of the magnesium metal and the intermetallic compound anodes will be presented.

11:20 AM

(ICACC-S6-041-2016) Thermal loss analysis in graphite anode based 18650 type lithium ion cells

M. Balasundaram*[1]; C. Yap[1]; V. Ramar[1]; L. Lu[1]; A. Tay[1]; P. Balaya[1]; 1. National University of Singapore, Singapore

The operation of lithium cobalt oxide (LCO) cathode based lithium-ion batteries combined with graphite anode poses potential safety concerns owing to unstable structure of the former especially at high potential. Studies in literature reported that mixed transition metal oxides derived from lithium cobalt oxide such as NMC and NCA show comparable electrochemical performance with improved thermal stability. Lithium iron phosphate (LFP) is another interesting cathode material which shows excellent thermal stability despite low specific capacity. Thermal studies are performed on stable cathode materials against graphite to determine heat generation characteristics under different testing conditions. Contribution of reversible and irreversible heat losses to the total heat loss in every cathode/graphite cell is reported. Co-rich NMC released more heat during a charge-discharge cycle compared to the other chemistries. Ni-rich NMC showed lesser reversible heat generation due to high structural stability. NCA/graphite battery showed nominal heat generation with good electrochemical performance. LFP is proved to be excellent in terms of thermal stability owing to lesser heat generation showing good electrochemical performance at higher C rates. Results obtained from thermal loss analysis can be used to develop an electrochemical-thermal model in order to understand the underlying mechanisms for thermal losses.

S7: 10th International Symposium on Nanostructured Materials: Functional Nanomaterials and Thin Films for Sustainable Energy Harvesting, Environmental and Health Applications

Nanomaterials for Sensing Applications I

Room: Coquina Salon A

Session Chairs: Yakup Gönüllü, University of Cologne; Shiping Song, Shanghai Institute of Applied Physics, Chinese Academy of Sciences

8:30 AM

(ICACC-S7-053-2016) Silicon Nano-Biotechnology for Biosensing and Bioimaging (Invited)

Y. He*[1]; 1. Institute of Functional Nano & Soft Materials (FUNSOM), Soochow University, China

Thanks to unique properties of silicon nanomaterials, many proof-of-concept studies have opened up promising avenues for establishing novel silicon nanotechnology-based biosensing and bioimaging techniques. Typically, silicon nanomaterials featuring unique electronic/optical/mechanical properties have been widely employed for constructing a number of biosensing devices with excellent sensitivity and specificity, high reproducibility, and multiplexing capabilities. On the other aspect, compared to well-established fluorescent proteins/organic dyes-based bioprobes of severe photobleaching property and II-VI fluorescent quantum dots (QDs)-based nanoprobes involving heavy metal-induced safety concerns, silicon nanoparticles (SiNPs) feature strong fluorescence, robust photostability, and excellent biocompatibility. Those attractive merits have triggered extensive exploration of SiNPs as potentially ideal biological fluorescent probes for long-term and real-time bioimaing. Here we review representative and promising achievement to highlight the remarkable development of silicon nanomaterials for biosensing and bioimaging applications in recent years, with the hope to promote the awareness of the state-of-art of silicon nano-biotechnology.

9:00 AM

(ICACC-S7-054-2016) Activating-with and activated vanadia. Semiconductor nanocrystals embedded in V_2O_5-like layers: solvothermal synthesis and gas-sensing enhancement (Invited)

M. Epifani*[1]; 1. CNR-IMM, Italy

Intensive research is under way for modifying the properties of semiconductor nanocrystals by suitable combinations with other structures. In this work the surface modification of TiO_2 and SnO_2 nanocrystals will be reviewed, through the solvothermal deposition of V_2O_5-like layers. TiO_2 modification resulted in both bulk doping by V(V) and surface deposition of dense V oxide species, with a local environment related to V_2O_5. SnO_2 nanocrystals, instead, were enwrapped by V_2O_5 layers providing a distinctive Raman signal, while the bulk of the nanocrystals did not show any appreciable structural modification. These nanocrystals can be easily processed for preparing gas-sensing devices. TiO_2 anatase nanocrystals were not buried in V_2O_5, and their remarkably enhanced gas-response to acetone and ethanol, by about two orders of magnitude with respect to pure TiO_2, was interpreted as synergistic result of interaction with activating surface vanadia species. SnO_2 nanocrystals were wrapped in the V_2O_5 layers, which then directly interacted with the gaseous analytes. In this case, the thin surface V_2O_5 layers showed remarkably enhanced ethanol response with respect to bulk V_2O_5, which was interpreted as vanadia activation by interaction with the underlying SnO_2 nanocrystals.

9:30 AM

(ICACC-S7-055-2016) Graphene and reduced graphene oxide decorated nanoparticules for electrochemical detection and electrogeneration of hydrogen peroxide (Invited)

M. Siaj*[1]; 1. UQAM, Canada

For this talk, two projects will be presented based graphene and graphene oxide decorated nanoparticules. The first project will be devoted to a tunable decoration of CVD- graphene with Rhodium nanoparticles for enhanced electrochemical detection of hydrogen peroxide (H2O2), in which a simple approach to the development of a single-layer graphene decorated with rhodium nanoparticles (RhNPs) will be presented. Graphene decorated with Rhodium Nanoparticles could be a sensitive sensor for hydrogen peroxide. For the second study, the Nb2O5 nanoparticles supported on reduced graphene oxide sheets as electrocatalyst for the H2O2 electrogeneration will be discussed. Hydrothermally prepared nanocomposites of Nb_2O_5 nanoparticles on reduced graphene oxide (rGO) were tested towards the oxygen reduction reaction (ORR), via the production of H_2O_2. Our results show that the ORR activity to H_2O_2 electrogeneration on the rGO catalyst, in both acid and alkaline media, occurs at lower overpotential and with higher selectivity with respect to Printex 6L catalyst. Thus, the high performance of Nb_2O_5-rGO electrocatalyst makes it viable alternative to Gas Diffusion Electrodes for hydrogen peroxide in-situ production for organic wastewater treatment applications.

9:50 AM

(ICACC-S7-056-2016) Rapid detoxification of water using organic-inorganic heterogeneous photocatalysts under visible irradiation via chemical approach

R. C. Pawar[1]; S. Kang[1]; C. Lee*[1]; 1. Hanyang University ERICA campus, The Republic of Korea

The rapid growth of various industries worldwide is a major concern because of its adverse effect on human health and environment. Photocatalysis is the most efficient and green technique that could be applicable in water purification. Number of photocatalysts such as TiO2, ZnO, WO3, BiVO4, Ag3PO4 have been reported successfully for effective degradation of organic pollutants. Nevertheless, the obtained efficiency of these photocatalysts is not sufficient to commercialize photocatalysis technology. Mainly, recombination of charge carriers and poor visible light absorbance limits their performance. Therefore, it is essential to develop new approach and heterojunctions which could provide superior performance. Hence, we explored photocatalysts based on g-C3N4, ZnO, Fe2O3, CNTs and graphene heterojunctions using chemical approach. The fabricated composites were characterized by different analytical tools and confirmed their phases. Then, these composites were used to degrade methylene blue and rhodamine B under visible light. It was found that heterogeneous composites exhibit higher photocatalytic activitycompared to single component material, which is attributed to effective charge separation and transportation of photo-electrons. Therefore, these nanocomposites can be used in water purification devices.

Nanomaterials for Sensing Applications II

Room: Coquina Salon A

Session Chairs: Mohamed Siaj, UQAM; Thomas Fischer, University of Cologne

10:30 AM

(ICACC-S7-057-2016) Functional Nanomaterials with Rare-Earth Doped Ceramics for Biomedical Applications (Invited)

K. Soga*[1]; M. Kamimura[1]; 1. Tokyo Univ. of Science, Japan

Rare-earth doped ceramics nanoparticels (RED-CNPs) has been known to emit efficient fluorescence in near infrared wavelength region. Namely, the region with a wavelength more than 1000 nm is called "second biological window (SBW)" with lower loss than in the first one in 800-1000 nm. The authors has developed nanostructured materials for biomedical photonics I the SBW by using the RED-CNPs. The paper will review the potential of the biophotonics in the SBW by using the RED-CNPs including nanothermal imaging.

11:00 AM

(ICACC-S7-058-2016) A novel miRNA biosensor based on the electrochemical catalysis triggered by the hybridization on a Nanotip electrode

Y. Wen[2]; L. Wang[2]; L. Li[2]; L. Xu[2]; Q. Xu[2]; G. Liu*[2]; N. Jia[1]; 1. Shanghai Normal University, China; 2. Shanghai Institute of Measurement and Testing Technology, China

Electrochemical biosensors have attracted plenty of research interest for their advantages of high sensitivity, low economy/time cost and portability. Whereas, the signal/noise ratio (S/N) of electrochemical biosensors is often limited by mass transport and the surface crowding effect at the water-electrode interface. Although the electrochemical catalysis has shown great potential in signal amplification to increase the S/N [1], the current enhancement is inevitably limited due to the high current background on microscopic electrode surface. Thus various nanostructured electrodes were developed and applied for electrochemical biosensors. One of our former study showed that a gold nanotip electrode with a 100 nanometer-sized cone shaped tip could help to regulate the DNA hybridization and ion translation in the self-assembling monolayer [2]. In this work, we studied the electrochemical catalysis reaction between $Ru(NH_3)_6^{3+}$ and $Fe(CN)_6^{3-}$ on the DNA self-assembling layer (SAM) on the surface of the nanoelectrode, and constructed a high S/N biosensor for the detection of microRNA (miRNA).

11:20 AM

(ICACC-S7-059-2016) DNA-mediated metal nanoprobes with SERS-active nanogaps for multiplex biosensing

S. Song*[1]; S. Mathur[2]; 1. Shanghai Institute of Applied Physics, Chinese Academy of Sciences, China; 2. University of Cologne, Germany

Uniform metal nanostructures with well-defined nanogaps hold great promise for ultrasensitive surface-enhanced Raman scattering (SERS) analyses. Nevertheless, the direct synthesis of such SERS nanotags with strong and stable SERS signals remains extremely

challenging. Here, we report a DNA-mediated approach for directly synthesizing gold-gold (Au-Au) and gold-silver (Au-Ag) nanostructures with interior nanogaps via orienting the growth of gold/silver on the surface of DNA-modified gold nanoparticles (AuNPs). The SERS intensities of these nanostructures were critically dependent on the area of the nanogap between the gold core and gold/silver shell. We found that the elimination of sodium chloride (NaCl) was critical for the formation of the interior nanogaps. We also found that the formation of nanogaps was finely tunable by controlling the surface density of the oligonucleotides on the gold nanoparticles. Thus, we obtained nanostructures in high yield with a high SERS signal enhancement factor of ~ 1.0×10^9, much higher than that of metallic nanostructures without nanogaps. Importantly, the nanostructures are easily biological functionalized or have the inherent ability for bio-recognition. We have developed a sensitive and specific SERS method for multiplex biosensing.

11:40 AM

(ICACC-S7-060-2016) Highly Selective p-n heterostructured TiO_2 nanotubes for gas sensing application

Y. Gönüllü*[1]; B. Saruhan-Brings[2]; S. Mathur[1]; 1. University of Cologne, Germany; 2. DLR - German Aerospace Center, Germany

In the last decades, atmospheric pollution in urban areas has achieved to critical levels. Processes involving combustion in aircrafts, energy and power production and automobile engines as well as through industrial settlement are the main sources of the pollution. Detection and control of the emission relies on the development of the precious and selective gas sensors. TiO_2 is non-toxic and low cost and has excellent chemical stability. It can pose semi-conductive properties on doping. Nevertheless, TiO_2 based gas sensors still need improvement for the achievement of high-temperature sensitivity, stability or efficiency. One of the methods to improve the performance of the TiO_2-based gas sensor devices is the increase of surface area by structuring the sensors. . Second solution for higher efficiency or sensitivity and better selectivity at the TiO_2 based gas sensor devices is the doping of TiO_2 with different valence elements. In this study, we report the synthesis of highly ordered TiO_2 nano-tubes by anodic oxidation. The as obtained TiO_2 NTs presented n-type behaviour. The TiO_2-NTs were modified by Cr doping in order to have p-type behaviour. The sensors produced using these nano-tubular layers are investigated for the sensing properties towards NO_2 and CO at the temperature range of 300°C – 500°C.

12:00 PM

(ICACC-S7-061-2016) Silicon nanowire field-effect transistor based biosensors for biomolecular detection and medical diagnostics (Invited)

A. Gao[1]; N. Lu[1]; Y. Wang[1]; T. Li*[1]; 1. Shanghai Institute of Microsystem and Information Technology, China

Quantification and detection of biochemical species are of utmost importance for biomedical applications. Silicon nanowire eld-effect transistors (SiNW-FETs) have recently drawn tremendous attention as a promising tool in biosensor design because of their ultrasensitivity, selectivity, and label-free and real-time detection capabilities. Here, we review the device fabrication and biomedical applications of SiNW-FET sensors. There are two major fabrication techniques in preparing SiNW-FETs: ''top-down'' and ''bottom-up''. The ''top-down'' method is normally carried out through lithographic processes combined with an electron-beam technique, while the ''bottom-up'' processes start with the growth of SiNWs followed by SiNW assembly and electrode fabrication. The applications of SiNW-FETs in the fields of biomedical sciences were discussed. SiNW-FETs have been employed in the detections of proteins, DNA sequences, small molecules, cancer biomarkers et al. Moreover, we show the integrated SiNW-FET arrays enable multiplexed detection for biomedical applications. The major limitations and future directions of SiNW-FET nanosensor were also discussed. This review clearly shows the great potential of SiNW-FET device for serving as powerful new tools in biological and medical diagnostics.

S8: 10th International Symposium on Advanced Processing and Manufacturing Technologies for Structural and Multifunctional Materials and Systems (APMT10)

Novel Ceramic Processing IV

Room: Coquina Salon B

Session Chairs: Francis Cambier, BCRC; Satoshi Tanaka, Nagaoka University of Technology

8:30 AM

(ICACC-S8-047-2016) Effect of acetate on the Coarsening, Processing and Sintering of ZnO nano-powder (Invited)

B. Dargatz[1]; J. Gonzalez-Julian[1]; O. Guillon*[1]; 1. Forschungszentrum Juelich, Germany

Zinc acetate in combination with water plays a key role during the coarsening of zinc oxide (ZnO) nanocrystals at moderate temperature (85 °C) in air. The growth of ZnO nanocrystals is well known in liquid phase systems, but this work shows that this process is strongly enhanced in powder form by the presence of residual acetate. In contrast, particle size stayed almost constant if pure zinc oxide powder was used. This growth is expected to slowly occur during storage even under ambient conditions. The retention of nanocrystallinity in dense ceramic materials is still a challenge, even with the application of external pressure during sintering.The compaction behavior of high purity and acetate enriched zinc oxide (ZnO) nano-powders was also investigated.

9:00 AM

(ICACC-S8-048-2016) Development of fabrication technique for microstructurally-controlled advanced nanocomposites (Invited)

H. Muto*[1]; 1. Toyohashi University of Technology, Japan

The mechanical mixing techniques have conventionally used for fabricating composite particles. However, these techniques are including several issues for designing the nano-structure of composite particles. In order to overcome these issues, novel processing technique was successfully developed to fabricate integrated composite powders by present author. The fabrication of integrated composite powder involves the sequential adsorption of oppositely charged polyelectrolytes, *i.e.*, PSS (Poly(sodium 4-styrene sulfonate)) and PDDA (poly(diallyldimethylanmoniumchloride)) on surface of matrix and additive grains, respectively in order to produce electrically charged particles. The integrated composite particles, i.e., large-sized-particles coated with nanoparticles were successively obtained by the mixing with oppositely charged particles in the solvent. In this study, the microstructurally-controlled advanced nanocomposites have fabricated via integrated composite powders.

9:20 AM

(ICACC-S8-049-2016) Advancements in Zirconia Technology

B. Farber*[1]; 1. Zircoa Inc, USA

Material development for high performance milling media tailored to specific application requirements will be described with an emphasis on QC testing, product consistency validation and application support tools.

9:40 AM

(ICACC-S8-050-2016) Fabrication of Magnesium Oxide Ceramics with Density Close to Theoretical Using Nanopowders

J. Yang*[1]; T. Lin[1]; B. Manett[1]; J. Young[1]; E. Medvedovski[2]; 1. SCI Engineered Materials, USA; 2. Consultant, Canada

Magnesium Oxide (MgO) ceramics has a proven high potential for thermal management, corrosion protection, semiconductor and electronic applications due to its superior mechanical and refractory properties, chemical inertness, thermal conductivity and specific electrical properties. In many industrial applications, high purity, highly dense ceramics should be used. However, achievement of fully dense MgO ceramics is still a challenge (using pressure-assisted and pressureless sintering) despite many years of research. In the present work, practically fully dense (99.5+% of TD with almost zero porosity) and high purity (99.95%) MgO ceramics have been attained using nanopowders without sintering aids. Sintering and the factors affecting densification and grain growth have been studied for the pressure-assisted process.

10:20 AM

(ICACC-S8-051-2016) Synthesis and characterization of lightweight ceramic foam core for sandwich TPS (Invited)

C. Tsai[2]; R. Bordia*[2]; S. Bland[1]; M. Chen[3]; S. P. Joshi[1]; 1. NextGen Aeronautics, USA; 2. Clemson University, USA; 3. Air Force Research Laboratory, USA

The light weight foam core is fabricated using an inexpensive manufacturing process from a pre-ceramic polymer that can be tailored for thickness and gradient of porosity without a substantial increase of weight of the structure. Ceramic foams of average density as low as 0.15 g/cc and hierarchical porosity ceramic foam of average density as low as 0.13 g/cc are synthesized. The processing parameters required to develop the core material that would improve the specific structural and thermal properties are described. The manufacture of different configuration of planner prototypes with uniform macro-porosity, gradient macro-porosity, and uniform macro-porosity with uniform micro-porosity porous ceramic cores is described. The density, macrostructure, microstructure, mechanical and thermal characterization of the foams are summarized. Comprehensive multi-scale characterization of the foams including 3D microstructure and strut microstructure are performed. Thermal exposure test result of a core sandwich with a ceramic matrix composite facesheet will also be presented.

10:50 AM

(ICACC-S8-052-2016) Graphene/silicon carbide cellular structures fabricated by robocasting

B. Román-Manso[1]; G. de la Osa[1]; M. I. Osendi[1]; P. Miranzo[1]; M. Belmonte*[1]; 1. Institute of Ceramics and Glass, CSIC, Spain

Silicon carbide (SiC) cellular ceramics have a wide range of applications like chemically inert filters, heat exchangers or catalytic supports. The incorporation of graphene nanoplatelets (GNPs) to these cellular structures could provide them additional functionalities, such as electrical conductivity, as well as adsorption of gas-phase molecules for sensors. Here, complex three dimensional (3D) cellular structures of GNPs/SiC with nanoplatelets contents ranging from 0 to 100 vol.% were assembled by Robocasting. Concentrated shear thinning colloidal inks of GNPs/SiC powders mixtures were formulated as a function of the GNPs content and, then, robocast following a designed cuboid or cylindrical pattern. The scaffolds were densified by pressureless spark plasma sintering. Lightweight GNPs/SiC cellular structures with densities ranging from 0.3 g•cm^{-3} (pure graphene monoliths) to 1.6 g•cm^{-3} (plain SiC) were developed. The electrical conductivity of the scaffolds increased with the GNPs concentration and showed anisotropy between the transverse and longitudinal directions relative to the extruded rods. Besides, the compression strength of the cellular structures decreased with the GNPs content. These functional 3D lattices are promising for applications where specific directional current flows are required.

11:10 AM

(ICACC-S8-053-2016) Investigation of comminution process of e-waste in drum type agitation mill using the discrete element method

Y. Tsunazawa*[1]; S. Fukui[1]; C. Tokoro[1]; 1. Waseda university, Japan

A printed circuit board (PCB) is an important constituent of e–waste, which has various kinds of electronic components with valuable and/or hazardous materials. Recycling of PCBs is an important subject from the viewpoint of the recovery of valuable metals and waste treatment. Since some of useful critical metals like Ta are concentrated in a specific component, a selective grinding such as parts detachment from the board is an effective method. However, the mechanism and the effectiveness of the selective grinding have been unclear. The objective of this study was evaluation of the comminution performance of drum type agitation mills. In this study, the behavior of PCBs was simulated by the discrete element method (DEM) coupled with computational fluid dynamics (CFD). Additionally, to model the shape of PCBs, the particle based rigid body model was included into the DEM. In this study, collision energy was calculated in order to qualitatively evaluate the detachment of parts and the breakage of boards. Simulation results indicated that the rotation speed of the agitator and the input number of PCBs had strongly influence on the comminution process. These result qualitatively corresponded to experimental results. Consequently, the comminution performance was qualitatively evaluated using the DEM

11:30 AM

(ICACC-S8-054-2016) A Study on Development of Stoneware Body Formulation Suitable for Fast Firing (Invited)

L. K. Sharma*[1]; 1. CSIR-Central Glass & Ceramic Research institute, India

Stoneware products being used worldwide commonly in hotel industry are manufactured in intermittent or continuous kilns in 20-30 hrs firing cycles. A comparative study was carried out to develop a formulation for Stoneware suitable for 180 minutes firing cycle in Roller Hearth Kiln. Fuel used was Liquidified Petroleum Gas. Fired rejection levels in stoneware crockery fired in 20-30 hrs firing cycle kilns are found to be in the range of 10-20%. A comparative study was conducted on one modern and three traditional formulations fired at 1200ºC for 180, 210, 240 and 270 minutes firing cycle (cool to cool) in LPG fired single deck roller hearth kiln. The rejection level of modern formulation was found to be at 6.9% for 180 minutes firing cycle whereas it was in the range of 13.4-22.8% for the traditional stoneware formulation. Water absorption of modern formulation was found to be 1.42% in comparison to 2.36% - 5.66% for traditional ones. Better processing practices in presence of talc resulted excellent physical properties at 1200ºC for 180 minutes firing cycle. It resulted the reduction in wastage 6.5 – 15.9%, increase in strength by 11% and increase in whiteness by 9%.

11:50 AM

(ICACC-S8-055-2016) A sustainable process for metal-ceramic castings through microwave hybrid heating

S. Singh*[1]; D. Gupta[1]; V. Jain[1]; 1. Thapar University, India

A sustainable process for developing metal matrix composite castings through microwave hybrid heating is investigated in present work. The unique characteristic of lower energy consumptions, lower processing time, volumetric and rapid heating through microwaves supports this work. Mixtures of metallic nickel based powder with 10% alumina and silicon carbide were placed in the graphite cavity, which was irradiated with microwaves of 2.45 GHz at 900 watt. Hybrid heating was carried out by using charcoal as susceptor which helps in raising the temperature of metallic powder such that microwaves starts interacting with nickel at elevated temperatures.

Hybrid heating causes rapid increase in temperature, which led to the melting of metallic powders. Results revealed that dense castings of the shape of cavity were produced having neligible visible defects. Microstructure revealed equiaxed grains of nickel with uniform distribution of ceramic reinforcements. Porosity content was lower in the range of 1.8% due to the volumetric heating; which reduces the temperature gradient throughout the castings. Hardness of the developed composites was in the range of 1200 Hv. The results of present investigation shows lot of potential in microwave casting process, which will target the manufacturing industries; owing to lower energy consumptions and shorter processing time.

S9: Porous Ceramics: Novel Developments and Applications

Innovations in Processing Methods & Properties of Porous Ceramics

Room: Coquina Salon G
Session Chair: Young-Wook Kim, University of Seoul

8:30 AM

(ICACC-S9-008-2016) Carbon periodic cellular architectures

A. Szczurek[2]; A. Ortona*[1]; L. Ferrari[1]; E. Rezaei[1]; G. Medjahdi[2]; V. Fierro[2]; D. Bychanok[3]; P. Kuzhir[3]; A. Celzard[2]; 1. SUPSI, Switzerland; 2. Université de Lorraine, France; 3. 3Research Institute for Nuclear Problems, Belarus

The first carbon periodic cellular architectures derived from 3D printing, in the form of new tetrakaidecahedra meshes, are reported and investigated in this work. They were prepared in hydrothermal conditions by a template method based on polymer periodic structures of the same geometry, and fabricated by a 3D printer using photocurable resin. Several formulations based on resorcinol–formaldehyde were tested, and the best ones were those using low concentrations of resorcinol at 150°C in a pressurized solution of nickel nitrate. After pyrolysis at 1000°C, catalytic graphitization was demonstrated by TEM, XRD and Raman studies. The higher was the amount of nickel, the higher was the resultant graphitization level. Mechanical tests were also carried out on such extremely lightweight periodic carbon structures, showing that these new materials present a much higher modulus than carbon foams of similar bulk densities.

8:50 AM

(ICACC-S9-009-2016) Thermal conductivity and mechanical properties of macroporous ceramics by gelation freezing method

M. Fukushima*[1]; C. Matsunaga[1]; Y. Tanaka[2]; F. Ozeki[2]; T. Ohji[1]; Y. Yoshizawa[1]; 1. National Institute of Advanced Industrial Science and Technology (AIST), Japan; 2. Mino ceramic Co., Ltd., Japan

Very large amount of porosity (70-98vol%) into ceramic monoliths could be introduced by strategically employing gelation freezing condutions such as type and amount of gelation agent and raw powder, and freezing temperature, in order to apply advanced ceramic thermal insulators. Two key parameters for gelation freezing processing have here been investigated: (1) the effect of gelation processing and antifreeze additives on nearly honeycomb like morphologies, unlike both of lamellar or dendritic microstructures created by conventional water based freeze casting routes; (2) the relationship between freezing conditions, microstructures, thermal conductivities and compressive strength, leading to tailored porosity, pore shape, pore size and thickness of struts. Thermal conductivities of insulators obtained well fitted with the Maxwell–Eucken 1 model to predict conductivities of insulators with internal porosities such as honeycombs and foams. The compressive strength was lower than upper limiting bound of theoretical values proposed by Gibson and Ashby, for honeycomb comprising of ideal hexagonal cells, out of plane motel, because lower sintering temperature, locally curved pore orientation and lower solid loading in the initial slurry. Commercial insulators will be also discussed as comparison of present insulators developred.

9:10 AM

(ICACC-S9-010-2016) High temperature steady state oxidation and thermal shock of SiC-based periodic cellular architectures: experimental observations on their thermal, mechanical, and mass transport properties evolution

L. Ferrari[1]; E. Rezaei[2]; M. Barbato[1]; S. Gianella[3]; A. Ortona*[1]; 1. SUPSI, Switzerland; 2. EPFL, Switzerland; 3. EngiCer, Switzerland

This work reports on the properties evolution of SiC based cellular architectures during their steady state oxidation at 1400°C and 1600°C in air and during thermal shock at 1400°C. Si-SiC and Si-SiC-ZrB_2 systems were employed as skeleton material because they, previously produced as monolithic bars, showed promising oxidation behavior at high temperatures. Regular arrays of different periodic structures were first designed by CAD, 3D printed, and finally converted into ceramic by replica and reactive silicon infiltration. The surface area of each sample was calculated and specific weight variations evaluated as a function of time. During oxidation and thermal shock, effective properties of each sample were measured and results discussed.

9:30 AM

(ICACC-S9-011-2016) Engineered aluminum titanate - based ceramics for diesel particulate filter applications

M. Backhaus-Ricoult*[1]; 1. Corning Incorporated, USA

Aluminum titanate enables the development of low thermal expansion ceramics, which can be processed into high porosity honeycomb and meet the specifications for diesel particulate filters, including low back pressure, high filtration efficiency and high thermal shock resistance. In the present work, a wide range of aluminum titanate – based composites with different compositions and porosity levels is processed. Reaction sequence, microstructure evolution and kinetics are studied during high temperature firing of powder mixtures. It is shown how the final microstructure is affected by starting materials and firing cycle and how the final phase arrangement drives the material properties. Permeability and tortuosity of the materials were measured experimentally and also derived by modeling from tomograms. The data were combined to provide trends for flow properties of diesel particulate filters. Thermomechanical material properties, such as strength and thermal expansion were measured on extruded honeycomb. They were found to be tightly linked to phase and pore distributions.. Key microstructural drivers for properties were derived that were used to engineer high porosity, high strength and low thermal expansion materials that are well suited for diesel particulate filter applications.

Membranes and High SSA Ceramics

Room: Coquina Salon G
Session Chair: Manabu Fukushima, National Institute of Advanced Industrial Science and Technology (AIST)

10:10 AM

(ICACC-S9-012-2016) Low-Temperature Processing and Characterization of Ceramic Membranes for Oily Wastewater Treatment (Invited)

Y. Kim*[1]; J. Eom[1]; I. Song[2]; 1. University of Seoul, The Republic of Korea; 2. Korea Institute of Materials Science, The Republic of Korea

The application of ceramic membranes is limited by the high cost of raw materials and sintering process at high temperatures. To overcome these drawbacks, this work investigated both the processing of ceramic membranes at low temperatures and the possibility of using cost-effective raw materials. Both clay-diatomite composite membranes and SiC membranes were successfully prepared by a simple pressing and dip-coating route at temperatures equal to or

lower than 1000°C in air. The changes of porosity, flexural strength, pore size, permeability, flux, and oil rejection rate of the membranes were investigated while changing the diatomite content and/or starting particle size. The membrane pore size could be tailored through controlling starting particle size and processing parameters during manufacturing. A simple burn-out process subjected to the used membranes in air completely recovered the permeability, steady state flux, and oil rejection rate of the virgin membranes. The recycled membranes showed an exceptionally high oil rejection rate (99.9%) at an applied pressure of 101 kPa. The flexural strength, permeability, oil rejection rate, and steady state flux of both the recycled clay-diatomite composite membranes and SiC membranes will be presented.

10:40 AM

(ICACC-S9-013-2016) Sorption-Induced Deformation of Silica Monoliths with Hierachical and Anisotropic Porosity

R. J. Morak*[1]; F. Putz[2]; A. Waag[3]; M. Elsaesser[2]; G. Popovski[1]; C. Balzer[3]; N. Hüsing[2]; G. Reichenauer[3]; O. Paris[1]; 1. Montanuniversität Leoben, Austria; 2. Paris-Lodron University Salzburg, Austria; 3. Bavarian Center for Applied Energy Research, Germany

A topic of increasing interest for novel actuator/sensor applications as well as for catalysis or medical diagnostics is a better understanding of the sorption-induced deformation of porous systems. In this study we investigated silica monoliths with hierarchical porosity built of a macroporous network of struts, which consists of well-ordered cylindrical mesopores arranged on a 2D hexagonal lattice. The analytical methods are in-situ Small Angle X-ray Scattering (SAXS) and in-situ dilatometry. The in-situ SAXS measurements are sensitive to the pore lattice spacing and therefore, to the sorption induced strain at the mesopore scale. Dilatometry probes the macroscopic deformation of the overall network. Comparison of these methods for systems with anisotropic mesoporosity but isotropic macroporosity allows new insights into the deformation transfer from the nanometer to the macroscopic scale. Moreover a new synthesis strategy makes monoliths with a macroscopically anisotropic network possible. Position resolved 2D-SAXS shows that the ordered cylindrical mesopores follow the macroscopic preferred orientation with a gradient from the center towards the rim. We present in-situ SAXS results of sorption induced deformation in these macroscopically anisotropic samples parallel and perpendicular to the cylindrical axis, and compare these data with the deformation obtained from in-situ dilatometry.

11:00 AM

(ICACC-S9-014-2016) Characterization of subnano-scale porous structures and gas permeation properties of microporous ceramic membranes (Invited)

T. Yoshioka*[1]; 1. Hiroshima University, Japan

Microporous ceramic membranes are very promising due to their thermal and chemical stability, and they are expected to be utilized to purification of several gas mixtures such as hydrogen separation, carbon dioxide separation from natural gas or flue gas, olefin gas separation from light hydrocarbons, and so on. In order to design effective microporous structures and surface chemistries for gas separation membranes, in-situ characterization of microporous membranes is of importance as well as the elucidation of gas permeation mechanisms. A non-equilibrium molecular dynamics (MD) technique was used to assist the study of gas permeation mechanisms for microporous silica and silica-based ceramic membranes. The effect of the gas molecular size and its affinity to the pore surface on gas permeation properties were well examined from a molecular scale point of view. MD simulations revealed that the effective diffusion length in a micropore depended on the gas molecular size, and that the pre-exponential coefficient of a modified gas translational (GT) model equation showed good correlation with the gas molecular size. Also presented is a simple method to estimate the mean pore size of microporous membranes. The "normalized Knudsen-based permeance (NKP)" method and "k_0-plot" method were easy to be utilized for subnano-pore size estimation on ceramic membranes.

11:30 AM

(ICACC-S9-015-2016) Polymer-derived amorphous silica-based inorganic-organic hybrids: intermediates for synthesizing microporous amorphous silica materials

Y. Iwamoto*[1]; M. Mohd Sokri[1]; T. Onishi[1]; Z. Mounline[1]; Y. Daiko[1]; S. Honda[1]; 1. Nagoya Institute of Technology, Japan

Alkoxy group-functionalized amorphous silica-based inorganic-organic hybrid materials were designed through polymer precursor route, in order to develop a novel route for the fabrication of microporous amorphous silica-based materials. Perhydropolysilazane (PHPS) was chemically modified with alcohols (R-OH, R=n-C_5H_{11}, n-$C_{10}H_{21}$), and subsequently oxidized to afford alkoxy group-functionalized amorphous silica by exposure to aqueous ammonia vapours at room temperature. Then, the oxidized materials were heat-treated at 600°C in air. Nitrogen sorption analysis revealed that micropore volume of the amorphous silica increased upon alkoxy group-functionalization prior to the heat treatment. As a result, higher micropore volume of 0.204 cm^3/g was achieved, with a specific surface area of 387 m^2/g for the amorphous silica derived from PHPS chemically modified with n-$C_{10}H_{21}OH$ at the Si/n-$C_{10}H_{21}OH$ molar ratio of 2/1. The in-situ formation of the microporosity will be further studied by the simultaneous TG-MASS spectrometry analysis, and the evolution of gaseous species during the heat treatment and the resulting microporosity will be discussed.

S10: Virtual Materials (Computational) Design and Ceramic Genome

Ceramic Genome and Integrated Materials Computational Engineering II

Room: Ponce DeLeon
Session Chair: Wai-Yim Ching, University of Missouri-Kansas City, USA

8:30 AM

(ICACC-S10-039-2016) Enabling the Materials Genome - The Materials Project and Beyond (Invited)

S. Ong*[1]; A. Jain[2]; S. Cholia[2]; P. Huck[2]; D. Winston[2]; D. Gunter[2]; K. Persson[2]; G. Ceder[3]; 1. \"University of California, San Diego\", USA; 2. Lawrence Berkeley National Laboratory, USA; 3. Massachusetts Institute of Technology, USA

A key enabler to probing the materials genome is the wide availability of high quality computational materials data and the necessary software tools to facilitate its analysis and generation. In this talk, I will present the efforts of the Materials Project (http://www.materialsproject.org) and the Materials Virtual Lab (http://www.materialsvirtuallab.org) in the development of open materials databases and software. Founded in Oct 2011, the Materials Project aims to remove guesswork from materials design by computing the properties of all known materials. A unique aspect of the Materials Project is its adoption of cutting edge information technology best practices, such as the Materials RESTful Application Programming Interface (API) for programmatic access to data, and a powerful open-source software suite (Python Materials Genomics, Custodian and FireWorks) for the automation of first principles calculations and analysis. I will present examples of how these tools have accelerated materials design in several application areas, including thermoelectrics, elastic properties of materials and lithium-ion batteries. Finally, I will also discuss the efforts of the Materials Virtual Lab in further extending these tools into new analyses and technological areas.

9:00 AM

(ICACC-S10-040-2016) The application of CALPHAD Approach in the Nano-sized YSZ (n-YSZ) Phase Diagram

M. Asadikiya[1]; Y. Zhong*[1]; 1. Florida International University, USA

Yttria-stabilized zirconia (YSZ) has a lot of applications as like as electrolytes for solid oxide fuel cells (SOFCs) and oxygen sensors, refractory materials for high temperature furnaces as well as protective coatings for metals. On the other hand, nano-sized YSZ (nYSZ) shows different properties since surface energy participates in the stability of different phases. Therefore, by changing the particle size, Gibbs free energy of each phase changes and as a result, the stability of that phase in different temperatures changes. In this situation, we need to have enough knowledge of the phase equilibria in the ZrO2-Y2O3 system when the particle size changes. Also, we need to know the phase stability behavior of the system by changing temperature. By having an extended map of nYSZ phase diagram, we have better understanding about the properties of this material versus particle size, composition and temperature. By having this information, we can better decide about the application of this materials. CALPHAD approach could be used to analyze the existent data and infer a good map from the thermodynamics point of view.

9:20 AM

(ICACC-S10-041-2016) Analysis of Multiplet States of CrO_6^{9-} and MnO_6^{8-} clusters with D_{4h} Symmetry Based on First-Principles Calculations

K. Ogasawara*[1]; 1. Kwansei Gakuin University, Japan

Mn^{4+}-doped oxides are drawing attention as promising candidates for the red phosphor of white LED. Although multiplet energies of transition metal ions in crystals are generally analysed based on the well-known Tanabe-Sugano diagrams, more practical diagrams without any empirical parameters are desired for the theoretical search of novel red phosphors. For this purpose, we recently created the multiplet energy diagrams using the bond length and the absolute multiplet energy for CrO_6^{9-} and MnO_6^{8-} clusters with O_h symmetry based on first-principles calculations. In this work, in order to investigate the effect of low-symmetry crystal field, the multiplet states of CrO_6^{9-} and MnO_6^{8-} clusters with D_{4h} symmetry were calculated and investigated in detail based on first-principles calculations. The CrO_6^{9-} and MnO_6^{8-} clusters with various combinations of two types of bond lengths were constructed. The multiplet energy calculations were performed based on the discrete-variational multi-electron method. In order to clarify the relationship between the local structure and the multiplet energy, multiplet energy maps in terms of the two types of bond lengths were created. The effects of electron correlation and covalency were also investigated quantitatively, by creating the maps of the correlation correction factor and the orbital deformation parameter, respectively.

9:40 AM

(ICACC-S10-042-2016) Exploring low thermal conductivity by tailoring chemistry composition and crystal structure in $AEAl_2Si_2O_8$ (AE = Ca, Sr, and Ba) ceramics

S. Luchao*[1]; J. Wang[1]; 1. Institute of Metal Research, China

One of the challenges in developing low thermal conductivity materials is searching novel low-cost and lightweight ceramic free of rare earth or heavy elements. Alkaline-earth aluminosilicates $AEAl_2Si_2O_8$ (AE = Ca, Sr, and Ba) exist low density and show three polymorphs (celsian, paracelsian, and hexagonal anorthite). They are ideal model systems to probe the relationship between chemical composition, crystal structure, chemical bonding, and lattice thermal conductivity. The present work investigates the lattice thermal conductivities of $AEAl_2Si_2O_8$ by combination of first-principles calculations method, and Debye approximation and Slack model. The results highlight some candidates with extremely low thermal conductivities, for example, the temperature dependent thermal conductivities of cel-$BaAl_2Si_2O_8$ and para-$BaAl_2Si_2O_8$ are 377 and 680 $W/m^{-1}K^{-1}$, and approaching to minimum values of 0.85 and 0.88 $W/m^{-1}K^{-1}$ at high temperature, respectively. In addition, we discuss the relationships among chemical composition, crystal structure, and thermal conductivity, as well as the origins of low lattice thermal conductivities (mainly due to intense anharmonicity of lattice vibrations and low phonon group velocity) of $AEAl_2Si_2O_8$ ceramics.

Ceramic Genome and Integrated Materials Computational Engineering III

Room: Ponce DeLeon

Session Chair: Jingyang Wang, Institute of Metal Research

10:20 AM

(ICACC-S10-043-2016) Electronic Structure and Interatomic Bonding in Bulk Metallic Glasses (Invited)

W. Ching*[1]; 1. University of Missouri-Kansas City, USA, USA

The electronic structure and bonding in a large number of binary (Zr_xCu_y) and ternary ($Zr_xCu_yAl_z$) bulk metallic glasses (BMG) are calculated using the first-principles orthogonalized linear combination of atomic orbitals (OLCAO) method. Each model contains 1,024 atoms and was first generated using classical molecular dynamics (MD) with long annealing steps followed by full relaxation with no constraints using VASP. The bond order (BO) values for each atomic pairs with a distance of separation up to 5 Å are calculated. The total bond order density (TBOD) is obtained as the sum of all BO values normalized by cell volume. Detailed analysis of the distribution of the TBOD and contributions from different partial components reveal intimate details of the short and intermediate range order in these BMGs. We have also explored correlations between TBOD and fundamental physical properties in BMG including the glass forming ability (GFA), chemical composition, density of states (DOS) at the Fermi level and partial DOS.

10:50 AM

(ICACC-S10-044-2016) Computational Exploration of ZrSiBCN Coatings

P. Kroll*[1]; A. Dasmahapatra[1]; 1. UT Arlington, USA

Recent synthesis of hard $Zr_{42}B_{30}C_8N_{20}$ coatings motivates this study to explore properties of ZrSiBCN materials. While an addition of Si_3N_4 targets to improve oxidation resistance of the ZrSiBCN coatings, an impact on mechanical properties is unknown. Our computational exploration starts from the experimental composition $Zr_{42}B_{30}C_8N_{20}$ and investigates systematically the impact of BN and Si_3N_4 to materials properties. All structures are generated and computed using density-functional theory calculations. Melt-quench models comprise 100 atoms and are repeatedly annealed to achieve low-energy amorphous and nano-crystalline structures. Subsequently, we compute elastic constants and estimate Vicker's Hardness and thermal conductivity. We consistently find ZrN(C) and ZrB_2 nuclei in our ZrSiBCN model structures, resembling TEM pictures of nano-structured ZrBCN coatings. The tendency to form such nuclei, decreases with increasing BN or Si_3N_4 phase content. High hardness appears for compositions low in Si_3N_4 and high in ZrN. Only if Si_3N_4 is added at the expense of ZrB_2, the system retains high hardness values. Therefore, we project that a balance between Si_3N_4 and ZrB_2 must be sought to achieve hard coatings with improved oxidation resistance.

11:10 AM

(ICACC-S10-045-2016) Modelling Amorphous Diamond-like Carbon

N. Dari*[1]; P. Rulis[1]; 1. University of Missouri, Kansas City, USA

Tetrahedral Amorphous carbon, commonly known as Diamond-like carbon (DLC), has become a widely used coating material in recent years due to its valuable properties and ease of use. DLC coatings have been shown to greatly enhance the lifetime of the coated

material, greatly reduce wear and tear due to acting as a dry lubricant, and increase the external hardness of materials to name only a few uses. However, one of the limitations that DLC coatings face is its propensity to delaminate due to poor adhesion to the substrate. This is seen as a large obstacle to the wider adoption of DLC films in industry and in biomedical applications. We will present our efforts to create accurate atomistic models of DLC, along with resultant electronic structure, bonding, and optical properties of the models. Initial efforts to address the delamination problem through the inclusion of tungsten dopants will also be presented. This approach is used because reducing the internal stress of DLCs is seen as an important avenue for increasing interfacial bonding and reducing the delamination of DLC films on non-carbide surfaces.

11:30 AM

(ICACC-S10-046-2016) First principles investigation of two-dimensional transition metal carbides (Invited)

Z. Sun*[1]; Z. Guo[1]; C. Si[1]; J. Zhou[1]; 1. Beihang University, China

Two-dimensional (2D) transition metal carbides $M_{n+1}X_n$s labeled as MXenes derived from ternary transition metal carbides MAX ($M_{n+1}AX_n$) phases attract increasing attention due to their promising applications as Li-Ion battery anodes, hybrid electro-chemical capacitors and electronic devices. Experimentally, most MXenes are synthesized by chemical extraction of "A" layers from MAX phases. To unravel the microscopic mechanism of forming MXenes from MAX phases, we have studied the chemical bonding changes of MAX phases in response to tensile and shear stresses. Our results demonstrate the possibility and microscopic process of mechanical exfoliating 2D M_2C from M_2AlC phases. Furthermore, we have shown that the mechanical failure of Mxenes under tension is due to the elastic instability induced by collapse of the surface metal layer, while surface functionalization could slow down the collapse, resulting in striking increase of the critical strain of MXene. We have also shown that surface functionalization can induce ferromagnetic (FM) to antiferrmagnetic (AFM) transition in Cr_2C MXene, which is accompanied by metal to insulator (MIT) transition. The surface functionalization induced localization of Cr *d* orbitals is responsible for the FM-AFM and MIT transition. Our results highlight the potential applications of MXenes in the spintronics and flexible electronics.

S11: Advanced Materials and Innovative Processing Ideas for the Production Root Technology

New Concept on Root Technology and Surface Technology

Room: Tomoka B

Session Chair: Tadachika Nakayama, Nagaoka Univ of Tech

8:30 AM

(ICACC-S11-001-2016) Introduction on The Role, Vision, and Strategic Goal of Industrial Root Technology (What is the Ppuri Technology?) (Invited)

J. Kim*[1]; 1. Korea Institute of Industrial Technology (KITECH), The Republic of Korea

"Industrial Root Technology (Ppuri Technology)" symbolically refers to an integration of six production technology groups; casting, molding, forming, welding, heat treatment, and surface treatment. The Ppuri Technology includes materials and process technologies, which are hidden behind products, and do not appear outward frequently, however, are very important fundamental backgrounds greatly influencing the features. For example, the valuable noble materials developed based on the basic materials science could be reformed into the valuable components and final products by the proper support of Preliminary Ppuri Technology. As the functions of components and products are becoming more and more complex and robust, the importance of the Ppuri Technology is growing even greater. In this presentation, the successful story about the change of Ppuri Technology from 3 D (Dangerous, Dirty, and Difficult) to ACE (Automatic, Clean and Easy) will be introduced. It is also introduced the role, vision, and strategic goal of the Ppuri Technology.

9:00 AM

(ICACC-S11-002-2016) New Development of root technology by GIGAKU concept (Invited)

K. Niihara*[1]; T. Nakayama[1]; H. Suematsu[1]; 1. Nagaoka Univ of Tech, Japan

Nagaoka University of Technology (NUT) was founded in 1976, with the aim of creating technology and science, namely, GIGAKU, as well as nurturing practical and creative engineers through whom it would attempt to realize a vision of strong cooperation between academia, industry, and government which was revolutionary at these years in Japan.Since the founding, NUT has continued to realize our goal of training and developing leading engineers and researchers, with practical and creative abilities, capable of making a contribution to our society. The results are borne out in the activities of our graduates in society, as well as the high esteem in which they are held. In order to continue to grow in the medium-and long-term, we are developing GIGAKU more deeply still to match the changes of a rapidly globalizing society. By sharing the results of this development both domestically and internationally, we will make the value of our research results more widely understood and appreciated and hasten the spread of the concept of GIGAKU. At the same time, through the training of GIGAKU Professionals, we aim to devote ourselves to the technological innovation of this nation's industry and the improvement of international competitiveness

9:30 AM

(ICACC-S11-003-2016) Tailoring the functional properties of niobium carbide (Invited)

M. Woydt*[1]; H. Mohrbacher[2]; 1. BAM Federal Institute for Materials Research and Testing, Germany; 2. Niobelcon BVBA, Belgium

The differences between the binary phase diagrams W-C and Nb-C illuminate several parameters for tailoring the properties of NbC. In the region of homogeneity of NbC_x (0,75< x <1.0), with Nb_4C_3 and Nb_6C_5 other niobium carbide phases occur. Properties, like micro-hardness, hot hardness, sliding wear, elastic modulus and toughness can be tailored by the C/Nb ratio, secondary carbides and the type of binder. Supporting results from different grades with varying C/Nb ratio or binder types will be illuminated. Thus, the NbC system offers to producers a wider parameter window, than WC.

Shaping Process with Powders

Room: Tomoka B

Session Chair: Kouichi Yasuda, Tokyo Institute of Technology

10:20 AM

(ICACC-S11-004-2016) Observation of development of internal pores in dry-pressed alumina ceramics during sintering (Invited)

S. Tanaka*[1]; T. Hondo[1]; F. Wakai[2]; K. Yasuda[2]; 1. Nagaoka University of Technology, Japan; 2. Tokyo Institute of Technology, Japan

The control of pore development is necessary for improving reliability in ceramic material. In general, ceramics are gradually sintered, where densification and grain growth occurred. Although fine pores in the powder compact are removed by sintering, some of them survive and become larger simultaneously. Until now, sintering behavior has been studied well, but, pore development during sintering has not been fully understood. Here, we have examined pore-coarsening during sintering by using Micro-CT, which is a useful tool for non-destructive visualization of ceramics. In experiments, alumina powder compacts were prepared by uniaxial

pressing and CIP from two kinds of granules with or without binder. Sample with 1mm^3 in size was observed by Micro-CT semi-sequentially in heating. The sample made from granules with 50-100μm in size and with binder segregation on the surface. As a results, powder compact after de-binder had crack-like pores with ~10 μm at the interface of granules. These pores gathers fine pores and developed by sintering. The pore coarsening was observed well in the sample made from granules with binder segregation.

10:50 AM

(ICACC-S11-005-2016) Fabrication of porous ceramics using inorganic binder (Invited)

J. Tatami*[1]; M. Iijima[1]; 1. Yokohama National University, Japan

Porous ceramics have been applied to filter, thermal insulator, catalyst support, and so on. Therefore, they are important for development of sustainable society. Although organic binder is added to improve the strength of the green body of porous ceramics, it is sometimes difficult to maintain the shape of the green body after dewaxing to fabricate the ceramics. Objective of this study is to fabricate porous alumina ceramics using basic aluminum lactate as an inorganic binder. The density of the porous alumina ceramics was independent of kind and amount of binder. After firing at 500 ^{O}C, the strength of the sample by adding polyvinyl alcohol was 0.5 kPa because of decomposition and oxidation of polyvinyl alcohol. On the other hand, addition of basic aluminum lactate improved the strength after dewaxing. Furthermore, it increased with an increase in the amount of added basic aluminum lactate. Porous alumina ceramics by adding basic aluminum lactate fired at 1600 ^{O}C also showed higher strength than that by adding only polyvinyl alcohol, which resulted from neck growth by alumina formed from the basic aluminum lactate. Consequently, it was shown that basic aluminum lactate as an inorganic binder is effective in the improvement of the strength of not only green body but also sintered body.

11:20 AM

(ICACC-S11-006-2016) Effect of Microstructure on the Properties of Porous Alumina (Invited)

S. Honda*[1]; T. Eda[2]; H. Watanabe[2]; K. Miyajima[2]; Y. Daiko[1]; S. Hashimoto[1]; Y. Iwamoto[1]; 1. Nagoya Institute of Technology, Japan; 2. Noritake Corporation Limited, Japan

The permeability and fracture properties of porous alumina structure for the support substrates for permselective microporous ceramic membranes were studied. To study the influence of grain necking or various parameters of porous microstructure systematically, porous alumina with different porous structure were fabricated by various sintering conditions. In order to estimate the effect of grain necking on thermal conductivity of porous alumina, the numerical analysis was performed using inverse of thermal conductivity. This research clarified quantitatively to the relation between properties of porous alumina and grain necking size.

11:50 AM

(ICACC-S11-007-2016) Pyrolysis of non- and pre-oxidized Polyacrylonitrile (PAN) characterized by TGA-GC-MS and TGA-FT-IR

E. Post*[1]; 1. NETZSCH Geraetebau GmbH, Germany

Polyacrylonitrile (PAN) is a semi-crystalline thermoplastic. Its main application is for textiles, membranes etc. High quality carbon fibers are produced by pyrolysis of pre-treated PAN fibers. A preliminary step is oxidation of the fibers at 200°C to 300°C for several hours prior to the pyrolysis in an inert gas atmosphere or vacuum. During the pyrolysis process, several toxic gaseous products can occur. The evolved gases can be simultaneously detected with the mass loss versus time and temperature by employing a TGA/STA coupled to an evolved gas analyzer. In this work, the pyrolysis of pre-oxidized and raw PAN material was investigated by TGA-GC-MS and TGA-FTIR. The TGA-GC-MS measurements can be performed in different acquisition modes delivering either an optimum time correlation to the mass change (quasi-continuous mode) or a better mass separation by the GC (cryo mode). Based on these sample measurements, the TGA-FT-IR coupling is especially helpful in identifying and confirming of the smaller gaseous molecules like HCN, NH_3 etc. In this contribution, the gaseous pyrolysis products of PAN raw material and pre-oxidized will be compared and shown versus temperature and mass loss.

S14: Crystalline Materials for Electrical, Optical and Medical Applications

Semiconductor III

Room: Tomoka C
Session Chair: Didier Chaussende, CNRS

8:30 AM

(ICACC-S14-036-2016) Preparation of Nitride Materials for Large Area Devices with Pulsed Sputtering (Invited)

H. Fujioka*[1]; K. Ueno[1]; A. Kobayashi[1]; J. Ohta[1]; 1. the University of Tokyo, Japan

It is generally believed that group III nitride devices exhibit high performance but the field of their applications are largely limited because their fabrication process involves expensive MOCVD growth. Nitride devices possibly prevail quickly among various new application fields once low cost fabrication process is established. Large area nitride devices such as solar cells and displays are among these applications. For this purpose, we have recently developed a new PVD-based growth technique called PSD (pulsed sputtering deposition). Various nitride devices such as LEDs solar cells, MISFET, and HEMTs were already fabricated by the use of PSD and operated successfully. In this technique, surface migration of the film precursors is enhanced and, therefore, the temperature for epitaxial growth is dramatically reduced. This reduction allows us to utilize various large area low cost substrates such as metal foils or glass that have not been used for growth of semiconductors so far due to their chemical and thermal vulnerability. In this presentation, we will discuss feasibility of large area nitride devices such as LED displays or solar cells fabricated with PSD on various low cost substrates. We will also show that PSD is quite promising for growth of high In concentration InGaN which is necessary for fabrication long wavelength optical devices.

9:00 AM

(ICACC-S14-037-2016) Realization of AlGaN based high performance UV lighti-emitting devices and detectors (Invited)

M. Iwaya*[1]; T. Takeuchi[1]; S. Kamiyama[1]; I. Akasaki[1]; 1. Meijo University, Japan

Because the UV light emitting devices and detectors are expected in the applications of the device such as a medicine, an industrial sources and a sterilization, the solid-sate UV light emitting devices and detectors will surely give a big impact on the optoelectronics industry. The AlGaN ternary alloys are one of the best candidates for realization of such UV devices, because of its direct wide bandgaps ranging from 3.4 to 6.0 eV. In this presentation, we discuss the realization of high crystalline quality AlGaN on AlN template and AlN freestanding substrate. We also discuss the behavior of a-type and a+c type threading dislocations in AlGaN on AlN template charactrized by transmission electron microscopy. And, we also discuss the internal quantum efficiency of UV and deep UV multi-quantum wells and injection efficiency of UVA laser diode and UV-LED. Moreover, we also discuss the high performance heterostructure field-effect transistor type UV detector using p-type GaN optical gate.

9:30 AM

(ICACC-S14-038-2016) Current status and future prospects of nitride semiconductors (Invited)

T. Matsuoka*[1]; T. Tanikawa[1]; K. Shojiki[1]; T. Kimura[1]; K. Prasertsuk[1]; T. Suemitsu[2]; 1. Institute for Materials Research, Tohoku University, Japan; 2. Research Institute of Electrical Communication, Japan

LEDs consisting of nitride semiconductors have been commercially available since 1996. A white LED built with a blue LED and a yellow phosphor has saved energy consumption a great deal because of their efficiency twice higher than that of fluorescent lamps. Transistors with high power and high frequency, solar cells with high conversion efficiency, and ultraviolet LEDs for sterilization have also been developed using nitride semiconductors. Although high quality of materials are required in these applications, the treading dislocation density of the GaN grown on sapphire, which is popularly used for a substrate to grow GaN-based materials, is so far five orders of magnitude higher than that of conventional III-V materials such as GaAs and InP. In addition, nitride semiconductors have unique characteristics different from conventional III-V semiconductors, i.e., a large polarization field strongly depending on the crystalline polarity and strain. We have successfully fabricated red LEDs by the polarity control. This is a key step enabling the white LEDs consisting of all three fundamental colors by nitride semiconductors. In solar cells, the polarity control enhances the extracted current density up to about ten times larger than that in the conventional nitride solar cells. In transistors, the polarity control will also pave the way to enhance intrinsic transistor performance and to reduce on-resistance.

Piezo/Ferro

Room: Tomoka C

Session Chair: Kiyoshi Shimamura, National Institute for Materials Science

10:20 AM

(ICACC-S14-039-2016) Recent developments on piezoelectric single crystal (Invited)

S. Zhang*[1]; 1. Pennsylvania State University, USA

Piezoelectric materials play an important role in electromechanical applications, such as medical imaging and structural health monitoring (SHM) /nondestructive evaluation. To improve the performance of electromechanical devices, the selection of piezoelectric materials with the optimized properties is a critical concern. In this presentation, the developments of piezoelectric crystals are surveyed, compared to conventional polycrystalline PZT ceramics. Special attentions are focused on the temperature dependence of electromechanical properties and related mechanisms of piezoelectric materials, where the discussion is divided into two parts, i.e., ferroelectric materials and nonferroelectric materials. The potential piezoelectric materials for cryogenic and ultra-high temperatures applications are discussed. The uniqueness of relaxor-PT crystals and nonferroelectric piezoelectric crystals are surveyed for possible electromechanical applications.

10:50 AM

(ICACC-S14-040-2016) Strain and Pyroelectric Energy Conversion of PLZST Antiferroelectric Single Crystal (Invited)

Q. Li*[1]; J. Gao[1]; F. Zhuo[1]; Y. Zhang[1]; Q. Yan[1]; 1. Tsinghua University, China

MPB La modified complex perovskite antiferroelectric Pb(Zr,Sn,Ti)O_3 (PLZST) single crystal, as an attractive candidate for pyroelectric energy conversion devices design, had been grown from a modified flux, with huge remnant polarization P_r and pyroelectric coefficient p alongside an induced AFE-FE phase transition PE loops and pyroelectric analysis indicated that the ferroelectric and pyroelectric properties of PLZST single crystals were both strongly orientation-dependent. From electric measurements, Raman study and observation of domain structures, an electric field induced antiferroelectric to ferroelectric phase transition could be found accompanying with fifteen times of strain difference. Via this induced phase transition, a metastable ferroelectric phase (FE_{in}) was preserved with soften of $A_1(TO_1)$ mode and increase of long-range force. Coexistence of Tetragonal (T) and Rhombohedral (R) domains could be observed in a virgin sample. Electric field induced T to R phase transition would be verified by both extinction angle and domain morphology changes. Clamping "polar" structure formed by the embedded R phase was believed to contribute to the increase of long-range force.

11:20 AM

(ICACC-S14-041-2016) Vertical Morphotropic Phase Boundary in Lead-Free Piezoceramics (Invited)

T. Karaki*[1]; 1. Toyama Prefectural University, Japan

In R&D of lead-free piezoceramics, one of the most important works is to find out a tetragonal-rhombohedral morphotropic phase boundary (MPB) composition with certain Curie temperature. In $BaZrO_3$-(K,Na,Li)NbO_3 binary system there is a temperature-dependent MPB, meaning that the MPB slope is negative in the phase diagram. In this work, we adjusted the MPB slope by adding a third component (Bi,Na)TiO_3. Sintered specimens were crushed and then the powders were measured by X-ray diffraction for phase transition determination. Ceramics with a composition of $0.075BaZrO_3$-$0.915(K,Na,Li)NbO_3$-$0.01(Bi,Na)TiO_3$ showed no phase transition between tetragonal and rhombohedral phases from room temperature to its Curie temperature about 270 °C. A temperature-independent MPB, so called vertical MPB was successfully formed.

11:50 AM

(ICACC-S14-042-2016) Observation of relaxation time in structural phase transformtaion in $Na_{0.5}Bi_{0.5}TiO_3$-(K,Na)NbO_3 piezoceramics

G. Wang*[1]; D. Hall[1]; Y. Li[1]; I. Calisir[1]; 1. University of Manchester, United Kingdom

High-energy synchrotron diffraction has been employed to demonstrate a structural phase transition in $Na_{0.5}Bi_{0.5}TiO_3$-x$KNbO_3$ (NBT-xKN) and $Na_{0.5}Bi_{0.5}TiO_3$-x$NaNbO_3$ (NBT-xNN). It is demonstrated that the rapid cycle in AC electric field (1 second per cycle per scan) induces a transformation from pseudo-cubic to rhombohedral symmetry in NBT-xKN system at x=0.01-0.03 and NBT-xNN system at x=0.02-0.04. When the electric field is applied steping AC field (25 second per step per scan), no transformation occurs, only showing peak broading and peak shift. Suprisingly, those specimen after applied stepping AC field,rhombohedral symmetry was observed clearly after 60 minutes and able to retain after. Due to energy barrier in nano-polar region (PNRs) of relaxor-ferroelectric NBT-(K,Na)NbO_3, rapid cycle AC field is able to induce structural transformation easier, while micro-domain switching is easier induced by stepping AC field instead. Also, with help of relaxation time, energetic PNRs is able to gradually align with each other and eventually transform structure from pseudo-cubic to rhombohedral phase.

EMERGING TECHNOLOGIES SYMPOSIUM - Carbon Nanostructures and 2D Materials, and Composites

Carbon Nanostructures and 2D Materials, and Composites I

Room: St. John
Session Chair: Gustavo Costa, NASA Glenn Research Center

8:30 AM

(ICACC-EMERG-001-2016) Thermochemistry of Carbon Nanomaterials (Invited)

A. Navrotsky*[1]; 1. University of California, Davis, USA

High temperature oxidative calorimetry has been used to study the energetics of formation of carbon based nanomaterials, including carbon onions, graphene,and nanodiamond. Their enthalpies of oxidation are less exothermic than that of graphite, suggesting they are more stable. However they contain significant concentrations of oxygen as surface functional groups, whose stability more than compensates for potentially destabilizing surface energies. Indeed these nanomaterials probably require the stabilization of surface functionalization for their formation and thus are intrinsically part of multicomponent systems rather than simply carbon materials. Quantitative trends of energetics versus functionalization will be discussed.

9:00 AM

(ICACC-EMERG-002-2016) Synthesis of Carbon/Sulfur Nanolaminates by Electrochemical Extraction of Titanium from Ti_2SC

M. Zhao*[1]; M. Sedran[1]; M. R. Lukatskaya[1]; M. Barsoum[1]; Y. Gogotsi[1]; 1. Drexel University, USA

The selective extraction processes to produce 2D materials has been attracted much attention due to its ability to achieve well-controlled morphologies and structures, and even generate new materials that cannot be produced by other methods. Recently, a family of new 2D materials, so called MXenes, were synthesized by selective extraction of 'A' layers from the MAX phases (a family of 3D layered, ternary carbides and nitrides). Carbide-derived carbons with tunable size were produced by extracting both the 'M' and 'A' elements from the MAX phases. Herein we electrochemically and selectively extract Ti from the MAX phase Ti_2SC to form carbon/sulfur, C/S, nanolaminates at room temperature. The products are composed of multi-layers of C/S flakes, with predominantly amorphous and some graphene-like structures. Covalent bonding between C and S is observed in the C/S nanolaminates, which render the latter promising candidates as electrode materials for Li-S batteries. We also show that it is possible to extract Ti from other MAX phases, such as Ti_3AlC_2, Ti_3SnC_2, and Ti_2GeC, suggesting that electrochemical etching can be a powerful method to selectively extract the 'M' elements from the MAX phases, to produce 'AX' layered structures, that cannot be made otherwise. The latter hold promise for a variety of applications, such as energy storage, catalysis, etc.

9:20 AM

(ICACC-EMERG-003-2016) CNTs and Ferroelectrics towards 3D Microelectronic Structures (Invited)

P. M. Vilarinho*[1]; 1. University of Aveiro, Portugal

As microelectronic systems become more complex/customized, standard approaches to fabricate semiconductors soon will not be anymore appropriate. Three-dimension (3D) design and integration is being considered as a key solution to the future of integrated circuits. In addition 3D structures offer extreme miniaturization and cost-effective fabrication for More-than-Moore products. Carbon based electronics may offer potential to fabricate 3D nano-arrays using one dimension (1D) FE nanostructures to increase memory capacity. Indeed use of CNTs as templates or as bottom electrodes is a potential strategy to realize 3D FE nanostructures. However, combining CNTs with FE is challenging. It starts with materials compatibility, since crystallization of FE and oxidation of CNT temperatures may overlap. Low cost processing of FE is fundamental. In this talk our work on the various aspects related to the fabrication of CNTs-FE structures using low cost low temperature methods, as effect on thermal stability of MWCNTs, FE phase formation in presence of MWCNTs and interfaces between CNTs/FE is presented. FE response locally measured by PiezoForce Microscopy evidenced that even at low processing temperatures FE on CNTs retain its ferroelectric nature. CNTs can be combined with FE and be used as next 3D generation of FERAMs

10:20 AM

(ICACC-EMERG-004-2016) Confocal and near-field Raman study of graphene, twisted bilayer graphene, and carbon nanotubes (Invited)

L. G. Cancado*[1]; A. Jorio[1]; R. Beams[2]; L. Novotny[3]; C. Achete[4]; 1. Universidade Federal de Minas Gerais - UFMG, Brazil; 2. National Institute of Standards and Technology, USA; 3. ETH Zurich, Switzerland; 4. Instituto Nacional de Metrologia, Qualidade e Tecnologia-INMETRO, Brazil

The presentation starts with an overview on the characterization of graphene and twisted bilayer graphene using Raman spectroscopy. For graphene, Raman spectroscopy delivers fast information about crystallite size, point defect density, electron and phonon coherence lengths. The Raman signal obtained from edges provides information about their atomic structures. For twisted bilayer graphene (TBLG), rich resonance effects make it possible to measure the twist angle and transition energies between superlattice-induced van Hove singularities in the electronic joint density of states. In the second part of the talk, the mechanism of tip-enhanced Raman scattering (TERS) in graphene and carbon nanotubes will be discussed. We investigate the Raman modes of carbon nanotubes and pristine monolayer graphene to determine how the scattered signal depends on the distance between the sample and a laser-irradiated gold tip. As the correlation length increases, we find increasingly different behaviors for the strengths of various bands present in the Raman spectrum. We note that the characteristic correlation lengths are nearly an order of magnitude smaller than optical wavelengths. As a result of coherence, we find that the Raman intensities on the nanoscale depend strongly on phonon symmetry and spatial confinement.

10:50 AM

(ICACC-EMERG-005-2016) SnO_2-Reduced Graphene Oxide Nanocomposites: Overview (Invited)

D. P. Volanti*[2]; C. D. Zito[1]; 1. UNESP, Brazil; 2. UNESP - São Paulo State University, Brazil

The research concerns the evaluation of the use of reduced graphene oxide (RGO) and tin oxide (SnO_2) nanoparticles in the SnO_2-RGO nanocomposites to improve the sensitivity, selectivity and response time of the volatile organic compounds (VOCs) sensors. The nanocomposites are synthesized in one step from the dispersion containing Sn precursor solution and graphene oxide at pH controlled by microwave-assisted crystallization. RGO act as electron acceptor to facilitate interaction between SnO_2 nanoparticles and VOCs via pi-pi interations type, in addition to increasing the surface area of the composite. The main benefits of RGO consist in increasing the adsorption, sensitivity, reversibility and detection limits of the sensor process. The nacomposites will be evaluated in the presence of different VOCs (e.g. acetone, ethanol and toluene) by conductometric measurements. As a challenge, the composite shall be tested in similar conditions of high human breathing (relative humidity between 90 to 95%). Indeed, the materials studied may

have potential to diagnose diseases such as diabetes and lung cancer.
Acknowledgement: FAPESP Grant number 14/17343-0.

11:20 AM

(ICACC-EMERG-006-2016) Optical and Electronic Properties of 2D MXenes Thin Films

J. Halim*[1]; L. Hultman[2]; J. Rosen[2]; P. Eklund[2]; Y. Gogotsi[1]; M. Barsoum[1]; 1. Drexel University, USA; 2. Linkoping University, Sweden

The discovery of graphene has influenced scientists to explore other 2D materials such as transition metal dichalcogenides, BN, among several others. The main quest of seeking other 2D materials is to explore various properties that would suit different applications. MXenes are a newly discovered 2D family of early transition metal carbides. MXenes are synthetized by selective chemical etching the A element from a MAX phase, such as Ti_3AlC_2, producing 2D layers of $Ti_3C_2T_x$ where T stands for O, OH and/or F terminations. We show the fabrication and characterization of several members of the MXene family as 2D thin films, such as $Ti_3C_2T_x$, using TEM, XRD, and SEM. Optical and electrical properties have been investigated. For instance, $Ti_3C_2T_x$ thin films show transparency up to 90% in the visible light range. They also show a conductive behavior from room temperature down to 100 K, whereas below that temperature, the resistivity of the films increases with decreasing temperature; this behavior is due to weak localization phenomenon characteristic of defective 2D metals. Negative magnetoresistance serves as another proof of the weak localization phenomenon, confirming that these are 2D materials. Based on these results, it is possible to consider MXene thin films as candidates for electronic and photonic sensing applications as well as transparent conductive electrodes.

11:40 AM

(ICACC-EMERG-007-2016) Effect of Synthesis Conditions on the Structure of Ti_3C_2-MXene and its Performance in Electrochemical Energy Storage Systems

M. Naguib*[1]; H. Wang[1]; K. L. Page[1]; Y. Gogotsi[2]; 1. Oak Ridge National Lab, USA; 2. Drexel University, USA

Two-dimensional transition metal carbides and carbonitrides, MXenes, are synthesized by etching atomically thin metal layers from MAX phases (ternary layered carbides/nitrides). The etching process is carried out using hydrofluoric acid (HF), or a mixture of an acid and a metal fluoride salt. So far, more than fifteen different MXenes have been synthesized, and many more are expected to be stable. Among all MXenes, Ti_3C_2 is the most explored one since it was the first produced experimentally. The structure of Ti_3C_2-MXene was resolved using neutron and X-ray diffraction. Different Ti_3C_2-MXene samples prepared by etching Ti_3AlC_2 using different processes were investigated, and it was found that a lower HF concentration led to more ordered structure and a lower fluorine content. The effect of etching conditions on the electrochemical performance of Ti_3C_2-MXene in energy storage systems, including Li-ion batteries, was studied and will be discussed.

FS1: Geopolymers, Chemically Bonded Ceramics, Eco-friendly and Sustainable Materials

Sustainable Materials

Room: Coquina Salon E
Session Chair: Hubert Rahier, Vrije Universiteit Brussel

8:30 AM

(ICACC-FS1-008-2016) Mixed alkali regional metakaolin-based geopolymer (Invited)

R. A. Sa Ribeiro*[1]; M. G. Sa Ribeiro[1]; W. M. Kriven[3]; K. Sankar[2]; G. P. Kutyla[3]; 1. INPA-National Institute for Amazonian Research, Brazil; 2. University of Illinois at Urbana Champaign, USA; 3. University of Illinois at Urbana-Champaign, USA

In the pursuit of sustainable construction, regional natural materials can be used as a base for geopolymer processing. For higher strength achievement, this study uses mixed potassium-sodium geopolymer. Geopolymer was synthesized using metakaolin produced from kaolinite extracted from Amazonian soil, and microscopically compared to a commercial, highly reactive, metakaolin-based geopolymer. Amazonian kaolin was converted into metakaolin by calcination up to 700 °C. X-ray diffraction (XRD) analysis showed the resulting amorphous metakaolin to be 76% pure, with 24% crystalline quartz impurity. Four-point flexural and compressive strength testing of the geopolymer were carried out according to ASTM standards. Energy dispersive x-ray spectroscopy and scanning electron microscopy were used to investigate the microstructure and the Si/Al ratio. In addition, XRD was used to confirm the formation of geopolymer.

9:00 AM

(ICACC-FS1-009-2016) Potassium-based Geopolymer Reinforced with Bamboo Fibers

R. A. Sa Ribeiro*[1]; M. G. Sa Ribeiro[1]; K. Sankar[2]; W. M. Kriven[3]; 1. INPA-National Institute for Amazonian Research, Brazil; 2. University of Illinois at Urbana Champaign, USA; 3. University of Illinois at Urbana-Champaign, USA

Bamboo is a fast growing, readily available natural material with tensile specific strength equivalent to that of steel. In the pursuit of a sustainable construction material, a composite was made with potassium geopolymer as the matrix and randomly oriented chopped bamboo fibers (*Guadua angustifolia*) from the Amazon region as the reinforcement. Four-point flexural strength testing of the geopolymer composite reinforced with bamboo fibers was carried out according to ASTM standard. Energy dispersive x-ray spectroscopy and scanning electron microscopy were used to investigate the microstructure and the Si/Al ratio. In addition, X-ray diffraction was used to confirm the formation of geopolymer and the presence of cellulose in the bamboo fibers.

9:20 AM

(ICACC-FS1-011-2016) Durability Performance of Alkali-activated Metakaolin, Slag, Fly Ash, and Hybrids (Invited)

F. Jirasit*[1]; C. Rüscher[2]; L. Lohaus[2]; P. Chindaprasirt[3]; 1. RMUTL, Thailand; 2. LUH, Germany; 3. KKU, Thailand

The durability performance of Alkali-Activated Cements (AAC) i.e., metakaolin (AAMK), slag (AAH), fly ash (AAB), and their hybrids (AAMK/H, AAMK/B) were carried out on carbonation test and degradation test in sulfuric acid pH 0.5. The effect of carbonation was followed by IR absorption spectroscopy, KBr method. Ordinary Portland Cement (OPC), modified-OPC, and AAC were monitored for 11weeks. Series of AAMK, AAH, AAB, and their hybrids were prepared using 2 types of alkaline activator (K0.5 & K0.64) and their deterioration were monitored for 9weeks. Any accelerated

carbonation can be ruled out in case of AAMK, while it occurs the more the higher the CaO content of the raw material. In those material carbonation occurs with the possible formation of vaterite which is split in the bands at about 1420 and 1490 cm^{-1} before exposure. The further reaction is detected by increasing of the intensity of vaterite phase after exposed to CO_2 of 3 vol%. For the sulfuric acid, the AAC reveal much better compared to OPC. A comparison between 2 types of alkaline activator reveals that the higher content of alkaline yielded more deterioration. As compared between sources of starting materials, AAFA tended to resist acid attack better than that of AAMK. However, the AAFA shows significant formation of cracks. The results are also discussed with respect to their long term mechanical properties followed over 5 years.

9:40 AM

(ICACC-FS1-012-2016) Inorganic polymers in the CaO – "FeO" – Al_2O_3 – SiO_2 system: precursors, engineered materials and real-life applications (Invited)

Y. Pontikes*[1]; R. Iacobescu[1]; 1. KU Leuven, Belgium

Inorganic polymers today are primarily synthesized from aluminosilicate-rich precursors, often containing calcium, and little emphasis is placed on synthesizing the precursor itself. An alternative set of precursors is presented in this work. These materials originate from a (s)melting/vitrification process that typically operates at a temperature not exceeding 1200 °C. Their chemistry is predominantly composed of Si, Al, Ca and Fe oxides, are produced under reducing conditions so that Fe^{2+} prevails, with FeO levels preferably higher than 30wt%. To illustrate the potential, inorganic polymers from originally different precursors are synthesized and characterised. Focus is placed on slags from non-ferrous metallurgical processes. The results show that the inorganic polymers produced can reach compressive strength >100 MPa, the inorganic polymer synthesis process can be tuned to engineer porosity and firing behavior, and their production process can be more sustainable when compared to ordinary Portland cement. A portfolio of final applications where these materials can be used is also presented.

Composites

Room: Coquina Salon E
Session Chair: Henry Colorado, UDEA

10:20 AM

(ICACC-FS1-013-2016) Cement paste with iron oxide powders obtained from an arsenic remediation process

H. A. Colorado*[1]; 1. UDEA, Colombia

Portland cement-iron oxide composite with arsenic contents were fabricated in this research. Iron oxide is the byproduct of the water filtration process to remove arsenic. Several countries have issues with drinking water contaminated with arsenic, which could lead to arsenic poisoning. Iron oxide waste used as filters for arsenic removal from water has been mixed with Portland cement to form composites with two main benefits: arsenic stabilization by fixing the iron oxide powder with the cement binder, and by working as a reinforcement for the cementitious matrix. Characterization was conducted scanning electron microscopy (SEM), X-Ray Fluorescence, and x-ray diffraction (XRD). Up to 50wt% of these particles where added to cement, which itself is environmentally friendly since reduces the necessary cement binder amounts, and therefore reducing the CO_2 footprint.

10:40 AM

(ICACC-FS1-014-2016) Bone Ash Reinforced Geopolymer: A route to enhance microstructural integrity and mechanical properties in geopolymer composites (Invited)

A. W. Bhuiya*[1]; K. Sankar[1]; W. M. Kriven[1]; 1. University of Illinois at Urbana-Champaign, USA

In this study, natural bone ash (calcined) has been investigated for the reinforcement of potassium-based geopolymer. Bone ash as a particulate reinforcement was added to an amorphous three-dimensional aluminosilicate binding material known as geopolymer. Di-calcium phosphate mineral of bone ash reacted with potassium based aluminosicate and developed an interface with reduced porosity and micro crack in the microstructure at relatively low temperature. A material composition of geopolymer composites with low density bone ash ranging from 5-15 wt % were investigated to design a relatively light weight structural material with enhanced impact and flexural strength. The geopolymer composites were also thermally treated to 1000^0 C to investigate the microstructure, thermal resistance and mechanical properties at elevated temperature. The mechanical properties such as compressive, tensile, flexure and impact strength were tested according ASTM standards and compared with those of pure potassium-based geopolymer. The microstructure of the geopolymer composites were invested by powder X-ray diffraction and scanning electron microscopy.

11:00 AM

(ICACC-FS1-015-2016) Potassium Geopolymer Reinforced with E-glass Leno Weaves

K. Sankar*[1]; S. McCormack[1]; W. M. Kriven[1]; 1. University of Illinois at Urbana-Champaign, USA

This study addresses the need for a high temperature, structural ceramic matrix composite that can be used as a refractory tile. E-glass fibers are cheap, readily available, resistant to heat, electricity and chemical attack. They have high specific strength, stiffness and retain these properties at elevated temperatures (< 500 C). Geopolymers can be processed at room temperature and can withstand high temperatures. However, pure geopolymers have low tensile strength and fracture toughness. In this work the tensile, flexure and impact strength of E-glass Leno weave-reinforced, potassium geopolymer was studied. In-situ flexure properties of the composites were also studied to find out the behavior of composites at elevated temperatures. SEM and EDS were performed to observe the fiber-matrix interface. XRD was performed to confirm the presence of the geopolymer.

11:20 AM

(ICACC-FS1-016-2016) Dolomite ($CaMg(CO_3)_2$) Particulate-reinforced Geopolymer Composite

P. F. Keane*[1]; W. M. Kriven[1]; 1. University of Illinois at Urbana-Champaign, USA

Dolomite powder ($CaMg(CO_3)_2$ or $CaCO_3$•$MgCO_3$) is an industrial waste material obtained as a sediment resulting from grinding of dolomite rocks. Representative microstructures, particle size and size distributions were measured. Increasing amounts of dolomite powder were dispersed in sodium and potassium-based geopolymer. The mechanical compressive and flexure properties were measured in three-point bending at room temperature, as well as four-point bending at high temperatures to 1000°C. The thermal conductivities were also measured as a function of solids loading. The microstructures were examined by XRD and SEM/EDS.

11:40 AM

(ICACC-FS1-017-2016) Sodium Geopolymer Reinforced with Cork

D. Roper*[1]; W. M. Kriven[2]; 1. University of Illinois Urbana-Champaign, USA; 2. University of Illinois at Urbana-Champaign, USA

Cork is a low-density natural bark produced by trees that can be harvested for hundreds of years. When chopped finely, this material can be used for crack deflection and toughening in geopolymers. The goal of this design was to create a sustainable, lightweight and reliable geopolymer composite. Its properties and viability as a structural material were determined through four-point flexure testing according to ASTM C78/C78M-10 and analyzed by Weibull statistics. Its refractory properties were tested by exposing samples to various temperatures, then testing for shrinkage and flexure strengths. Scanning electron microscopy (SEM) was used to characterize the size and geometries of the cork, and to determine its viability as a reinforcement for sodium geopolymer.

FS4: Additive Manufacturing and 3D Printing Technologies

Selective Laser Sintering

Room: Coquina Salon C

Session Chairs: Thomas Mühler, Clausthal University of Technology; Eric Schwarzer, Fraunhofer Gesellschaft

8:30 AM

(ICACC-FS4-009-2016) Selective Laser Sintering in Combination with Layerwise Slurry Deposition for the Additive Manufacture of SiC Ceramics (Invited)

J. Guenster*[1]; A. Zocca[2]; C. M. Gomes[2]; 1. BAM, Germany; 2. BAM Federal Institute for Materials Research and Testing, Germany

The selective laser sintering of SiC ceramic powders has been studied extensively in the past. Despite its low sintering activity, SiC is particularly suited for the selective laser sintering process, because of the possibility to form SiO_2 at elevated temperatures in oxidizing ambient. The SiO_2 formed can act as a binder within the laser sintering process. In the present work densely packed powder beds generated by the Layerwise Slurry Deposition (LSD) technology are selectively sintered by a cw. fiber laser. The layerwise slurry deposition is an innovative process for the deposition of layers in additive manufacturing. A slurry with no or very small organic content is repetitively spread as thin layers on each other by means of a doctor blade. During the deposition process, the ceramic particles settle to form thin layers of about 100 μm which have a high packing density (typical 55-60%). This high powder packing density is the result of a slip casting process: When a layer is deposited on a previously dried porous layer, the water is drawn into the pores by capillary forces. The LSD process therefore shares aspects of tape casting and slip casting. An additional benefit of the LSD technology is the free choice of the size of the ceramic particles used. Compared to the processing of dry flowable powders, especially small particles can be very well processed.

9:00 AM

(ICACC-FS4-010-2016) Development of Advanced Ceramic Fuel Cells using Additive Manufacturing Technology (I): Design and Modeling

Y. Du*[1]; A. Maar[1]; K. Zhao[1]; 1. Kent State University, USA

Fuel cells are one of the most efficient clean technologies to convert chemical energy in fuel into electricity. A fuel cell consists of two electrodes separated by electrolyte to realize the energy conversion function. A novel spiral fuel cell has been invented. The cell consists of two features, a spiral shell with a closed spiral cross-section, and two spiral manifolds for fuel distribution and current collection. This work is to develop a spiral solid oxide fuel cell (SOFC) using additive manufacturing process, and to study the effects of processing parameters on the microstructure and performance. Firstly, the spiral cell will be designed using a 3D modeling program and the theoretical power output will be calculated. Secondly, the model will be printed using a plastic 3D printer for checking design defects or revisions. The final approved model design(s) will be produced using ceramic anode materials and selective laser sintering (SLS) or lithography-based ceramic manufacturing (LCM) process. Microstructure of the anode will be examined to optimize the process parameters. The application of additive manufacturing in SOFC will add new aspects to ceramics, enabling the manufacturing of the complex ceramic designs. This talk will discuss our design and modeling part of the work.

9:20 AM

(ICACC-FS4-011-2016) Generation of ceramic green bodies in the additive manufacturing by Laser Induced Slip-casting (LIS)

T. Mühler*[2]; J. Guenster[1]; A. Zocca[1]; 1. BAM Federal Institute for Materials Research and Testing, Germany; 2. Clausthal University of Technology, Germany

For the additive manufacture of large components usually powder-based methods are used. A powder is deposited layer wise by a recoater, then, the component structure is printed to the powder bed or sintered by a laser. In slurry based methods, the slurry is deposited by a doctor blade and dried before the printing of binder or the laser treatment. The new method of laser-induced slip casting is also a slurry-based method and the layers deposited sequential. However the slip is not dried and the structure is written directly by a laser into the suspension. The wall thickness of the ceramic material can be adjusted by the laser spot size and treatment time. The water is evaporated by the laser and a green body is formed locally. Because of its porosity, water is taken from the surrounding suspension and the wall thickness of the green body increases with treatment time. Due to the use of highly filled suspensions, the green body is stable in the ceramic slurry. Large green bodies can be built which have no visible layers in the microstructure.

9:40 AM

(ICACC-FS4-012-2016) Layerwise slurry deposition: an approach for dense powder-beds in Additive Manufacturing and its application to technical ceramics

A. Zocca*[1]; T. Mühler[2]; J. Guenster[1]; 1. BAM Federal Institute for Materials Research and Testing, Germany; 2. Clausthal University of Technology, Germany

Several Additive Manufacturing (AM) processes are based on the deposition of a powder to form a powder-bed layer-by-layer which typically has a low packing density (35-50%) and consequently hinders the ability of sintering ceramic parts to full density. The layerwise slurry deposition (LSD) is an innovative process for the deposition of layers in AM. In the LSD, a slurry with no or small organic content is repetitively spread as thin layers on each other by means of a doctor blade. During the deposition, the ceramic particles settle to form thin layers with a high packing density (55-60%). When coupled with a printing head or with a laser, the LSD enables novel AM technologies inspired to the 3D printing or selective laser sintering, but taking advantage of having a highly dense powder-bed. This approach has been successfully applied to silicate ceramics, but implementing technical ceramic slurries is more challenging, because the water is drained too quickly from the suspension into the pores of the previous porous layer. In this presentation, the variables involved in the LSD will be analyzed and the latest improvements in the deposition setup will be described. The application of the LSD to technical ceramics has the potential of generating additive manufacturing parts which in the green state are comparable to those produced by slip casting.

Stereolithography

Room: Coquina Salon C

Session Chairs: Jens Guenster, BAM Federal Institute for Materials Research and Testing; Johannes Homa, Lithoz GmbH

10:20 AM

(ICACC-FS4-013-2016) Additive manufacturing of ceramics – myths and facts

J. Homa*[1]; M. Schwentenwein[1]; 1. Lithoz GmbH, Austria

In recent years additive manufacturing (AM) has created a regular hype; some people even see the next industrial revolution in this technology and claim that a new age has risen and we will see a democratization of industrial production, where huge factories will disappear and everybody will manufacture his required goods at home. Will this really happen or is it just a newspaper hoax or a far too enthusiastic outlook in the future? While some of these expectations will not be fulfilled in the foreseeable future, AM has begun to play an integral role in today's ceramic research and also became an important methodology in ceramic industry. This contribution tries to elaborate and differentiate between facts and potentials of this new manufacturing paradigm on one side, and the myths and expectations generated by the media on the other. By showcasing different examples where AM was able to complement existing ceramic production methods the actual potential and strength of this method is highlighted. It is shown that AM provides an undisputable potential for customization, small-scale series and highly complex designs making it a valuable complement in the ceramic industry to existing manufacturing techniques but not to a substitute.

10:40 AM

(ICACC-FS4-014-2016) Stereolithographic Additive Manufacturing of Micro Ceramic Components by Variable Diameter Laser Scanning

S. Kirihara*[1]; 1. Osaka University, Japan

Stereolithographic additive manufacturing system has been customized to create ceramic components with micro functional structures at higher processing speed. A laser scanner with automatic collimator was newly equipped to realize precise micro pattering and high speed drawing by fine and thick beam spots, respectively. Photo sensitive acrylic resins with hydroxyapatite and β-tricalcium phosphate of 3 μm in particle diameter at 50 vol. % were spread on a glass substrate with 10 μm in layer thickness by a mechanical knife edge. An ultraviolet laser beam of 355 nm in wavelength was adjusted from 10 to 100 μm in variable diameter and scanned on the pasted resin surface. Irradiation power was changed automatically from 10 to 200 mW to obtain enough solidification depth for layer by layer joining. Cross sectional patterns were laminated to create solid objects. Composite precursors were dewaxed and sintered under the crystal phase transition temperatures to prevent loss of their biocompatibilities. Bioceramic implants in centimeter order with graded and fluctuated patterns in micrometer order were designed and fabricated to realize vital fluid distributions and geometrical osteogenesis.

11:00 AM

(ICACC-FS4-015-2016) Additive manufacturing of high performance ceramics – new materials and new developments

M. Schwentenwein*[1]; J. Homa[1]; 1. Lithoz GmbH, Austria

Using the Lithography-based Ceramic Manufacturing (LCM) process the fabrication of precise and strong ceramic objects in a layer-by-layer manner becomes possible. The outstanding properties of this process are the high resolution as well as the isotropic microstructure and mechanical properties at the level of conventional formed ceramics. The use of a high resolution optical system allows the production of very precise and complex geometries with minimum feature sizes down to 100 μm. Since LCM is a slurry-based process, the technology can be adapted to the given ceramic powder, hence this process allows in principle the use of any conventional ceramic material. However, due to problems associated with light absorption, materials for lithographic processes are usually limited to ceramic powders very light in color. Thus, this paper focuses on the latest developments towards ceramic powders such as silicon nitride, cordierite or magnesia as addition to the existing alumina and zirconia materials. By broadening the available range of materials into these directions, lithographic AM of high-performance ceramic shall gain potential for a more widespread application. In combination with its high precision and accuracy the LCM process can provide interesting opportunities in fields such as biomedical applications, catalysis or refractories.

11:20 AM

(ICACC-FS4-016-2016) Additive Manufacturing of Polymer-Derived Ceramics

T. Schaedler*[1]; Z. C. Eckel[1]; C. Zhou[1]; J. H. Martin[1]; A. J. Jacobsen[1]; W. B. Carter[1]; 1. HRL Laboratories, USA

Additive manufacturing of ceramics enables fabrication of architected materials and complex shaped structures that are not feasible with conventional ceramic processing routes. We report UV curable pre-ceramic monomers that are exposed with UV light in a commercial stereolithography system or through a patterned mask, forming a three-dimensional polymer structure that can have complex shape and cellular architecture. These polymer structures can be pyrolyzed to a ceramic with virtually no porosity and defects. Silicon oxycarbide microlattice and honeycomb materials fabricated with this approach exhibit strength of 9 – 163 MPa at densities of 0.05 – 0.8 g/cm^3 - 10X higher than ceramic foams of similar density. The materials exhibit good oxidation performance and survive 3h at 1700°C in air with less than 1 mg/cm^2 weight change. Additive processing of such materials is of interest for thermal protection systems, porous burners, biomedical devices and lightweight, loadbearing sandwich structures.

11:40 AM

(ICACC-FS4-017-2016) Suspension-based additive manufacturing of ceramic, metal and metal-ceramic components

E. Schwarzer*[1]; U. Scheithauer[1]; A. Härtel[1]; H. Richter[1]; T. Moritz[1]; A. Michaelis[2]; 1. Fraunhofer Gesellschaft, Germany; 2. Fraunhofer IKTS, Germany

Different additive manufacturing (AM) procedures with new degrees of freedom introduce the possibility of innovative function oriented designs. Various material properties determine the type of methods. Lithography-based ceramic manufacturing (LCM, Lithoz) enables additive manufacturing of high performance, dense (>99 %) oxide ceramic components. Now, innovative functional ceramic designs have been produced with LCM. One application for example are complex shaped static mixers made of alumina with changing channel diameters and honeycomb structures with perforated walls and spoilers to regulate incoming fluids. Until now, no AM-process exist to generate e.g. metal-ceramic components. Metals are not applicable in the LCM process due to their high light absorption. Therefore, we follow a new approach of a novel AM-process, called thermoplastic 3D-printing (T3DP), which allows the processing of metal, ceramic and metal-ceramic components. The developed process is nearly independent from the used materials due to the solidification mechanism working temperatures up to 100 °C. Every powder, which is dispersible in a thermoplastic suspension, can be used in T3DP. Hence, this method is applicably for producing multi-material (e.g. metal-ceramic) components. First test structures made of alumina, zirconia, stainless steel and steel zirconia were manufactured by T3DP, thermal processed and characterized

FS6: Hybrid Materials and Processing Technologies

Hybrid Materials and Processing Technologies I

Room: Coquina Salon H
Session Chairs: Seungbum Hong, Argonne Nat Lab; Takashi Shirai, Nagoya Institute of Technology

8:30 AM

(ICACC-FS6-001-2016) Hybrid Materials for Energy Storage and Conversion (Invited)

J. Kang*[1]; 1. Korea Advanced Institute of Science and Engineering (KAIST), The Republic of Korea

The presentation will report materials for energy storage and conversion. Chemical and physical properties of traditional inorganic materials are governed by electron /spin behavior of the materials. They are primarily dependent on constituent atoms and their arrangement. These aspects of the materials have been intensively studied for bulk crystals (infinite periodic systems). Elementary particles, nuclei, atoms and condensed matter are forming hierarchical structure both in space and energy. Of course I am interested in condensed matter, including both hard- and soft-materials. Material science to pursue/find the universality, diversity & complexity requires us new strategy both in solving structures and in designing the materials. Recently, my main concern is to realize development of high performance materials relating to energy and environmental issues. On this invited talk, I will discuss new paradigm approaches to realize next generation energy storage and conversion technologies that we could demonstrate via development of materials beyond the conventional concepts.

9:00 AM

(ICACC-FS6-002-2016) Development of Hydrothermally Stable Metal-Organic Frameworks for Water Sorption Technologies (Invited)

J. Chang*[1]; U. Lee[1]; Y. Hwang[1]; 1. KRICT, The Republic of Korea

Water sorption technologies are widely used commercially in many areas, including industrial or indoor desiccant applications such as desiccant dehumidifiers, gas dryers, adsorptive air-conditioning systems, fresh water production, adsorption heat transformation, etc. In this context, there is nowadays a growing interest to search for novel porous solids able to achieve high uptakes of water at low relative pressure, which is one of the major requirements for adsorption-driven heat pumps and chillers. Such a process based on reversible adsorption/desorption of a fluid rather than conventional vapour compression is a promising alternative to exploit low-grade waste thermal energy for heat and cold allocation. In spite of this importance, a concentrated effort on the development of advanced water adsorbents is still necessary since the working capacities of commercial porous solids at low pressure (p/p_0 = 0.17-0.20) are not sufficient to compete with the performances of commercial absorption chillers based on LiBr-water as the working fluid pair. In this work, we present the great promise that some of hydrothermally stable metal-organic frameworks (MOFs) can be used for adsorption-drive heat pump applications and desiccant dehumidification. These MOFs exhibit higher thermodynamic efficiency, volumetric working capacity and lower desorption temperature than conventional sorbents.

9:20 AM

(ICACC-FS6-003-2016) Plasma Deposition and Modification of Semiconducting Thin Films for Photoelectrochemical Hydrogen Production (Invited)

Y. Gönüllü*[2]; T. Fischer[1]; M. Pyeon[2]; A. Kaouk[2]; S. Mathur[2]; 1. University of Colgne, Germany; 2. University of Cologne, Germany

The PE-CVD is a unique technique for thin film deposition, since it provides a good control over several parameters (time, plasma power and reactive gas composition) and therefore over the properties of the resulting films. In addition PE-CVD processes show a high reproducibility and they are scalable for large area productions. It finds applications in growth and processing of nano-materials, such as semiconductor thin films or carbon structures like graphene, carbon nanotubes (CNT), or DLC. Since the PE-CVD is a low temperature process it is possible to deposit under mild conditions onto sensitive materials like polymers. In this work we present the deposition and modification of semiconducting metal oxides (TiO_2, Fe_2O_3, SnO_2) and their heterostructures for photoelectrochemical (PEC) hydrogen production. Furthermore the as deposited films were modified using plasma techniques or supporting with graphen layer. Namely those modifications were the partial reduction of the metal oxides by hydrogen plasma, the doping with different metal cations. All this techniques allowed the selective tuning of the optical and electrical properties of the films and therefore lead to a substantially enhanced PEC performance.

9:40 AM

(ICACC-FS6-004-2016) Multiscale Modeling of Hybrid Interface in Energy/Environmental Materials (Invited)

H. Kim*[1]; 1. Korea Advanced Institute of Science and Engineering (KAIST), The Republic of Korea

To achieve the improved sustainability through the development of renewable and clean energy source, it is required to understand the operational mechanism of the complex materials to improve their own intrinsic and extrinsic properties. However, such materials often consist of complicated Multiscale/Multiphysics natures characterized by energy inter-conversion processes, sequential electron/charge transfers, multistep catalytic reaction pathways, subtle balance of thermodynamic driving forces, ill-defined structural characteristics, etc.; thus, it is often difficult to unveil the underlying mechanism and improve the desired material properties. For the systematic improvement with tailored material properties, we use first-principles based multi-scale computational methods to understand, predict, and design the material structures and processes. In this talk, I will discuss our recent works demonstrating how the computational simulations can aid understanding complicated chemo-physical properties of materials.

10:20 AM

(ICACC-FS6-005-2016) Formation of polymer/metal nanoparticles hybrid nanowires by single particle nanofabrication technique (Invited)

S. Tsukuda*[2]; M. Sugimoto[3]; T. Sekino[1]; S. Seki[4]; 1. Osaka University, Japan; 2. Tohoku University, Japan; 3. Japan Atomic Energy Agency, Japan; 4. Kyoto University, Japan

High energy ion beam can achieve high-density energy deposition within a cylindrical area along the passage of a single ion. The ion beam irradiation of a polymer thin film has been shown to cause cross-linking reactions along ion paths, yielding a nanogel with reduced solubility in solvents. Subsequent washing procedure using a solvent to remove a non-cross-linked polymer affords isolated nanowires with uniform size. This direct fabrication technique of polymer nanowire is called single particle nanofabrication technique (SPNT). Several kinds of polymer nanowires such as poly(vinylpyrrolidone) and polycarbosilane have been fabricated using SPNT. We also fabricated hybrid nanowires based on the polymer and metal nanoparticles by reduction treatment in a solution containing

a metal salt. Au, Ag, and Pd nanoparticles were selectively formed on the polymer nanowires, and the particle size and number density could be easily controlled by the reduction conditions. The formation mechanism of metal nanoparticles on the nanowires were discussed in terms of reduction reaction, nucleation, and growth. The catalytic and optical properties of the hybrid nanowires were also investigated.

10:50 AM

(ICACC-FS6-006-2016) Ubiquitous Magneto-Mechano-Electric Generators with Piezoelectric Single Crystal Fibers and Ni laminate composites (Invited)

J. Ryu*[2]; D. Jeong[3]; S. Choi[1]; W. Yoon[2]; J. Choi[2]; J. Kim[2]; B. Hahn[2]; C. Ahn[2]; 1. Korea Institute of Materials Science, The Republic of Korea; 2. Korea Institute of Materials Science (KIMS), The Republic of Korea; 3. Inha University, The Republic of Korea

Magnetoelectric (ME) composites exploit the product property of magnetostriction and piezoelectricity. The ME effect is the result of multiple energy transduction starting from magnetic energy to mechanical energy and finally to electrical energy, i.e, magneto-mechano-electric (MME) transduction. In this presentation we report the energy harvesting performance of self-biased ME laminate composite with anisotropic piezoelectric single crystal fiber composites (SFC) and magnetostrictive Ni plate. The flexibility of SFC represents high compliance of the sample and it is ideal for achieving low resonance frequency in cantilever structure. Flexibility also imparts durability and ability to apply increased strain magnitudes. Ni can be easily self-biased and generates linear strain response in low level magnetic field environment. ME properties and MME generator performance were evaluated under 60 Hz low level magnetic noise to clarify the performance metrics and illustrate the uniqueness of this architecture. In addition, we demonstrate the energy harvesting from the real power line for vacuum pump and 60 LEDs lighting under the weak magnetic field of 700 mT at 60 Hz. Furthermore, this MME harvester can operate wireless sensor networks (WSN) composed of TI-MSP430-CC2500 module.

11:10 AM

(ICACC-FS6-007-2016) Improvement of Thermoelectric Properties of Electrodeposits by Nanoinclusion (Invited)

N. Heo[1]; J. Kim[2]; Y. Song[1]; N. V. Myung[2]; K. Kim[3]; J. Lim*[1]; 1. Korea Institute of Materials Science, The Republic of Korea; 2. University of California, Riverside, USA; 3. Pusan National University, The Republic of Korea

The many advantages of Themoelectric (TE) devices include solid-state operation, zero-emissions, vast scalability, no maintenance and a long operating lifetime. However, due to their limited energy conversion efficiencies, TE devices currently have a rather limited set of applications. Recently, there is a renewed interest in the field of TE materials because of the remarkable efficiency improvement by means of nanostructured materials. Among many synthesis methods that facilitates the formation of embedded nanostructure, Electrodeposition of thermoelectric materials, including binary and ternary compounds, have been attracting attentions because its many advantages including low-cost, rapid deposition rate, and ease of control their microstructure and crystallinity by adjusting electrodeposition parameters. However, little works on the inclusion of low dimensional structure by spontaneous formation has been done to improve the thermoelectrical property. Herein, we performed systematic studies to electrodeposited binary and ternary compounds using pulse-plating and post-annealing process, and correlate their materials/structural properties to thermoelectrical/electrical properties. The details will be presented.

11:30 AM

(ICACC-FS6-008-2016) High-Capacity Cathode Material for Next-Generation Lithium-Ion Batteries (Invited)

Y. Sun*[1]; 1. Hanyang University, The Republic of Korea

Ubiquitously present in mobile society, have driven the ever-increasing demands for light portable power sources with large capacity. Although lithium-ion batteries are the standard choice for powering mobile electronics, successful use of LIBs in the automotive sector requires significant improvements in energy density, cycle life, and safety characteristics. A layered lithium transition metal oxide, $Li[Ni_xCo_yMn_z]O_2$ (x+y+z = 1) have been extensively utilized and studied as cathode materials for lithium-ion batteries due to their high capacity. One of the most promising oxides is full concentration gradient (FCG) lithium nickel-cobalt-manganese oxide composed of a Mn-rich outer surface providing excellent safety and Ni-rich center achieving high capacity. Here, we extended the FCG concept and report a new novel $Li[Ni_{0.65}Co_{013}Mn_{0.22}]O_2$ cathode material with two-sloped full concentration gradients (TSFCG) of Ni, Co, and Mn ions throughout the cathode particles to maximize the average Ni concentration at the core as active redox species and the Mn concentration in the area near the particle surface. The Ni-rich TSFCG delivers a discharge capacity in excess of 200 mAh g^{-1} (at 4.3 V cutoff voltage and 0.1 C rate) with excellent cycle life and thermal stability. Comparison of electrochemical and thermal properties of the TSFCG with those of NCA and conventional cathode $Li[Ni_{0.65}Co_{013}Mn_{0.22}]O_2$ is presented.

S1: Mechanical Behavior and Performance of Ceramics & Composites

Ceramic Matrix Composites II

Room: Coquina Salon D

Session Chairs: Jacques Lamon, CNRS; Dietmar Koch, Institute of Structures and Design

1:30 PM

(ICACC-S1-059-2016) Monitoring damage in ceramic matrix composites using waveform-based modal acoustic emission (Invited)

E. Maillet*[1]; G. N. Morscher[2]; 1. GE Global Research, USA; 2. The University of Akron, USA

Ceramic matrix composites (CMCs) are being implemented in the hot section of commercial jet engines. In order to predict life in service of CMC parts, it is necessary to understand the nature and extent of damage in given conditions of stress, temperature and environment, and how such damage initiates and further propagates throughout service life. Extensive laboratory testing is carried out for that purpose. The use of acoustic emission (AE) monitoring during these tests provides valuable information about damage in terms of location and mode. However, only a waveform-based analysis of acoustic emission can validate and precisely examine the recorded AE data with a view to damage localization and identification. In the present work, a procedure was developed that fully integrates wave initiation, propagation and acquisition in the analysis of AE waveforms recorded at various sensors, therefore providing more reliable information to determine the relation between AE and damage modes. The waveform-based analysis of AE allows accurate selection of AE events originating from damage, accurate determination of their location, and offers the possibility to account for effects of propagation on the recorded AE signals. Correlations between AE and damage will be presented for various ceramic matrix composite systems.

2:00 PM

(ICACC-S1-060-2016) A Multiscale-Multiphysics Framework for Linking Coupon to Component Behavior of CMCs

M. Bailakanavar*[1]; 1. Weidlinger Associates Inc., USA

Manufacturing of CMC components inadvertently results in manufacturing defects such as porosity and matrix rich regions in the vicinity of the ply drops and ply wrinkling that act as potential sources for damage. The current approaches to characterize the thermo-mechanical behavior in CMCs is mostly based on flat coupon testing and fail to accurately predict failure and fatigue life. A multiscale-multiphysics finite element analysis methodology is currently under development for design and analysis of CMC components. The multiscale-multiphysics analysis methodology is envisioned to effectively capture the complex multi-axial stress states in SiC-SiC based CMC sub-elements and components under relevant operating conditions. The unique features of the Multiscale-Multiphysics analysis tool are as enumerated below: 1. Ability to model manufacturing defects and upscale their effect on the component response 2. Micromechanics models at the fine scale of interest to characterize damage and failure in the CMC constituent phases The multiscale model will predict the thermo-mechanical behavior of CMCs through a two step-hierarchical procedure: Step 1 - Utilize the multiscale mechanical model in flat coupon analysis to calibrate model parameters Step 2 - Predict failure and fatigue life of actual CMC sub-elements and components based on the calibrated material models

2:20 PM

(ICACC-S1-061-2016) Modeling of Delamination Growth in Ceramic Matrix Composites

R. Kumar*[1]; G. Ojard[1]; 1. United Technologies Research Center, USA

Initiation and propagation of delaminations is an important failure mode in complex-shaped Ceramic Matrix Composite (CMC) components subject to thermomechanical loads such as those experienced in gas turbine engines. This paper will present recent work on computational modeling of delamination propagation in CMCs under both quasi-static and impact loading conditions. Simulation results from both simple and complex geometries will be presented and compared against experimental data. The paper will also discuss challenges associated with modeling and testing of delamination crack growth in CMCs.

2:40 PM

(ICACC-S1-062-2016) Matrix Cracking, Detection and Micromechanics of Pre-Preg Laminate SiC/SiC Composites (Invited)

G. Morscher*[2]; N. Gordon[3]; E. Maillet[1]; 1. GE Global Research, USA; 2. The University of Akron, USA; 3. NobleTek, USA

Pre-preg laminate ceramic matrix composites are soon to be entered into service for jet engine applications. The damage development in SiC/SiC composites is necessary to understand the stress-strain properties for this important class of materials. To this end, matrix cracking was determined due to tensile stress for pre-preg SiC/SiC composites consisting of Hi-Nicalon Type S fibers, a BN interphase and Si-SiC matrix. Three of different laminate architectures were studied: unidirectional, [90/0]2s and [0/90]2s. Matrix cracking was monitored during tensile testing using acoustic emission (AE) and electrical resistance (ER). The numbers of cracks for the different composite architectures were determined for different stress/strain exposures by polishing lengths of tested composites. The AE and ER results were analyzed with respect to the cracking behavior within the different plys of the different composite architectures and used to estimate stress-dependence for matrix cracking. The stress-dependent cracking results were then used in conjunction with micromechanics approaches to model the stress-strain behavior for the different composites.

3:30 PM

(ICACC-S1-063-2016) Development of an Interlaminar Fracture Testing Technique for Ceramic Matrix Composite at Ambient and Elevated Temperatures

R. Mansour*[1]; G. Morscher[1]; 1. The University of Akron, USA

For fiber-reinforced ceramic matrix composites, interlaminar fracture properties play a vital role in predicting failure of structural components. Elevated temperatures induce more severe conditions for interlaminar properties resulting in a weaker interlaminar toughness. In a 2D-based architecture material, fibers are generally aligned in one of the orthogonal axial directions, therefore, only few of the fibers bridge interlaminar cracks resulting in a higher probability of failure in the interlaminar direction. Detecting crack initiation and in-situ crack growth measurements are the main challenges in evaluating interlaminar fracture properties. Hence, a non-visual crack monitoring technique has been successfully developed to estimate crack length in a melt-infiltrated woven SiC/SiC composite using electrical resistance. This method was also applied to obtain preliminary interlaminar fracture properties at high temperatures. Acoustic emission was used as well to determine crack initiation and damage accumulation accurately during the test.

3:50 PM

(ICACC-S1-064-2016) Fatigue Behavior of Double-Edge Notched Oxide/Oxide Ceramic Matrix Composite in a Combustion Environment

A. K. Singh*[1]; V. Sabelkin[1]; S. Mall[1]; 1. Air Force Institute of Technology, USA

Tension-tension mechanical fatigue tests were performed on double-edge notched specimens of NextelTM/720 alumina ceramic matrix composites. Tests were performed in a gas turbine combustion environment which was simulated by the state-of-the-art combustion chamber developed at the Air Force Institute of Technology. The combustion environment test temperature was 1250 ± 50°C, with the mechanical loadings applied simultaneously at a frequency of 1 Hz and a stress ratio of 0.05. The test results were compared to published results performed in laboratory air environment at 1200°C on specimens made out of the same material and tested under the same mechanical loading conditions. The S-N curves developed from the test results showed that for a particular number of cycles to failure, the maximum cyclic stress in the combustion environment was approximately 30% less than that of the same number of cycles in the laboratory air environment.

4:10 PM

(ICACC-S1-065-2016) Fatigue property of SiC/SiC Ceramic Matrix Composites

T. Nakamura*[1]; T. Manabe[1]; S. Muto[1]; 1. IHI Corporation, Japan

CMC is a promised candidate material for next generation aero-engine. SiC/SiC was chosen as the material for application study of turbine nozzle. Fatigue property is important to consider the applicability of CMC parts. So, tensile fatigue tests were conducted for both of LCF and HCF region, from 10^3 to 10^7 cycles, at elevated temperature up to 1100 degrees Celsius. Fatigue test with notched coupons were also conducted to consider the stress concentration effect. Properties change during the tests and the micro structural observation were investigated.

4:30 PM

(ICACC-S1-066-2016) Synchrotron studies of Ceramic Matrix Composites under extreme loading conditions

A. Manero*[1]; K. Artzt[2]; J. Wischek[2]; S. Sofronsky[1]; S. Hackemann[2]; J. Almer[3]; J. Okasinski[3]; P. Kenesei[3]; S. Raghavan[1]; M. Bartsch[2]; 1. University of Central Florida, USA; 2. DLR - German Aerospace Center, Germany; 3. Argonne National Laboratory, USA

This study presents the findings of in-situ synchrotron studies on high temperature ceramic matrix composites. The application of high intensity synchrotron X-Rays characterization of ceramic matrix composites has shown great promise to unlock complex material behavior in response to extreme conditions. Synchrotron studies provide micron resolution examination of material behavior and performance. This study utilized synchrotron radiation to conduct 3D Computed Tomography and 2D diffraction on an all-alumina ceramic matrix composite (WHIPOX™) under extreme environments. Quasi-unidirectional composites with varying fiber orientation were investigated to identify load partitioning between the fibers and matrix, and the influence of specimen aging compared with the as processed composite. Radiography and Diffraction studies were conducted on specimens under compression loading and extreme temperatures. Results show segregation of fiber and matrix diffraction rings under loading and distinct texturing variation due to grain size and growth. In-situ strain analysis provides insight into mechanical properties of matrix material and the varying fiber orientation composites, while computed tomography sheds light on macro-porosity and the role of processing. Together the synchrotron studies provide valuable material information on the structural capability of these ceramic matrix composites.

4:50 PM

(ICACC-S1-067-2016) Electrical resistance and acoustic emission during fatigue testing of high velocity impact SiC/SiC composites

Z. Han*[1]; G. N. Morscher[1]; 1. University of Akron, USA

Electrical resistance (ER) is a feasible approach of real-time monitoring and evaluating damage in SiC/SiC composites for a variety of loading conditions. In this study, two types of woven silicon carbide fiber-reinforced silicon carbide (SiC/SiC) composite systems, HNS and SA, were impacted by projectiles with the velocities ranging from 320m/s to 360m/s. The post-impact specimens were cycled (1Hz) at both room and elevated temperature (1200C). In addition, modal acoustic emission was also monitored, which can reveal the occasion of matrix cracks and fiber breaks which can then be related to the changes of ER. A method based on the slope of the ER evolution has been developed. It allows a second damage phase to be identified. Mechanical and electrical-mechanical models are also considered and compared with the experimental data.

S3: 13th International Symposium on Solid Oxide Fuel Cells (SOFC): Materials, Science and Technology

Thermomechanical Properties / Modeling and Evaluation of Material Properties

Room: Crystal

Session Chairs: Norbert Menzler, Forschungszentrum Juelich GmbH; Tatsumi Ishihara, Kyushu University

1:30 PM

(ICACC-S3-050-2016) Mechanical and Thermal Properties of Anode Materials for SOFCs under Redox Cycle Conditions (Invited)

K. Sato*[1]; 1. Tohoku University, Japan

Effects of redox cycling on the mechanical and thermal properties of the Ni-YSZ cermets for SOFCs anode were investigated by using a small punch (SP) testing method and differential dilatometer. The porosity range in the Ni-YSZ cermets tested in this study was 25-46%. Experimental results obtained from the in-situ SP tests demonstrated that elastic modulus and fracture stress of Ni-YSZ composite decreased with Ni contents increasing testing condition-independent, moreover Ni-YSZ composites are suggested that Ni particles formed a network-like structure at the Ni content greater than 30 vol.% by electrical resistivity measurement. So, the ductile-like behavior under SOFC operating condition could be attributed to the formation of Ni network in composite. On the other hand, in re-oxidized NiO-YSZ composites case, all composites surface already have a lot of facial cracks formed like spider net by re-oxidation treatment. This study revealed that porosity makes a key contribution to the durability of Ni-YSZ cermets by the redox cycling.

2:00 PM

(ICACC-S3-051-2016) Complete Relaxation of Residual Stresses During Reduction of Solid Oxide Fuel Cells Through Accelerated Creep

H. L. Frandsen*[1]; C. Chatzichristodoulou[1]; T. Heiredal-Clausen[2]; T. K. Petersen[3]; M. F. Madsen[4]; P. V. Hendriksen[1]; 1. Technical University of Denmark, Denmark; 2. Haldor Topsoe A/S, Denmark; 3. Topsoe Fuel Cell A/S, Denmark; 4. Resolvent I/S, Denmark

One challenge for commercialization of the solid oxide fuel cell (SOFC) technology consists of ensuring mechanical reliability over the desired lifetime of an SOFC stack. To evaluate the reliability of the SOFC stacks during operation a thermo-mechanical model can be used to determine the the stress field in the stack. The stresses in a stack evolve over time depending on the operational conditions, external pressures, mechanical properties of the stack components. In this work we present the impact of a newly discovered mechanical phenomenon, accelerated creep, for anode supported (Ni(O)-YSZ) SOFCs, which significantly changes the current estimates of the residual stresses in the SOFC stacks. The occurrence of the phenomena does however also make it simpler to estimate the residual stresses. The phenomenon has been studied by loading samples of Ni(O)-YSZ anode supports during the reduction and measure the residual stresses in simulated stack assembly by XRD. The anode support showed extreme compliance, i.e. with deformational rates, which are ~$\times 10^4$ of the typical creep rates of these materials. The extreme deformation rates can be understood on the microstructural scale of the porous metal-ceramics. Based on the findings, a guide for a simpler analysis of the residual stress field in a SOFC stack is established for practical use.

2:20 PM

(ICACC-S3-052-2016) Improved Redox Stability of Novel Inert-Substrate Supported Tubular Single Cells

K. Zhao*[1]; Y. Du[1]; 1. Kent State University, USA

Solid oxide fuel cells (SOFCs) have been considered as the most attractive energy conversion devices, due to their high efficiency and environmental compatibility. Ni-containing anode supported tubular SOFCs have been intensively investigated because of their low ohmic and polarization losses together with high maximum power densities. The Ni-containing anode supporters, however, suffer from poor mechanical stabilities under redox cycling conditions, arising from the reduction and re-oxidation of the nickel. This issue causes the expansion of anode supporters, the occurrence of cracks in the electrolyte, and ultimately performance degradation or even failure of the cells. To improve the redox cycling stability, we designed an inert-substrate supported tubular cell with a configuration of porous yttira-stabilized zirconia (YSZ) supporter/Ni anode current collector/Ni-$Ce_{0.8}Sm_{0.2}O_{1.9}$ (SDC) anode/YSZ/SDC bi-layer electrolyte/$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) cathode. The rigid porous YSZ supporter improves the mechanical strength and reduces the dimensional change upon anode reoxidation. Meanwhile, the porous YSZ supporter inhibits the propagation of delamination in the anode, thus improving the bulk volume stability of the single cell. These functions may pave a way for solving the redox cycling stability problem of SOFCs.

2:40 PM

(ICACC-S3-053-2016) Strengthening cathode contact strength by surface texture engineering for solid oxide fuel cells

Y. Chou*[1]; J. F. Bonnett[1]; J. W. Stevenson[1]; 1. Pacific Northwest National Lab, USA

In planar SOFC cell test the weakest link has been identified at the cathode contact interface. Results of ohmic resistance during routine thermal cycling and fractography have presented direct evidence. To improve the mechanical integrity of contact, we have proposed mechanism of mechanical interlocking by engineering a rough/textured cathode surface. Several processing techniques will be evaluated and strength tested: (1) pressing with a metallic mesh and a SiC grit paper, (2) using ink with sacrificial carbon, (3) deposition of large granules onto wet screen printed surface. Two of the treated bilayers will be joined with the nominal LSM contact paste and sintered to typical SOFC stack firing temperatures (<=950°C). Uniaxial tensile strength will be conducted on joined couples at room temperature. In addition, the effect of particle size, sintering temperature, and thermal cycling will be investigated. The intrinsic bulk strength of contact materials as a function of sintering temperature as well as elastic properties and Weibull modulus will also be reported to facilitate the fracture analysis and assessment of the surface texturing effect. The engineered surface will also be tested in a generic stack fixture test at 800°C followed by several thermal cycles.

3:20 PM

(ICACC-S3-054-2016) Role of Thermodynamics and Transport in Mechanical Reliability of Fuel Cells and Electrolyzer Cells (Invited)

A. V. Virkar*[1]; 1. University of Utah, USA

It is well known that fuel cells and electrolyzer cells degrade under certain operating conditions, thus affecting their electrical and structural reliability. Degradation is known to be more severe in the electrolysis mode compared to the fuel cell mode. It typically manifests as electrode delamination, electrolyte cracking, change in electrolyte stoichiometry (and thus change in defect chemistry), and electrolyte decomposition. The most fundamental entity is the magnitude of the local chemical potential of electrically neutral species corresponding to the mobile ion (e.g. μO_2 in O^{2-} ion conductor, μH_2 in proton conductor). This presentation will discuss the role of transport on local chemical potentials within the electrolyte and how a system (an electrochemical cell) can move away from equilibrium, affecting both electrical and mechanical reliability. Experimental work on how the electrolyte can be moved away from equilibrium and how the transport properties are affected will be presented. Samples of YSZ were fabricated with embedded Pt screen electrodes and porous surface electrodes. By electrochemically pumping oxygen into or out of the sample, the local μO_2 was varied over a wide range. The corresponding changes in transport properties will be discussed. Also presented will be the results of experiments on samples containing ceria.

3:50 PM

(ICACC-S3-055-2016) Improvement in electrochemical performance of micro-/nano-structure controlled electrodes for ceramic cells (Invited)

H. Shimada*[1]; T. Suzuki[1]; T. Yamaguchi[1]; H. Sumi[1]; K. Hamamoto[1]; Y. Fujishiro[1]; 1. National Institute of Advanced Industrial Sience and Technology (AIST), Japan

We have investigated various type electrochemical ceramic cells such as fuel cells and electrolysis cells and have developed processes to fabricate them. Micro-/nano-structure controlled electrodes showed improvement in their electrochemical performance. For example, highly porous electrode substrates prepared via extrusion process led to good gas diffusion property, resulting in low gas diffusion resistance and high reactant utilization in both fuel cell and electrolysis modes. Also, the use of nano-composite powder prepared via spray pyrolysis for electrode material led to achievement of extremely fine electrode structure and high activity. We will introduce these results in detail in our presentation.

4:20 PM

(ICACC-S3-056-2016) Mechano-chemical engineering: Can strained oxide ion conductors provide a route to next-generation SOFC devices for energy conversion?

G. Harrington*[1]; A. Cavallaro[3]; D. McComb[4]; S. Skinner[3]; J. Kilner[3]; K. Sasaki[1]; B. Yildiz[2]; H. L. Tuller[2]; 1. Kyushu University, Japan; 2. Massachusetts Institute of Technology, USA; 3. Imperial College London, United Kingdom; 4. The Ohio State University, USA

Traditionally, the development of new materials for electrochemical devices, such as solid oxide fuel cells (SOFCs), has been based upon new chemical compositions and structures. Yet in recent years the effects of mechano-chemical coupling, via strain engineering, has received considerable interest for improving ion transport and surface reactivity in SOFCs. In this presentation, we assess the effect of lattice strain on the oxide ion conductivity and the chemical stability of oxides of importance to SOFCs. We study the effects of strain on the transport properties of oxygen ion based electrolytes such as yttria-doped zirconia and gadolinia-doped ceria, when grown in thin film geometries. Here, we investigate oxygen ion conductivity as a function of substrate induced tensile and compressive strain, both electrically and using a novel isotope tracer diffusion technique. Given the significant interest in the ionic transport in strained oxides, there has been surprisingly little work studying the stability of such systems, despite devices being required to operate at high temperatures for extended lengths of time. To address this issue, we assess the implications of lattice strain on materials degradation from dopant segregation in typical fluorite and perovskite structures, as a path towards identifying strain states for optimal device performance.

4:40 PM

(ICACC-S3-057-2016) Thermodynamic Modeling of the Phase Stability of LSCF Perovskite

S. Darvish[1]; Y. Zhong*[1]; 1. Florida International University, USA

The quantitative calculation regarding the phase formation and the effect of atmospheric carbon dioxide and on Sr segregation on

the surface of $La_{0.6}$-$Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF-6428) is calculated using La-Sr-Co-Fe-O-C database with respect to the compound energy formalism model by applying CALPHAD approach. The results were compared with the available experimental data under a range of carbon dioxide levels and different temperatures. Based on the quantitative calculation, the most efficient atmospheric condition and temperature in equilibrium for this cathode were proposed.

5:00 PM

(ICACC-S3-058-2016) Thermal Management Study of Planar SOFC by a Computational Approach

S. Tang*[1]; A. Amiri[1]; V. Periasamy[1]; M. Tade[1]; 1. Curtin University, Australia

Solid oxide fuel cell (SOFC) operates at a high temperature typically ranging from 600°C to 800°C. Temperature is not identical in all parts of the cell due to various non-homogeneities in physicochemical properties, heat and mass transfer and subsequently reaction rate. It is well known that the role of temperature profile inside the cell is striking for SOFC design, operation and durability. Excess amount of air is commonly used for regulating temperature and its distribution in SOFC. This approach, however, causes some disadvantages in terms of pressure and efficiency losses as well as operation costs. In this work, other factors such as the heating methods (cell heating versus inlet gas heating) and physical parameters (heat transfer coefficients), that will also influence the cell temperature profile are investigated. A validated computational model for a planar SOFC is utilized to study the interactions of these factors with the air flow rate in influencing the cell temperature gradient under different operating conditions. The results from this work will provide an understanding of the influence of the thermal aspects of the cell and system design on the temperature profiles inside the cell.

5:20 PM

(ICACC-S3-059-2016) MEA performance evaluation using different methods for area specific resistance estimation

M. Kusnezoff*[1]; W. Beckert[1]; N. Trofimenko[1]; S. Megel[1]; C. Dosch[1]; A. Michaelis[1]; M. Rachau[2]; C. Wieprecht[2]; D. Gipp[2]; 1. Fraunhofer IKTS, Germany; 2. FuelCon AG, Germany

Membrane-electrode-assembly (MEA) is a key component of solid oxide fuel cell and electrolyzer and defines the limits for power density, efficiency and durability available for exploitation in stacks and systems. Most widespread way to communicate the MEA performance is to present the U-I-characteristic at a constant temperature and to estimate the area specific resistance from its slope. Other methods for characterization of performance like current density at constant operating voltage, electrochemical impedance (EIS) and local resistance measurement under defined operating conditions also have been used for this purpose. Fuel composition (defines OCV) and fuel utilization strongly affect the obtained power density. For these reasons the area specific resistance (ASR) has been defined to compare the results achieved by different researchers. ASR values obtained using different methods such as U-I-characteristic, EIS and current density and operating voltage at stationary conditions with and without correction to fuel utilization are compared for dry and humidified fuel. It was found that at temperatures above 750°C the area specific resistance of the cell corrected to the fuel utilization only weakly depends on fuel composition and current density. Favourable testing conditions as well as influence of operating conditions on estimation of ASR are discussed.

S5: Next Generation Bioceramics and Biocomposites

Bioceramics IV

Room: Coquina Salon F

Session Chairs: Akiko Obata, Nagoya Institute of Technology; Andraz Kocjan, Jozef Stefan Institute; Akiko Obata, Nagoya Institute of Technology; Anne Leriche, University of Valenciennes

1:30 PM

(ICACC-S5-025-2016) Development of hypoallergenic ceramic based implants and their properties

K. Balazsi*[1]; N. Olah[1]; Z. Fogarassy[1]; T. Csanadi[2]; A. Sulyok[1]; C. Balazsi[3]; 1. Centre for Energy Research HAS, Hungary; 2. IMR SAS, Slovakia; 3. Bay Zoltan Nonprofit Ltd. for Applied Research, Hungary

There are more than 400 000 artificial hip joint operations made every year in the word and there are some 25 million people who have either a partial or a total hip replacement. The wear and risk of the implant loosening increases so that after 10 years 10-20% of the implants have to be renewed. The used materials are TiAl6V4, Ti or CoCrMo. Biomaterials used for implant should possess some important properties in order to long-term usage in the body without rejection with excelent biocompatibility, superior corrosion resistance, and combination of high strength and low modulus. This new line research is focused to examination of ceramic based nanocomposites. The three different types of bioceramics (TiC/a:C thin films, hydroxyapatite based coating on TiC/a:C thin film and HAP composite) are developed from the same based material. The sputtered TiC/a:C thin films are developed as an optimal solution for protective applications. The formation of TiC based surface coating has a passivation effect to titanium implant and Ti ions will kept in the bulk implant introduced in the living organism. The nanosized hydroxyapatite coating on TiC thin films will help the quick and inflammation-free osiffication. Structure and other properties of bioimplants will be showed.

1:50 PM

(ICACC-S5-026-2016) Micro-wave sintering of hydroxyapatite ceramics for biological applications (Invited)

A. L. Leriche*[1]; S. Chamary[1]; A. Thuault[1]; E. Meurice[1]; F. Bouchart[1]; J. Hornez[1]; D. Hautcoeur[2]; M. Lasgorceix[2]; V. Lardot[2]; F. J. Cambier[2]; 1. University of Valenciennes, France; 2. BCRC, Belgium

Hydroxyapatite (HA) is widely used as a scaffold material to repair and restrict damaged parts of the human skeleton. Its chemical composition is close to the mineral part of the human bone and it shows good osteoconduction. However, its weak mechanical properties limits its use for load bearing applications. One way to overcome this limitation consists in decreasing the grain size while achieving high density of the scaffold walls. Several studies have shown that besides the mechanical properties, the biological ones are also enhanced by decreasing the grain size of HA ceramic. Among numerous sintering processes tested, microwave sintering seems very promising. The first goal of this study consisted in confirming the positive effect of the direct microwave sintering of HA on the microstructure development. Stoichiometric HA powders were synthesized by a co-precipitation method from di-ammonium phosphate and calcium nitrate solutions and shaped by slip casting. Dense pellets with fine microstructures and improved mechanical properties were successfully obtained in short sintering times. The second goal was to apply the direct and hybrid microwave sintering methods to various CaP scaffolds processed by different shaping methods: replica from PMMA beads skeleton, ice-templating and 3D-printing and to test the impact of the macroporosity geometry and size, and of the grain size on the cell proliferation.

2:10 PM

(ICACC-S5-027-2016) Nature's Design Wisdom and Smart Manufacturing of Biocomposites (Invited)

X. Li*[1]; 1. University of Virginia, USA

Nature's design wisdom in seashells lies in multiscale hierarchical structure, ranging from micro lamellae down to nanoparticles, rendering seashells multilevel strengthening and toughening mechanisms such as crack deflection, interlocking, lamellae's deformability, biopolymer's viscosity, nanoparticle rotation, deformation twining in nanoparticles, and amorphization, jointly contributing to seashell's ultra-high mechanical robustness. To realize nature's performance in engineering materials, we need to intelligently design and select materials. This talk will present several case studies in which nature's multiscale design strategies and materials selection principles are applied through smart manufacturing.

2:40 PM

(ICACC-S5-028-2016) Advanced Cermet Ceramic Composites for Medical Applications

R. Dittmer*[1]; J. Trötzschel[1]; J. Fischer[1]; U. Hausch[1]; 1. Heraeus Medical Components, Germany

Strict requirements apply for implantable medical devices as they reside for years within the body. Hence, materials applied in this field have to feature not only biocompatibility but also high reliability. In addition, they often have to provide a number of additional properties vital for the respective application. We present a material system that enables a highly complex profile of properties by means of a dual composite approach. An electrical conductor is embedded into a ceramic matrix using multilayer technology to create conductive paths, so-called vias, that are insulated from each other. These vias are not composed of a single metallic phase but a cermet, *i.e.*, a ceramic-metal mixture. Owing to its interpenetrating structure, the cermet allows for a strong and hermetic integration of the conductor into the ceramic matrix otherwise impossible due to mismatch in thermal expansion. Thus, these composites provide new ways to hermetically encapsulate electronic components as required for medical implants. It will be shown that the composite exhibits a higher strength than the pure ceramic and provides highly conductive vias. In addition, the dual composite is biocompatible, non-magnetic, and chemically inert, rendering it suitable also for other fields of application. Beside the general fabrication route, we present the structural, microstructural, functional, and mechanical properties of these composites.

3:20 PM

(ICACC-S5-029-2016) Ageing-Resistant Coarse-Grained 3Y-TZP Zirconia Bioceramics (Invited)

A. Kocjan*[1]; A. Samodurova[1]; T. Kosmac[1]; 1. Jozef Stefan Institute, Slovenia

We have prepared a coarse-grained, ageing-resistant, 3Y-TZP zirconia bioceramic by alumina and silica co-doping, preserving its intrinsic mechanical properties on the account of the *t*–*m* transformability. The effect of small amounts of dopants on the microstructural evolution, and partitioning process, having a direct impact on the material's mechanical properties and ageing resistance, were investigated. The alumina increased the grain-boundary cohesion, increasing the amount of transgranular fracture and reduced microcracking, upon *t*–*m* transformation, while silica was concentrated at multiple grain junctions, increasing the material's resistance to ageing. Moreover, alumina also has an impact on the composition and properties of the silica glassy phase. We observed a temperature-related (>1550 °C) penetration of the silica phase from the grain junctions into grain boundaries, which was further accompanied by the emergence of a fraction of clearly larger grains, possessing yttria-lean heterogeneities in the co-doped material. Additionally, it resulted in a slower overall partitioning process into the equilibrium assemblage compared to the alumina-single-doped 3Y-TZP, where the partitioned yttria-rich phase was found to be $t`$-$ZrO_2$ upon cooling. Consequently, the much smaller amount of $t`$-ZrO_2 phase in the co-doped 3Y-TZP resulted in a less-depleted yttria-lean $t`$-ZrO_2, increasing the overall resistance to ageing.

3:40 PM

(ICACC-S5-030-2016) From Crystalline Nanorods to Hierarchical Biomorphs (Invited)

E. Nakouzi*[1]; P. Knoll[1]; Y. Ghoussoub[1]; O. Steinbock[1]; 1. Florida State University, USA

Silica-carbonate biomorphs are complex inorganic microstructures that assemble life-like morphologies with non-crystallographic symmetries. At the nanoscale, biomorphs consist of crystalline nanorods that arrange in hierarchical architectures reminiscent of biominerals. We report a novel method for synthesizing biomorphs in a single-phase, isolated system. The precipitating structures assemble millimeter-sized leaves, cones, and helices. Our analyses reveals characteristic timescales and lengthscales for biomorph assembly, and their relevance to the mesoscopic growth process. In addition, we report the existence of an additional level of self-organization that creates oscillatory height variations in the biomorph sheets. These topographic features are accompanied by a systematic out-of-plane displacement of the crystalline nanorods. Our results are analyzed in the context of a recent hypothesis that suggests the occurrence of local pH oscillations at the biomorph crystallization front.

4:00 PM

(ICACC-S5-031-2016) Combined effects of silicate, calcium and magnesium ions on osteoblast-like cell functions (Invited)

A. Obata*[1]; T. Ogasawara[1]; S. Yamada[1]; T. Kasuga[1]; 1. Nagoya Institute of Technology, Japan

Several inorganic ions released from bioceramics have been reported to stimulate osteogenic cell functions and to promote bone formation in body. In particular, a trace amount of silicate and calcium ions released from 45S5-type bioactive glass were reported to enhance several functions of human osteoblasts by many researchers. Additionally, magnesium ions have been reported to enhance cell adhesion to materials, along with the differentiation and biomineralization of osteoblasts. The aim of the present work was to examine combined effects of the three different ions, silicate, calcium and magnesium ions, on osteogenic cell functions. Human or mouse osteoblast-like cells were cultured in media containing different amounts of the three ions and their abilities of adhesion, proliferation, *etc*. were evaluated. The rate of adhesion of the cells was significantly higher in the medium containing magnesium and silicate ions than that containing each single ion. Thus, the combined effects of the ions were observed for the cell adhesion.

4:20 PM

(ICACC-S5-032-2016) Silica-bonded hydroxyapatite scaffolds from indirect and direct 3D printing of silicone/calcite mixtures

E. Bernardo*[1]; L. Fiocco[1]; H. Elsayed[1]; 1. University of Padova, Italy

Silica-bonded hydroxyapatite 3D scaffolds were developed from silicone polymers filled with calcite micro-particles. More precisely, highly porous components were prepared starting from "highly loaded" commercial silicones, designed to yield ceramics with a final $CaCO_3$ content of 70 wt%. Low viscosity calcite/silicone mixtures, based on polymers with low silica yield upon firing, were infiltrated in sacrifical "inverse" 3D-printed PLA scaffolds, later decomposed (at 350 °C), whereas viscous calcite/silicone mixtures, based on a polymer with significant silica yield, were subjected to direct 3D printing. In both cases, the binding phase turned from polymeric to ceramic by thermal treatment (ceramization) at low temperature, not exceeding 600 °C. The calcite filler, practically unchanged upon ceramization, was effectively converted into carbonate apatite by immersion in a phosphatizing solution (14 days in solution of Na_2HPO_4, at 60 °C). The transformation was optimized in samples

from infiltration of calcite/silicone mixtures, due to the enhanced micro-porosity of the struts, in turn favoring the calcite-solution interaction, and in samples from the use of natural calcite (calcined egg shell waste) instead of mineral calcite. These samples, with a porosity of about 70 %, exhibited a remarkable compressive strength, in the order of 10 MPa.

S7: 10th International Symposium on Nanostructured Materials: Functional Nanomaterials and Thin Films for Sustainable Energy Harvesting, Environmental and Health Applications

Integration & Device Applications of Nanostructures I

Room: Coquina Salon A
Session Chairs: Bonex Mwakikunga, National Centre for Nano-Structured Materials - CSIR; Daniel Chua, National University of Singapore

1:30 PM

(ICACC-S7-062-2016) 3D printing of porous structures from preceramic polymers (Invited)

P. Colombo*[1]; 1. University of Padova, Italy

Preceramic polymers are precursors for ceramic phases of different composition. They convert into nano-structured ceramic materials in the system Si(X)OCN (with X = Al, Ti, Zr, etc.) by high temperature pyrolysis (PDCs or Polymer-Derived-Ceramics). This paper will report on the fabrication of porous structures starting from pure preceramic polymers (e.g. silicone resins) and of silicone resins plus reactive fillers (to produce advanced silicate ceramic phases suitable for different applications). Different types of additive 3D manufacturing techniques were employed, including: a) direct printing using a stereolithographic printer; b) direct printing using a paste extrusion printer (Robocasting); c) direct printing using a fused deposition printer; d) indirect printing using a powder bed-based printer (in collaboration with researchers from BAM, Berlin, Germany). Advantages and disadvantages of the different processing techniques employed, in relation to the use of preceramic polymers, will be discussed, and examples of produced and characterized porous structures for potential use in different applications will be presented.

2:00 PM

(ICACC-S7-063-2016) Single-Source-Precursor Synthesis of Novel Functional Polymer-Derived Ceramic Nanocomposites (PDC-NCs) for Energy-Related Applications (Invited)

E. Ionescu*[1]; 1. Technical University Darmstadt, Germany

Polymer-derived ceramic nanocomposites (PDC-NCs) have been addressed in the last decades and were shown to possess intriguing properties which make them excellent candidates as structural and multifunctional materials. PDC-NCs can be synthesized via polymer-to-ceramic conversion of suitable single-source precursors, leading in a first step to amorphous single-phase materials, which subsequently undergo phase separation and crystallization processes to furnish bi- or multi-phase ceramic nanocomposites. In the present work, the conversion of the single-source precursors into single-phase inorganic materials, which are of amorphous nature, as well as subsequent phase separation and crystallization processes occurring at high temperatures will be addressed in detail. Special emphasis will be set on describing the intimate relationship between the molecular architecture of the single-source precursors and the phase composition / microstructural features of the resulting PDC-NCs. Preparative concepts for the knowledge-based design of PDC-NCs with tailored phase compositions and property profiles as well as selected energy-related applications will be highlighted and discussed.

2:20 PM

(ICACC-S7-064-2016) Three-dimensional structural control of graphite nanosheets assembly for highly conductive polymer based composites (Invited)

S. Ryu[1]; H. Cho[1]; S. Kang[1]; Y. Choa*[1]; 1. Hanyang University, The Republic of Korea

In order to achieve high electrical conductivity with the lower filler contents in the electrical conductive polymer composites, the surfaces of carbon-based fillers and polymer particles have been conventionally modified through various complicated multistep surface-treatment processes. Here, we report a simple and facile approach electrostatically coupling the surface charges of graphite nanoplates (GNPs) fillers and poly(methylmethacrylate) (PMMA) polymer particles using an electrostatic coupling agent of ethylene maleic anhydride (EMA) copolymer. By switching the intrinsic repulsive electrostatic interaction between the GNPs-fillers and the PMMA particles to the attractive electrostatic surface interaction, the electrical conductivity of composites dramatically increased by a factor of 16.7 in the EMA-coupled GNPs/PMMA composites compared with that of the EMA-free GNPs/PMMA composites. In addition, the percolation threshold could be also notably reduced from 0.32 vol.% to 0.159 vol. % upon the electrostatic coupling of GNP-fillers and PMMA particles.

2:40 PM

(ICACC-S7-065-2016) Stabilization and nanoscale alignment techniques of functional nanoparticles for wet material processing in non-aqueous solvent systems (Invited)

M. Iijima*[1]; J. Tatami[1]; H. Kamiya[2]; 1. Yokohama National University, Japan; 2. Tokyo University of Agriculture and Technology, Japan

Technologies to control the dispersion and alignment state of nanoparticles in desired media is quite essential to tune the properties of particle based composite materials through material processing. Herein we report examples of processing protocols to homogeneously disperse nanoparticles in various organic media and to form nanoscale alignments in these organic matrixes. Techniques to improve stability of nanoparticles in various solvents involves a design of anionic surfactant having organic chain branched into hydrophobic and hydrophilic segments near the head group. Their attachment on nanoparticles with an assistance of polyethyleneimine (PEI) resulted to achieve nanoparticles completely dispersible in various types of solvents regardless of their polarities. These nanoparticles modified with PEI and anionic surfactant were also found to have effective adsorption properties on many templates such as raw fine particles (metal oxides, carbon related materials and metals) and polymer nanofibers in organic solvents through simple mixing process. The prepared composites covered with surface modified nanoparticles were also dispersible in many types of solvents and polymers which is quite useful phenomena to control nanoscale alignment of nanoparticles along the templates in composite materials.

Integration & Device Applications of Nanostructures II

Room: Coquina Salon A
Session Chairs: Paolo Colombo, University of Padova; Emanuel Ionescu, Technical University Darmstadt

3:20 PM

(ICACC-S7-066-2016) Multifunction metal oxides utilizing carbon nanotubes as a base template with for clean energy and other applications (Invited)

D. H. Chua*[1]; 1. National University of Singapore, Singapore

Depending on different metals, metal oxides formed have far-wide ranging material properties. In this review, we show that when carbon nanotubes are used as a base template, forming hybrid core-shell nanostructures, this effectively enhances and extends the range of applications. There are two unique properties of carbon nanotubes which the first is its versatility in structural tubular forms and second, the possibility in enhancing the properties of carbon nanotubes itself. Several applications will also be reviewed here. For example, metal oxide tip-coated carbon nanotubes (such as MoO3 and WO3) have proved to be excellent schottky electron emitters while platinum coated carbon nanotubes formed excellent catalytical activity for PEM fuel cell applications. Other metal-oxide composites such as ZnO can have dual-functional properties allowing good electron emission with photoluminescence properties. We can further extend the applications into biomedical materials where carbon nanotubes can be used as the seed layer for hydroxyapatite growth. We will further show that 2D structures can be incorporated on these carbon nanotubes with clean energy applications such as PEM fuel cell and hydrogen evolution reactions.

3:40 PM

(ICACC-S7-067-2016) Synthesis and Characterization of Monodisperse Nano-Particles and Core-Shell Particles using Flow Reactors (Invited)

M. Miyahara*[1]; S. Watanabe[1]; 1. Kyoto University, Japan

We applied a micromixer to the flow synthesis of monodisperse and core-shell nanoparticles. First example is nickel Nanoparticles: Hydrazine aqueous solution and aqueous solution of nickel(II) chloride and CTAB were mixed in the first micromixer, whose outlet was then mixed in the second micromixer with sodium hydroxide aqueous solution. Through intensive investigation, nickel nanoparticles were successfully synthesized with narrow size distribution. The key to the success was found to be the sub-second order of residence time AFTER the first mixer BEFORE the mixing in the second one. The micromixers with quite high mixing performance, which can attain milliseconds of mixing time, can provide this kind of fast process to assure the monodisperse nanoparticles. As for the second example of silica with gold shell, again the intensive mixing played a key roll to the successful synthesis, which will be discussed in detail in the presentation.

4:00 PM

(ICACC-S7-068-2016) MOCVD: a simple approach from molecules to functional nanostructures (Invited)

G. Malandrino*[1]; 1. Universita' degli Studi di Catania, Italy

The interest in nanoscale materials stems from the fact that new properties are acquired at this length scale and that these properties change with their size or shape. The bottom-up strategies represent the most used routes to prepare nanostructures, and the metal organic chemical vapor deposition (MOCVD) processes may be envisaged as a natural bottom-up approach starting from molecules towards the formation of nanosystems. This synthetic approach has proven suitable for the fabrication of nanosystems going from the simplest in chemical nature, such as metals, to the most complex multi-component oxides. Results on the growth of nanorod arrays of Pt, using a template-free and seedless approach, will be reported. Attention will be also devoted to binary oxides of transition metals in form of thin layers (ZnO, NiO, Mn_3O_4) and template fabricated nanotube arrays (CuO, NiO, Co_3O_4). Nanoscaled materials with a perovskite based structure show great potentialities in several technological fields. MOCVD results on various perovskite based films ($La_{2-x}Ba_xCuO_4$, $Pr_{0.7}Ca_{0.3}MnO_3$,$BiFeO_3$, etc.) will be presented as well. In summary, the possibility to tailor the nanostructure either using processing parameters or template systems and the potentiality of the used bottom-up approach to likely fabricate any type of materials, make MOCVD a very promising route to the formation of nanostructures of simple and complex chemical nature.

4:20 PM

(ICACC-S7-069-2016) Single nanofiber vs multiple nanowire devices in sensing applications (Invited)

B. Mwakikunga*[1]; 1. National Centre for Nano-Structured Materials - CSIR, Zimbabwe

This presentation outlines the progress made since 2011 when the projects of building nano sensors at the CSIR in Pretoria started up to the present time. The time line starts with our attempts to establish electrical contacts to single WO_3 nanowires by focussed ion beam coating in Carl Zeiss SEM equipped with nano-manipulators [1]. Next are the attempts for on-chip growth SnO_2 nanowires on Au patterned alumina substrates [2] and lastly the Au/Ti contacts to individual SnO_2 nanowires by electron-beam lithography protocols [3]. All these approaches led to harnessing the nanowire devices into a micro-nano chip which became the first CSIR technology demonstration in 2013.

4:40 PM

(ICACC-S7-070-2016) Application of Atomic Layer Deposited TiO_2 Films for Solar Cells (Invited)

D. Kim*[1]; 1. Chonnam National University, The Republic of Korea

Direct utilization of sunlight into electrical power is of great interest as a clean and safe energy source. Among various types of solar cells, Si-based solar cells can yield high power conversion efficiency and thus, is in mass production for practical usage. However, the expensive fabrication cost of the Si-based solar cells stimulated a research for alternative types of solar cells. Dye-sensitized solar cells (DSSCs) and polymer solar cell (PSC) are considered as the promising candidates for the partial replacement of Si-based solar cell due to its advantages of low cost, easy fabrication, and moderate power conversion efficiency compared Si-based solar cells. Recently, atomic layer deposition (ALD) which uses alternating cyclic pulses of reactants has received great attention in energy research. Here, the effect of atomic layer deposited-TiO_2 thin films on the device performance of DSSC and PSC will be presented.

5:00 PM

(ICACC-S7-071-2016) 15 Years of Commercializing Medical Devices Using Nanotechnology (Invited)

T. Webster*[1]; 1. Northeastern University, USA

The synthetic materials used in tissue engineering applications today are typically composed of millimeter or micron sized particles and/or fiber dimensions. Although human cells are on the micron scale, their individual components, e.g. proteins, are composed of nanometer features. By modifying only the nanofeatures on material surfaces without changing surface chemistry, it is possible to increase tissue growth of any human tissue by controlling the endogenous adsorption of adhesive proteins onto the material surface. In addition, our group has shown that these same nanofeatures and nano-modifications can reduce bacterial growth without using antibiotics, which may further accelerate the growth of antibiotic resistant microbes. Inflammation can also be decreased through the use of nanomaterials. Finally, nanomedicine has been shown to stimulate the growth and differentiation of stem cells, which may

someday be used to treat incurable disorders, such as neural damage. This strategy also accelerates FDA approval and commercialization efforts since new chemistries are not proposed, rather chemistries already approved by the FDA with altered nanoscale features. This invited talk will highlight some of the advancements and emphasize current nanomaterials approved by the FDA for human implantation.

S8: 10th International Symposium on Advanced Processing and Manufacturing Technologies for Structural and Multifunctional Materials and Systems (APMT10)

Novel Ceramic Processing V

Room: Coquina Salon B

Session Chairs: Rajendra Bordia, Clemson University; Hiroyuki Muto, Toyohashi University of Technology

1:30 PM

(ICACC-S8-056-2016) Spark Plasma Sintering of ceramic particulate composites for wear applications (Invited)

F. J. Cambier*[1]; L. Boilet[1]; M. Demuynck[1]; V. Lardot[1]; J. Erauw[1]; 1. BCRC, Belgium

Advanced ceramics and cermets are increasingly appreciated in tribological applications due to their excellent mechanical properties. Cemented carbides reinforced by cubic boron nitride (cBN), have gained attraction over the last few years. However, cBN is difficult to densify by natural sintering due to the strong covalent bonding of BN and the phase transformation of cBN in the hexagonal, graphite-like phase (hBN) at high temperature leading to an important decrease of the hardness. As SPS allows the densification at lower temperature and shorter dwell time than conventional sintering, the technique seems suitable to fully densify cBN-tungsten carbides composites (without the hBN phase appearance) and to improve mechanical properties by limiting the grain growth. In this study, cBN / WC-Co (with 6 and 12% of Co) composites containing up to 35% vol. of cBN were then densified by spark plasma sintering (HPD10 equipment from FCT System GmbH). For all compositions, SPS parameters (temperature, pressure, holding time) have been optimised to achieve near theoretical density values. X-Ray diffraction measurements have confirmed the stability of the cubic phase of BN. SEM observations have shown the maintaining of a fine microstructure and the homogeneous dispersion and good bonding of the ~ 10 μm size cBN particles in the WC-Co matrix. No trace of the low-hardness hexagonal boron nitride was found.

2:00 PM

(ICACC-S8-057-2016) Hexagonal OsB_2: Mechanochemical synthesis, spark plasma sintering, structure and mechanical properties

Z. Xie[1]; R. Blair[1]; N. Orlovskaya*[1]; D. Cullen[2]; A. Payzant[2]; 1. University of Central Florida, USA; 2. Oak Ridge National Lab, USA

Hexagonal OsB_2 has been synthesized by mechanochemistry. High energy ball milling was used to introduce high shear and normal impact forces on raw Os and B materials, which resulted in mechanochemical reactions forming hexagonal OsB_2. X-ray diffraction indicated that OsB_2 starts to form after 2.5 hours of milling, and the reaction reaches equilibrium after 18 hours of milling. No phase transformation was observed after OsB_2 powder was annealed at 1050 °C *in vacuo* for 6 days. The lattice parameters of the hexagonal OsB_2 are a=2.916 Å and c=7.376 Å, with P63/mmc space group according to the refinement of the powder XRD pattern. TEM results have confirmed the appearance of hexagonal OsB_2 phase. The synthesized hexagonal OsB_2 powder was sintered with spark plasma sintering at 1500 °C and 50 MPa for 5 minutes. The sintered OsB_2 contains ~80 wt.% of hexagonal and ~20 wt.% orthorhombic phases. It has a density of 9.46 g/cm^3 and porosity of 26.9%. Hardness and Young's modulus were measured to be 31 ± 9 GPa and 574 ± 112 GPa, respectively by nanoindentation.

2:20 PM

(ICACC-S8-058-2016) Low Temperature Synthesis and Densification of Magnesium Aluminate Spinel by SPS

L. Zarazua[1]; H. Balmori*[1]; G. Bonnefont[2]; G. Bonnefont[2]; L. Tellez-Jurado[1]; 1. Instituto Politecnico Nacional, Mexico; 2. INSA-Lyon, France

Precursor powders (in spinel's stoichiometric composition) were obtained using aluminum tri-sec-butoxide and magnesium nitrate hexahydrate reacted by sol-gel. The synthesis was performed at 80°C with an agitation speed of 600 RPM, using as solvent isopropyl alcohol and chloridric acid as catalyst. The powders obtained were characterized by SEM and XRD. The results show that the powder obtained by sol-gel is a mixture of boehmite and magnesium nitrate nanoparticles (20-50 nm) with a semicircular homogenous morphology. The SEM analysis also shows an homogenous mixtures of aluminum and magnesium elements. Powders were calcined at 550°C for 2h and sintered by SPS without additive at 1150°C, 1200°C, 1300°C and 1400°C in a graphite die at 72 MPa of pressure, a heating rate of 100°C/min and a holding time of 10 min at final temperature. Spinel phase was obtained at 1150°C according to XRD results. Density measurements were performed by Archimedes method obtaining 98.84 g/cm^3 at 1400°C. Density showed an increase with the temperature due to porosity reduction according to SEM micrographs. In addition at the increase on density, an increase on grain size could be observed

2:40 PM

(ICACC-S8-059-2016) Formation of graphite nanolayer on Ti(C,N) nano-grains in Si_3N_4 matrix prepared by spark plasma sintering

C. Lee*[1]; H. Lu[2]; W. Jang[3]; C. Dong[3]; J. Huang[1]; 1. National Cheng Kung University, Taiwan; 2. National Chin-Yi University of Technology, Taiwan; 3. National Synchrotron Radiation Research Center, Taiwan

In our previous work, we have demonstrated superior anti-wear resistance of Si_3N_4/Ti(C,N) nanocomposites under low Hertzian stresses, preliminarily contributing to their nanostructured grains for both crystal phases. In order to further reveal their distinguishable features of microstructures, the interfacial nanostructures were identified in this work. The substitutional $TiC_{0.4}N_{0.6}$ solid solution in Si_3N_4 based nanocomposites is identified by XRD and estimated by Vegard's law. D, G, and 2D band of carbon in Si_3N_4/Ti(C,N) were found in Raman spectroscopy, while 2D band is absent in as-received $TiC_{0.8}N_{0.2}$ nanopowder, implying that the observed graphite nanolayer is probably stimulated after experiencing spark plasma sintering. A graphite nanolayer with a thickness 20~50 nm can be frequently observed on Ti(C,N) grains by transmission electron microscopy. The EELS technique is conducted to characterize bonding configuration of carbon in graphite nanolayer and Ti(C,N) grains, revealing σ and σ/π bonding, respectively. Moreover, X-ray absorption near edge structure of titanium based phases is applied to extend the related discussion on the bonding configuration of the interests. These findings enable us to better understand the current activated phenomena and phase evolution of nano Ti(C,N) encompassed in the present Si_3N_4 based sintering system.

3:20 PM

(ICACC-S8-060-2016) Hybrid Coating with Combination of Aerosol Deposition and Thermal Spray (Invited)

J. Akedo*[1]; K. Shinoda[1]; M. Mori[1]; 1. National Institute of Advanced Industrial Science and Technology (AIST), Japan

The Aerosol Deposition (AD) method is obtained to form dens ceramic and metal coating layer at room temperature by impacting

of gas conveyed solid fine particles under vacuuming, which is induced room temperature impact consolidation (RTIC) of the raw materials particle. In principle AD layer has a strong adhesion with a substrate, because the anchoring effect of layer materials to a substrate is very high due to mainly use the high pressure loading without heating. However, the deposition properties greatly depend on the raw materials fine particles properties and leave many problems unfinished for the deposition efficiency, the coating cost, and the layer coverage. For such problems of the conventional AD method, we tried to develop the plasma assisted AD method and confirmed the improvement effect of the deposition efficiency and layer function. Therefore, for the purpose of developing these research results in a more practical level, we propose the hybrid AD (HAD) method as newly hybrid coating, which can variably change the deposition principle by the thermal fusion effect in conventional thermal spray process and by the high pressure loading effect in the AD process as the particle deposition coating to interpolate the fault of both principles. By examining such a technique, conventional problems solution of composites structured layer and gradient structured layer are expected.

3:50 PM

(ICACC-S8-061-2016) Understanding of low temperature fabrication process of oxide thin films in excimer laser-assisted metal organic deposition

K. Shinoda*[1]; T. Katsuki[2]; T. Nakajima[1]; T. Tsuchiya[1]; A. Yumoto[2]; J. Akedo[1]; 1. National Institute of Advanced Industrial Science and Technology (AIST), Japan; 2. Shibaura Institute of Technology, Japan

Irradiation with pulsed ultraviolet (UV) lasers is an attractive tool for the synthesis and modification of functional oxide thin films. In excimer laser-assisted metal organic deposition (ELAMOD) process, oxide films are crystallized with the assistance of irradiation from excimer laser sources, instead of employing thermal energy from high-temperature furnaces used in conventional metal organic deposition process. Control of process parameters such as a selection of wavelength, fluence, number of pulses, and repetition rate is required in the ELAMOD process in order to obtain a proper film. Here, understanding of a temperature field during pulsed UV laser irradiation is the key to the setting of proper process windows. This temperature evolution is expected to be on the order of a few tens of nanoseconds. Therefore, we have developed an in situ monitoring technique utilizing radiation thermometry at a nanosecond time scale. A case study on monitoring of fabrication process of tin oxide thin films will be shown.

4:10 PM

(ICACC-S8-062-2016) Development of a Plasma Arc Welding Technique for joining SiC based Composites

J. Watts*[1]; G. Hilmas[1]; W. Fahrenholtz[1]; S. Landwehr[2]; 1. Missouri University of Science & Technology, USA; 2. Rolls-Royce, USA

The desire for improved performance from turbine engines has resulted in a continuous push to operate at higher temperatures. This allows for improved efficiency and increased power output. Maximum operating temperatures in civil engines exceed the melting point of nickel based superalloys requiring the use of large amounts of cooling air. Reducing the use of cooling air for increased efficiency, or increases in operating temperature, will necessitate the use of ceramics and ceramic fiber reinforced ceramic matrix composites. SiC based composites have become the preferred material for use in high temperature turbine applications. Forming complicated shapes and assemblies out of these composites, however, creates many difficulties. The ability to join composite pieces together would allow for use of simpler shapes and their subsequent fabrication into larger complex assemblies. The goal of this research is to develop a plasma arc welding (PAW) technique capable of joining SiC/SiC composites, and reaction bonded SiC to themselves and to each other without preheating the entire component above the melting point of silicon. Research has focused on the use of SiC based filler materials and Si based braze materials in conjunction with PAW. Joint microstructures have been characterized and preliminary mechanical characterization has been performed.

4:30 PM

(ICACC-S8-063-2016) Combustion synthesis assisted friction spot stir welding (FSSW) for automotive & aerospace applications

R. Mahmoodian*[1]; P. Lin[2]; F. Yusof[1]; M. Hamdi[1]; 1. University of Malaya, Malaysia; 2. National Chung Cheng University, Taiwan

In this paper the combustion synthesis assisted friction spot stir welding (FSSW) is proposed to weld dissimilar lapped materials (steel and aluminum sheet). Ten different experimental setups were designed to evaluate the process over the range of 50 specimens. The tensile strength and characteristics revealed by optical microscope were investigated. A steel tool was used to make stir punching with 10 mm shoulder diameter and 3 mm tip step. Joining of steel and aluminum 6061-T6 sheet using combustion synthesis assisted friction spot stir welding (FSSW) was performed. The conventional FSSW process was modified by applying a powder mixture of the Ti+Al; Ti+C; Ti+Ni; Al+Ni on the steel surface. The surface was in contact with the aluminum sheet during friction, stir welding. The particles undergo severe plastic deformation where some amount of heat is generated. Microstructure and phase analysis was performed using FESEM-EDS, EPMA. The highest average tensile strength of 5.40 kN was obtained from galvanized Ti+C dispersed powder, but the highest peak load was detected for a galvanized steel sheet with no powder dispersed on the surface.

S9: Porous Ceramics: Novel Developments and Applications

Membranes and Filters

Room: Coquina Salon G

Session Chair: Enrico Bernardo, University of Padova

1:30 PM

(ICACC-S9-016-2016) Understanding strength, reliability, and gas transport in anisotropic porous structures (Invited)

A. J. Stevenson*[1]; J. Seuba[1]; C. Guizard[2]; 1. Laboratoire de Synthèse et Fonctionnalisation des Céramiques (LSFC), France; 2. Institut Européen des Membranes, France

Porous structures are frequently required to combine different functional properties, and these properties are usually inversely impacted by changing pore volume. For example, gas flow through a porous structure increases with increasing pore volume while strength decreases significantly with increasing pore volume. In order to better understand these trade-offs and provide predictive microstructure design criteria that can be applied across diverse applications, we explore the relationships between gas transport and strength in anisotropic porous structures made by ice templating. We report strength and reliability as a function of pore volume, pore size, and pore morphology. This data is then linked with similar data for gas flow through the same structures in order to map the functional properties with respect to the morphology of the pores. Finally, we will also introduce a Bayesian statistical approach that significantly enhances our understanding of the Weibull modulus of the structures and allows us to quantitavely discern between different models that predict strength in porous solids.

2:00 PM

(ICACC-S9-017-2016) Complex Freeze-cast Pore Structures and their Effects on Permeability

M. Naviroj*[1]; P. Colombo[2]; K. Faber[3]; 1. Northwestern University, USA; 2. University of Padova, Italy; 3. California Institute of Technology, USA

Freeze casting has been shown to be a reliable method for fabricating porous ceramics with unique pore architectures. In this work, a preceramic polymer is dissolved using a range of organic solvents and freeze cast directionally to create an anisotropic porous ceramic. Since the solidified structures of one solvent can vary significantly from another, a wide range of pore architectures can therefore be generated. In particular, lamellar, dendritic, and cellular pore morphologies were achieved in this study. The highly complex and varied pore structures are then characterized and compared between each other for differences in their properties, such as specific surface area and hydrodynamic permeability.

2:20 PM

(ICACC-S9-018-2016) Numerical Modelling of Evaporation-Driven Transport of Water from a Multi-Layered Ceramic

M. Jabbari*[1]; V. Jambhekar[2]; J. H. Hattel[1]; R. Helmig[2]; 1. Technical University of Denmark, Denmark; 2. Universität Stuttgart, Germany

In this paper, we present a coupled free-flow-porous-medium model for mass, momentum and energy exchange between a porous medium (Ω^{pm}) and a free-flow (Ω^{ff}) region describing an evaporation-driven water transport for ceramics. We describe the model initially for a single layer of a ceramic, where a Representative Elementary Volume (REV)-scale model concept is used for coupling non-isothermal multi-phase compositional porous-media flow—for the ceramic layer—and single-phase compositional laminar free-flow—for the air above it. We elaborate and discuss the characteristic diagram for the drying-rate curve for a single layer ceramic, and compare with that of a multi-layered ceramic. We, moreover, show the influence of the intrinsic permeability (**K**) of each single ceramic layer on the drying behavior of a multi-layered ceramic.

2:40 PM

(ICACC-S9-019-2016) Effect of membranes in exhaust particulate filtration

J. Adler*[1]; U. Petasch[1]; 1. Fraunhofer Institute for Ceramic Technologies and Systems, Germany

Diesel particulate filters are state of the art technology, and filters for direct injecting gasoline motor exhaust are subject of intensive R&D activities. But it is essential to have future developments of particle filters that focus on lowering pressure drop and increasing filtration efficiency. Therefore, experimental studies were carried out to identify the role of material porosities and a thin membrane on the properties of particulate filters. Filters with increased pore sizes are advantageous in decreasing initial pressure drop and back pressure during soot loading. However, materials with smaller pores show higher filtration efficiency since inefficient deep-bed filtration phase is less pronounced. Therefore, an additional fine porous membrane was applied on the filter wall. However, this not only influences the filtration efficiency but the back pressure, too. Microstructure simulation based on experimental and analytic results of particulate deposition were used for further development. An optimal balance between filtration efficiency and back pressure were obtained on a filter whose top pore layer is filled with fine ceramic particles. Initial pressure drop was slightly affected only. In contrast, back pressure offset caused by soot deposition is lower than for homogeneous filter material since depth filtration was completely avoided. The efficiency stays at about 99 % during the overall filtration process.

Innovations in Processing Methods & Synthesis of Porous Ceramics II

Room: Coquina Salon G

Session Chair: Joerg Adler, Fraunhofer Institute for Ceramic Technologies and Systems

3:20 PM

(ICACC-S9-020-2016) Meso/Macrostructure Porous Ceramics using Template method (Invited)

S. Manocha*[1]; 1. GGSIP UNIVERSITY, India

Porous ceramics have been synthesized through template methods. It could be carbons polymer template methods or carbides using biomorphic templates or silica foams by infiltration of silica sol in to commercial available polymeric foams template having well-ordered structure. Each method has its unique characteristics by way of choosing the template or the processing method etc. The polymeric foams with three dimensional interconnecting strut networks have been used as a macrostructure scaffold. By controlling processing conditions, choice of bio/synthetic templates & studs carbonaceous resins porous silica monoliths with interconnecting porosity with various macroporous structures can be obtained at 550 °C. The characterisation of foams was carried out for crystallinity, surface characteristics, surface morphology and acids resistance. The porous silica foam exhibits interconnected macropores having pore diameter from 100 – 500 μm in diameter, facilitating the fluid flow. Materials organized with such macropores structures can minimize the channel blocking for fast diffusion of bulky molecules in industrial catalysis, adsorption, separation, chromatographic separation and waste-disposing process, etc. The prepared silica foam shows good acid resistance. The present procedure used is very simple, reproducible, requires short periods, yields pure products, and highly suitable for large scale mass production.

3:50 PM

(ICACC-S9-021-2016) Foam-reinforced Thermal Insulation for High Temperature and Cryogenic Temperature Applications

J. Stiglich*[1]; B. Williams[1]; V. Arrieta[1]; 1. Ultramet, USA

Ultramet has developed a highly insulating and lightweight thermal protection material composed of open-cell carbon or ceramic foam with an ultralow-density aerogel filler. The foam serves as an easily machinable structural reinforcement for the low-strength aerogel insulator and defines the shape of the component. The aerogel exists in discrete cells and is supported by the foam skeleton. The combined density of the composite insulator is as low as 0.1 g/cm^3, and the thermal conductivity is ⟨1 W/m•K at 2000°C. Aerogel-filled foam has also been shown to be beneficial for cryogenic insulation applications. Single panels up to 30" square are feasible and can be press-fit over complex features. The benefit of reinforcing chopped fiber phenolic ablators with structural foam has also been demonstrated in arcjet testing to heat flux levels of >1000 W/cm^2 in which low erosion rates and heat transfer were indicated. The foam helps retain the char layer by physical reinforcement, and the network of passages allows pyrolysis gases to escape with minimal disruption of the char layer.

4:10 PM

(ICACC-S9-022-2016) Porous nano-SiC as thermal insulator: wisdom on balancing high strength and low thermal conductivity

P. Wan*[1]; J. Wang[1]; 1. Institute of Metal Research, China

Porous silicon carbide (SiC) was suggested as potential candidate for high-temperature thermal-energy conversion because of its unique combination of excellent mechanical properties, good chemical stability, as well as oxidation resistance at elevated temperature. However, SiC ceramic intrinsically has very high thermal conductivity which will frustrate the high efficiency of energy conversion. Increasing the porosity of bulk material can lower thermal

conductivity, but meanwhile greatly sacrifice mechanical strength. We herein show that by integrating specific nano-scale phonon scattering mechanisms in porous SiC, this outstanding material could demonstrate promising thermal insulation property. It is interesting to find that porous nano-SiC sintered at 1500 °C exhibits a specific balanced mechanical strength (compressive and flexural strength are 26 MPa and 13 MPa, respectively, with 57% porosity) and very low thermal conductivity (2 $Wm^{-1}K^{-1}$ at 300K); and sample sintered at 1800 °C shows excellent mechanical strength but also relatively high thermal conductivity. Our work shed a light on the novel thermal insulation property of porous nano-SiC for the first time.

4:30 PM

(ICACC-S9-023-2016) Fabrication of Functional Porous Ceramics by In-situ Solidification Process for Mitigating Environmental Issues (Invited)

T. Shirai*[1]; H. Razavi[1]; M. Fuji[1]; 1. Nagoya Institute of Technology, Japan

Porous ceramics are very widely used in many industrial applications, such as filters, catalyst for chemical industries and automobiles, light weight structural materials, biomaterials and so on. Among various processing technologies to fabricate porous ceramics, gel casting has gained much attention due to easy processing and easy to develop any complicated shape. We have successfully developed several materials with tailored pore structure such as ceramic filter, super-porous construction materials, and electrically conductive ceramics. Controlling the pore shape and size by gelcasting of slurry involving bubbles provides an effective and cheap way in fabricating porous ceramics. Various types of foamed slurries can be in-situ solidified by polymerization of monomer. One of these is cordierite ceramic filter which is fabricated by conventional gelcasting in nitrogen atmosphere. In an attempt to reduce the industrial and mining wastes, we have fabricated super-porous construction materials with the aid of natural gelformer. The use of Japanese gelatin, as a gelling agent, enabled the solidification of mechanically foamed slurry under ambient atmosphere.

S11: Advanced Materials and Innovative Processing Ideas for the Production Root Technology

Coating Process for Low Friction and Energy Solution I

Room: Tomoka B

Session Chair: Tim Hosenfeldt, Schaeffler Technologies GmbH & Co. KG

1:30 PM

(ICACC-S11-008-2016) A Combinatorial Approach to Achieving Ultralow Friction and Wear with Graphene and other Carbon-based Nanomaterials (Invited)

A. Erdemir*[1]; D. Berman[1]; A. Sumant[1]; S. Deshmukh[1]; S. Sankaranarayanan[1]; 1. Argonne National Laboratory, USA

Graphene has lately been attracting an overwhelming interest from both the industrial and scientific communities mainly because of its unusual electrical, thermal, optical, and mechanical properties. In our laboratory, we have been exploring the friction and wear characteristics of graphene for quite a while and recently confirmed that even one-atom-thick graphene can last thousands of sliding cycles while at the same time maintaining a very steady and superlubric friction values between macro-scale sliding surfaces. These studies have also confirmed that the wear behavior of graphene is far less sensitive to test environments; while ultralow friction can be achieved in dry and inert gases in combination with other types of carbon materials including nanodiamond and DLC. To understand the underlying superlubric sliding mechanism of graphene, we used large-scale molecular dynamics simulations that linked the collective nanoscale mechanics of combined carbon materials to macroscopic observations in in our friction and wear experiments. Overall, we determined that graphene is a very unique solid lubricant material that can be exploited for a variety of critical tribological applications. In this talk, we will present our research findings on the unusual friction and wear behavior of graphene as supported by large-scale MD simulations.

2:00 PM

(ICACC-S11-009-2016) Tetrahedrally bonded amorphous carbon (ta-C) – Coating Production Technology and Application Development (Invited)

T. Schuelke*[1]; 1. Michigan State University, USA

Tetrahedrally bonded amorphous carbon coatings (ta-C) are among the hardest diamond-like carbon (DLC) materials. The covalent C-C bonds in ta-C coatings are predominantly sp^3 hybridized similar to the carbon atom bonding in diamond. The balance of carbon atoms forms sp^2 carbon bonds as found in graphite. The ta-C films contain almost no hydrogen (<1 %) and are produced by physical vapor deposition (PVD) processes at low substrate temperatures (< 100°C). This paper presents the latest status of a scalable industrial PVD solution to deposit ta-C coatings based on the so-called Laser Arc technology. This technology was developed by researchers at the Fraunhofer Institute for Materials and Beam Technology in Dresden, Germany. At its core lies a cylindrical and rotating graphite target. The primary carbon evaporation mechanism is a pulsed cathodic vacuum arc discharge. However, a pulsed laser controls the arc's position on the graphite cylinder target. The combination of cylinder rotation and longitudinal laser scanning enables the uniform evaporation along the entire length of the graphite target. This principle has now been implemented in industrial coating technology solutions, so that a Laser Arc equipped PVD machine is commercially available for high volume production applications.

2:30 PM

(ICACC-S11-010-2016) Industrial Development of Carbon-based Coatings (Invited)

G. Franssen*[1]; R. Tietema[1]; D. Doerwald[1]; R. Jacobs[1]; I. Kolev[1]; 1. IHI Hauzer Techno Coating B.V., Netherlands

In the past decade, automotive, racing, petroleum, aviation, as well as, aerospace and wind industries have shown interest in improving the efficiency, viability and life time of their products by applying coatings using PVD technology. This paper reports the properties of various DLC coatings, produced by various deposition technologies. Special attention will be given to microwave technology. The advantages of the microwave technology include, among others, higher productivity, based on the much higher deposition rate in comparison to the conventional methods, improved etching performance, lower thermal load and ability to coat on nonconductive substrates, like plastics. Much focus is also on hydrogen-free ta-C coatings, as well as on the combinations of coating and lubricants. Ta-C coatings combine highest hardness with lowest friction and are potentially considerably better in friction reduction than hydrogenated DLC-coatings. Since ta-C coatings are commonly produced with arc technology, the surface roughness must be decreased by technological measures, to levels which are accomplished by hydrogenated DLC.

Coating Process for Low Friction and Energy Solution II

Room: Tomoka B
Session Chair: Ali Erdemir, Argonne National Laboratory

3:20 PM

(ICACC-S11-011-2016) Integrated tribology for higher energy efficiency by tailored coating technology (Invited)

Y. Musayev[1]; N. Bagcivan[1]; T. Hosenfeldt*[1]; 1. Schaeffler Technologies GmbH & Co. KG, Germany

The focus areas of future mobility are environmental drives, urban and interurban mobility and the corresponding energy chain. Environmental drives are one of the major factors that determine energy efficiency and environmental compatibility of mobility. Therefore, development of energy-efficient tribological systems continues to take top priority. The surface properties of engine components must be adjusted to more stringent environmental requirements while friction losses can be minimized by coating technology. Innovative thin film technology has the ability to reduce the friction losses of vehicle components by mandatory lightweight design, improved fuel efficiency and reduced CO_2-emissions. The presented Triondur® amorphous carbon based coating systems (a-C:H; a-C:H:Me; a-C:H:X and ta-C) are excellent examples for customized tribological systems like bucket tappets, roller fingers and roller bearings. Triondur® carbon coatings offer the following advantages: super low friction with highest wear resistance, customized surface energy, optimized wetability and interaction with formulated engine oils and low adhesion to the counterpart. Close collaboration between research and production, industry and academia is required to achieve this challenging goal. In the future, the role of thin film coatings as a design element will strongly increase in further technical applications.

3:50 PM

(ICACC-S11-012-2016) Design of flexible ceramic coatings (Invited)

J. Musil*[1]; 1. University of West Bohemia, Czech Republic

The flexible ceramic coatings represent a new generation of hard nanocomposite coatings. The lecture describes a design of the formation of flexible hard coatings with enhanced resistance to cracking. This design is based on the correlations between the material properties, the plasma parameters of magnetron discharge and the energy delivered to the coating during its growth. These correlations, which are described in detail, make possible to form flexible hard ceramic and multi-functional coatings. It is shown that a key role in the formation process of flexible coatings plays the energy delivered to the growing film. It is shown that the flexible hard coatings with enhanced toughness and resistance to cracking represent a new class of advanced protective and functional coatings with a huge application potential. As examples, the robust, flexible antibacterial coatings with long lifetime and the protective over-layers preventing to cracking of hard brittle coatings are given. Reported results can be used in the development of the flexible ceramic coatings, the surface strengthening of brittle materials, the prevention of (i) cracking of the functional coatings and (ii) the cracks formation on surfaces of bended materials. At the end, trends of next development of the advanced hard nanocomposite coatings with unique properties are outlined.

4:20 PM

(ICACC-S11-013-2016) Sintering and Binder Burnout of a Zirconia Green Body Investigated by Thermal Analysis Methods (Invited)

E. Post*[1]; 1. NETZSCH Geraetebau GmbH, Germany

Zirconia ceramics cover a lot of high temperature applications because of its high temperature stability, chemical resistance and electrical properties. It is used as refractory material, in electro ceramics, as high temperature solid oxide fuel cell (SOFC) or as oxygen sensor. The ceramic body is produced by sintering a zirconia green body containing about 2 to 4% of organic binder and some oxide additives. The organic binder is burned out at around 200 to 400°C, followed by the sintering process above 1000°C. The burn-out and sintering parameters are influencing the quality of the ceramics. Thermal Analysis methods belong to the classical investigations. With thermogravimetry (TG) coupled to evolved gas analysis methods (EGA) the binder amount and the evolved gases can be determined. With differential scanning calorimetry (DSC) the energetic effects and the specific heat can be analyzed. The sintering and density change of the zirconia green body is traditionally studied by dilatometry. With the laser flash method the thermal diffusivity and the thermal conductivity of the sintered and the raw material can be determined. This contribution will show the binder burnout and sintering results of a zirconia green body investigated by TG-DSC-EGA methods, dilatometry and LFA.

4:50 PM

(ICACC-S11-014-2016) Thick Ceramic Coating by Laser-Plasma Hybrid CVD (Invited)

T. Goto*[1]; 1. IMR Tohoku University, Japan

Thick coating such as thermal barrier coating and hard coating is a root technology to produce high performance materials. Among various coating methods, CVD (Chemical Vapor Deposition) can fabricate highly hard, heat-resistant and anti-corrosive ceramic coatings. CVD and CVI (Chemical Vapor Impregnation) can be also essential techniques to develop bulky ductile structural ceramics such as SiC/SiC composite (Ceramic Matrix Composite, CMC). However, CVD needs high-temperature to deposit coatings degrading substrate materials and its deposition rate is generally low. To overcome these disadvantages of CVD, auxiliary energy such as plasma and light (laser) can be adopted to accelerate chemical reactions increasing deposition rate and reducing deposition temperature. We have prepared various coatings by laser enhanced CVD, and demonstrated that highly oriented coatings can be prepared at temperatures several 100 K lower and at deposition rates of several 100 times higher than those of conventional CVD. By using diode laser, 3C-SiC film was prepared at 3.0 mm/h (at 1500 K). With combining laser and plasma in CVD, the deposition temperature can be further decreased. Microwave (2.45GHz, 0-1.5kW) was introduced in the laser CVD forming plasma, and 3C-SiC film was prepared at 138 μm/h (at 942 K) by using hydoridopolycarbosilane as a precursor.

EMERGING TECHNOLOGIES SYMPOSIUM - Carbon Nanostructures and 2D Materials, and Composites

Carbon Nanostructures and 2D Materials, and Composites II

Room: Tomoka A
Session Chair: Gustavo Costa, NASA Glenn Research Center

1:30 PM

(ICACC-EMERG-008-2016) Discovery of Two-Dimensional, Ordered, Double Transition Metals Carbides (MXenes) (Invited)

Y. Gogotsi*[1]; 1. Drexel University, USA

The higher the chemical diversity and structural complexity of two-dimensional (2D) materials the higher the likelihood they possess unique properties. MXene is a family of 2D transition metal carbide and nitrides with general formula of $M_{n+1}X_n$, where M is an early transition metal and X is carbon and/or nitrogen and n=1 to 3. In MXenes, n+1 layers of M are interleaved with n layers of C or N, such as in Ti_2C, Ti_3C_2, Nb_2C, V_2C, etc. Herein, we present two new

families of 2D ordered MXenes - $M'_2M''C_2$ and $M'_2M''_2C_3$ - where M' and M" are two different transition metals, such as Mo, Cr, Ta, Nb, V, and Ti. In these solids, M' layers are sandwich M" carbide layers, forming an ordered structure, such as Mo_2TiC_2, Cr_2TiC_2, $Mo_2Ti_2C_3$, etc. Their ordered structures are confirmed by high-resolution scanning transmission microscopy. Moreover, density functional theory (DFT) is used to explain why ordered structures are more stable than the random mixtures of the M elements. These ordered double transition metal MXenes have contrastive electrochemical and electrical behavior than their single M element MXenes end members. This work enlarge the family of 2D materials, offering neoteric choices of structures, chemistries, and ultimately advantageous properties.

2:00 PM

(ICACC-EMERG-009-2016) Hybridization of MXene and Transition Metal Oxides for High Performance Li-Ion Storage

M. Zhao*[1]; M. Torelli[1]; C. Ren[1]; M. Ghidiu[1]; M. Barsoum[1]; Y. Gogotsi[1]; 1. Drexel University, USA

Recently, MXenes, a new family of 2D carbides, have shown promise for electrodes in Lithium-ion batteries and supercapacitors. The goal of this study was to determine if a combination of MXenes, which have high metallic conductivity but moderate capacity, and transition metal oxides (TMOs) with high lithium storage capacity but poor conductivity may result in improved performance. Three different methods, including alternating filtration, spray coating, and *in-situ* growth, were employed to achieve the hybridization of MXenes and TMOs. Flexible and free-standing MXene/TMO papers were obtained. In these composites, the 1-nm thin flakes of Ti_3C_2-MXene provide superior conductivity, ensure mechanical integrity and flexibility, as well as some Li-ion storage capacity; the TMOs (e.g. Co_3O_4, $NiCo_2O_4$) nanosheets/nanorods serve as spacers between MXene flakes to improve the accessibility of electrolyte ions and provide additional capacity. The synergetic effect of the two materials leads to much improved performance compared to pure MXene or TMOs. The MXene/TMO paper electrodes achieved high reversible capacities of 1200-1400 mAh/g at 0.1C (10-hrs discharge). These paper electrodes also exhibited excellent rate performance and superior cycling stability. A highly stable capacity around 500 mAh/g was retained for >1000 cycles at 1C rate (1-hr charge/discharge), with no obvious decay.

2:20 PM

(ICACC-EMERG-010-2016) Polymer-derived-ceramic composites of graphene and carbon nanotubes (Invited)

L. Zhai*[1]; 1. University of Central Florida, USA

Graphene and carbon nanotubes (CNTs) have been extensively used in composites because of their intriguing mechanical and electrical properties. The presentation reports our recent effort in incorporating graphene and carbon nanotubes to SiCN polymer-derived-ceramics (PDCs). The fabrication and characterization of two types of SiCN PDCs, ceramic fibers with CNTs and bulk PDCs composites with anisotropic graphene fillers, will be discussed. CNTs and graphene in SiCN ceramics have greatly increased the electrical conductivity.

2:50 PM

(ICACC-EMERG-011-2016) Synthesis, processing, and optoelectronic devices of van der Waals heterostructures (Invited)

X. Li[1]; M. Lin[1]; O. Akinola[1]; A. Puretzky[1]; C. Rouleau[1]; I. Juan Carlos[1]; D. Geohegan[1]; K. Xiao*[1]; 1. Oak Ridge National Laboratory, USA

The discovery of novel phenomenon has come from heterostructures consisting of various individual 2D crystals. Our group has focused on building the 2D heterostructures by using various methods from the determined dry transfer of exfoliate crystals, the wet transfer of CVD synthesized monolayer crystals, to the direct van der Waals epitaixal growth of 2D layers and their heterostructures. The direct synthesis process provides superior interfaces and coupling compared to their exfoliated counterparts. In this talk, I will discuss recent breakthroughs for direct growth of two-dimensional atomic layers and heterostructures with scalable techniques such as chemical vapor deposition. The persistent photoconducting behavior and photovoltaic properties were observed from these van der Waals heterostructures.

3:40 PM

(ICACC-EMERG-012-2016) Synthesis and electrodepositing of zinc oxide nanostructures supported in graphene oxide sheets for application in energy harvesting

N. Jacomaci[1]; L. R. Canal[1]; N. Azana[1]; P. Shieh[1]; M. A. Zaghete[2]; T. Mazon*[1]; 1. CTI, Brazil; 2. Chemistry Technological/Institute of Chemistry of Araraquara, Brazil

Zinc oxide/graphene oxide (ZnO/GO) composites powders were synthesized by chemical bath deposition. Different experimental conditions were applied in order to prepare nanocomposites with different morphologies. Scanning electron microscope (SEM), Raman spectroscopy and X-Ray diffraction were carried out to confirm the effect of the use of GO on the structure and morphology of ZnO nanostructures and characterize the graphene oxide/ZnO interactions. The analysis of SEM microscopy were realized at LME/LNNANO/CNPEM. Morphological control was obtained by the influence of the graphene oxide in aqueous solution, in specifically condition. The ZnO nanorods/GO composites powders were used to prepare films on FTO/PET substrates by electrodeposition approach. Electrodeposition was performed at constant cathodic potential, in ZnO/GO alcohol solution at room temperature. The resulting ZnO/GO uniform layer was characterized by SEM and by the output voltage of the films. The results reveal that is possible to obtain oriented nanopastructures films by varying the voltage range from 500 to 3,000 V during the electrodeposition. These results pave the way for simple and low-cost routes for the production of ZnO nanostructures supported in graphene oxide sheets with potential for energy harvesting devices.

4:00 PM

(ICACC-EMERG-013-2016) Chemically Modified Graphene/PDC Electrodes for Long-cycle Lithium-ion Batteries (Invited)

G. Singh*[1]; L. David[1]; 1. Kansas State Univ, USA

Chemically modified graphenes (CMG) have garnered intense research interest as potential standalone as well as composite electrode materials for rechargeable alkali metal-ion batteries. CMG based electrodes offer high surface area, improved electrical conductivity and mechanical strength along with added value of mass production. Here, we will present data on recent success in synthesis of 2-D layered composites composed of molecular precursor-derived ceramic (PDC) and chemically modified graphenes. We will show that interfacing PDCs with graphene derivatives is an effective strategy in improving PDC's Li-ion electrochemical capacity, first cycle efficiency, and long-term cyclability. Flexible, lightweight, and mechanically robust nanostructured paper electrodes deliver Li-capacity of approximately 550 mAh/g (total electrode weight) with nearly 100 % coulombic efficiency for over 1000 cycles.

FS1: Geopolymers, Chemically Bonded Ceramics, Eco-friendly and Sustainable Materials

Novel Applications

Room: Coquina Salon E
Session Chair: Sylvie Rossignol, Laboratoire SPCTS

1:30 PM

(ICACC-FS1-018-2016) Development of a Mold for Thermoplastics based on a Phosphate Cement (Invited)

J. Blom[1]; H. Rahier*[1]; J. Wastiels[1]; 1. Vrije Universiteit Brussel, Belgium

In case of limited series or prototypes of thermoplasts, metallic molds are too expensive and time consuming to build. For that reason, a production strategy was developed to build a textile reinforced phosphate based cement mold. The requirements are: stability up to 400°C with limited shrinkage/expansion, sufficient stiffness, and reduction of the permeability. In this research, a composite mold is developed, based on glass fibre textile reinforced phosphate cement (TRC). This tooling system is combining the advantages of a thermoset mold with elevated temperature use. Since cement based molding systems contain water, major challenges are the reduction of porosity, the sealing of the surface and the limitation of the thermal shrinkage. The development of an isothermal curing method resulted in a more stable P-cement, as confirmed by shrinkage measurements, X-ray Diffraction and Scanning Electron Microscopy. By adding fillers to the top coat, the surface permeability was decreased. The effect of thermal loading, composition of the matrix and the curing conditions was provided by an experimental study including accoustic emission. To illustrate the potential of the proposed method, a thermoplastic prepreg was processed in both the conventional metal and the TRC equivalent. The proof of concept showed that a textile reinforced cement mold can be used to thermoform a thermoplastic prepreg, to an acceptable part.

2:00 PM

(ICACC-FS1-019-2016) Investigations of the thermally induced hydrogen release of NaBH4, NH3BH3 and their geopolymer composites (Invited)

C. Rüscher*[1]; Z. Assi[1]; L. Schomborg[1]; 1. Leibniz University Hannover, Germany

Some new applications in geopolymer research concerning hosting hydrogen storage materials have been reported recently. According to this sodiumboronhydride (SB = NaBH4) and aminoborane (AB = NH3BH3) could be re-crystallized within a geopolymer matrix. In this study an investigation of the thermally induced hydrogen release reactions and destruction products of these new materials in comparison to the behavior of SB and AB were carried out at temperatures up to 500°C. New results are obtained in temperature dependent infrared absorption (TIR) experiments, where the different materials were diluted with KBr and NaCl and pressed in pellets. The effect of hydrogen release could be followed using the reduction reaction of NaNO3 and KNO3 added in the KBr/NaCl pressed pellet. As an example the rather fast transformation of SB into DADB ([(NH3)2BH2]BH4]) could be observed between 115 and 120°C, probably via an ion exchange of the BH4/Br-anion exchange between DADB and the KBr matrix. Hydrogen release occurs in parallel. Similar effects are also observed for AB embedded in the geopolymer. For SB the effect of significant hydrogen release could be obtained above about 250°C whereas for SB enclosed in the geopolymer the hydrogen release occurs above about 350°C.

2:30 PM

(ICACC-FS1-020-2016) Effect of calcium addition on alkaline silicate binders: various applications (Invited)

F. Allali[3]; J. Cornette[1]; E. Joussein[2]; N. Idrissi[3]; S. Rossignol*[1]; 1. Laboratoire SPCTS, France; 2. GRESE, France; 3. Laboratoire de Chimie Appliquée, Morocco

This paper focuses on the influence of calcium on sodium silicate solutions activated with three additives: sodium carbonate, sodium hydroxide and boehmite. The calcium was added in two forms, calcite sand and slaked lime, as these two materials are widely used to restore historical coatings in Morocco. This aim of this work was to synthesize potential coatings from mixtures of a sodium silicate solution and traditional restoration materials. Several mixtures were synthesized and characterized by XRD, FTIR, SEM and the Vickers hardness test. Primary results demonstrated that lime was a highly reactive component in the mixtures when compared with calcite. Moreover, FTIR showed that the evolution of the Si-O-M band is different for these multiple mixtures. The mixtures composed of calcite, sodium silicate solution and boehmite presented good adherence to several supports.

3:20 PM

(ICACC-FS1-021-2016) Mica Platelet-reinforced Geopolymer Composites

P. F. Keane[1]; G. P. Kutyla[1]; J. F. Wight[2]; W. Rickard[3]; W. M. Kriven*[1]; 1. University of Illinois at Urbana-Champaign, USA; 2. Corning Incorporated, USA; 3. Curtin University, Australia

The mica flakes were obtained from the Cogebi Company as phlogopite mica paper type Cobebi P160 containing no organic or inorganic binder. Mica can withstand temperatures in excess of 1000°C. Phlogopite, of composition $(KMg_3(AlSi_3O_{10})(OH)_2$ is flame-retardant, non-flammable, does not give off fumes. It conducts very little heat, especially perpendicular to its strata. Natural mica has a dielectric strength greater than 25 kV/mm (625 V/mil), has good resistance to arcing and electrical erosion, and is permeable to microwaves. Mica has good compressive strength. It behaves well in the presence of tensile and bending stresses. It has a high modulus of elasticity. Geopolymer composites based on Na or K where fabricated having a matrix composition $M_2O{\bullet}Al_2O_3{\bullet}4SiO_2$ where M = Na or K. Increasing amounts of mica were dispersed in the geopolymer matrix under vibration, and the composites were set under ambient conditions. The mechanical properties were measured in 4-point flexure as a function of in situ and post mortem temperature to 1,000 °C and their Weibull moduli were analyzed from the statistical data. The microstructure was examined by SEM/EDS. The dielectric constants and thermal conductivity were measured perpendicular to the platelet casting direction.

Construction Materials

Room: Coquina Salon E
Session Chair: Abdul Bhuiya, University of Illinois at Urbana-Champaign

3:40 PM

(ICACC-FS1-022-2016) Inorganic phosphate with additions of steel slag powder

H. A. Colorado*[1]; 1. UDEA, Colombia

Inorganic phosphate cements based on wollastonite were mixed with steel slag powders. Steel slag is hazardous waste of constant concern to the slag industry. The addition of steel slag to cement is very beneficial to the environment because the cementing process decreases the possibility of water contamination. Second, the process conducted in this research was entirely conducted at room temperature reducing the impact on the global warming. Up to 50wt% of these particles where added to cement. The characterization was conducted by scanning electron microscopy (SEM), x-ray diffraction

(XRD), compressive strength and density tests. Up to, which itself is environmentally friendly since reduces the necessary cement binder amounts, and therefore reducing the CO_2 footprint.

4:00 PM

(ICACC-FS1-023-2016) Recycling of Grog by addition into heavy clay ceramic manufacturing

C. F. Vieira*[1]; L. Amaral[1]; 1. State University of the North Fluminense, Brazil

In the county of Campos dos Goytacazes, north of the State of Rio de Janeiro, Brazil, there is a large production of heavy clay ceramic for civil construction, mainly perforated bricks. A percentage of these bricks are damaged during the firing stage and after crushing is a powder waste denoted as grog. The amount of damaged ceramics generated after the firing stage is estimated to be at least 850 ton per month. This work investigates the recycling in the proper heavy clay ceramic processing. The characterization of the grog was performed by XRD, XRF, sieving and sedimentation method to determine its particle size distribution, DTA/TG and SEM. Grog originated from bricks produced at 500-600 C, was added up to 20 wt.% into the clayey body. Cylindrical test specimens, with a diameter of 31 mm and 11 mm thick, were prepared by uniaxial pressing at 20 MPa, with 8 wt.% water, dried at 110 C until constant weight and then fired at temperatures varying from 500 to 1100 C. Body samples were initially tested for plasticity. After firing, samples were then tested for linear shrinkage, water absorption and mechanical strength. The results have shown that grog addition improves the workability of the clay and 5 wt.% of grog does not damage the fired properties at all temperatures. These results indicate the possibility of recycling fired brick waste into the own ceramic processing.

FS4: Additive Manufacturing and 3D Printing Technologies

Emerging Technology

Room: Coquina Salon C

Session Chairs: Naoki Kondo, National Institute of Advanced Industrial Science and Technology (AIST); Surojit Gupta, University of North Dakota

1:30 PM

(ICACC-FS4-018-2016) Challenges and issues for indirect selective laser sintering of ceramics (Invited)

N. Kondo*[1]; M. Hotta[1]; A. Shimamura[1]; T. Ohji[1]; 1. National Institute of Advanced Industrial Science and Technology (AIST), Japan

(This abstract content will be available online January 24, 2016.)

2:00 PM

(ICACC-FS4-019-2016) Development of Novel Additive Manufacturing (AM) Practices

R. Dunnigan*[1]; S. Ghosh[1]; M. Habib[1]; S. Gupta[1]; 1. University of North Dakota, USA

The integral process of depositing thin layers of material, one after another, until the designed component is created is collectively referred to as Additive Manufacturing (AM). In this presentation, we will report some of the recent studies for developing novel polymer matrix composites for multifunctional applications. We will present the microstructure analysis, mechanical, and tribological behavior of composites fabricated by AM. These results will be compared with materials fabricated by conventional methods. Some of the polymer systems which will be explored during this study are High Impact Polystyrent (HIP), Nylon, PLA, ABS, among others.

2:20 PM

(ICACC-FS4-020-2016) Powder preparation for indirect selective laser sintering of alumina-binder composite powder

M. Hotta*[1]; A. Shimamura[1]; N. Kondo[1]; T. Ohji[1]; 1. AIST, Japan

(This abstract content will be available online January 24, 2016.)

2:40 PM

(ICACC-FS4-021-2016) Additive manufacturing of alumina ceramic part by indirect selective laser sintering

A. Shimamura*[1]; M. Hotta[1]; T. Ohji[1]; N. Kondo[1]; 1. National Institute of Advanced Industrial Science and Technology (AIST), Japan

(This abstract content will be available online January 24, 2016.)

3:20 PM

(ICACC-FS4-022-2016) Tribology of Polymer Matrix Composites (PMCs) fabricated by Additive Manufacturing

S. Gupta*[3]; R. Dunnigan[3]; A. Salem[4]; L. Kuentz[5]; M. C. Halbig[1]; M. Singh[2]; 1. NASA Glenn Research Center, USA; 2. Ohio Aerospace Institute, USA; 3. University of North Dakota, USA; 4. Hawken School, USA; 5. Lake Ridge Academy, USA

The integral process of depositing thin layers of material, one after another, until the designed component is created is collectively referred to as Additive Manufacturing (AM). Fused deposition process (FDP) is a type of AM where feedstock is extruded into filaments which then are deposited by 3D printing, and the solidification occurs during cooling of the melt. Currently, complex structures are being fabricated by commercial and open source desktop 3D printers. Recently, metal powder containing composite filaments based on polylactic acid (PLA) and acrylonitrile butadiene styrene (ABS) have emerged, which could be utilized for multifunctional applications. For further deployment in the field, especially for aerospace and ground-based applications, it is critical to understand the tribological behavior of 3D printed materials. In this presentation, we will report the tribological behavior of different polymer matrix composites fabricated by fused deposition process. These results will be compared with the base polymer systems. During this study, the tribological behavior of all the samples will be evaluated with tab-on-disc method and compared for different metallic powder reinforcements.

3:50 PM

(ICACC-FS4-023-2016) A Three-Dimensional Printing Rapid Prototyping Method for Complex Ceramic Parts

W. Jia*[1]; X. Wang[1]; Y. Chenglong[1]; Y. Yang[1]; L. Hui[1]; 1. Shaanxi University of Science and Technology, China

Ceramic parts with complex internal structure and fine ceramics is difficult to be printed by the three dimensional printing method. A new method of rapid manufacturing for ceramic parts, which used a special material as the support based on the ceramic three dimensional printing method, will solve this problem. Ceramic clay was extruded by the nozzle of the equipment. After printing each layer, a thin layer of a special material would be put on it. The special material has to be fixed by a certain device. A lifting platform of the printing equipment would drop a certain height at Z direction after printing the first clay layer. And the second layer of clay on the special material would be printed after the second special material was lay. This action was cycled until finishing printing the whole clay parts. By this way, the three dimensional molding with single nozzle can print complex structure ceramic parts and fine ceramic parts. Special characteristic of this special material can promote the mutual penetration between different layers of clays, which guarantee the product performance of ceramic parts. The three dimensional printing method with the special material as a support for ceramic parts is a new research idea, which has a good application value.

FS5: Field Assisted Sintering and Related Phenomena at High Temperatures

Sintering I

Room: Ponce DeLeon
Session Chair: Rishi Raj, University of Colorado

1:30 PM

(ICACC-FS5-001-2016) How far can classical ideas explain the flash sintering of ceramics? (Invited)

R. I. Todd*[1]; M. Yoshida[2]; E. Zapata Solvas[3]; R. Bonilla[1]; J. Zhang[4]; Z. Fu[4]; 1. University of Oxford, United Kingdom; 2. Gifu University, Japan; 3. CSIC-Universidad de Sevilla, Spain; 4. Wuhan University of Technology, China

"Flash sintering" occurs when a closed circuit electric field is applied across a ceramic powder compact and is characterised by an electrical power surge at a specific temperature, accompanied by rapid densification. The phenomenon is easy to reproduce but the mechanisms responsible remain controversial. This presentation begins from a classical perspective and examines separately the thermo-electrical response and densification at high heating rates of 3YSZ. First, the resistivity vs. temperature relationship is used to construct a dynamic model for Joule heating under conditions of non-uniform temperature. Comparison of the model predictions and experimental results showed that the flash event can be quantitatively explained in detail by classical thermal runaway resulting from the observed negative temperature coefficient of resistivity. Next, the sintering response and grain size of flash sintered specimens are compared with those of specimens starting with identical powder compacts and heated at similar rates but without the application of an electric field. The mechanisms involved are discussed and areas requiring further investigation are highlighted.

2:00 PM

(ICACC-FS5-002-2016) Flash Sintering of ZnO and Other Oxide (Invited)

Y. Zhang*[1]; J. Nie[1]; J. Luo[1]; 1. University of California, San Diego, USA

Flash sintering of ZnO has systematically been investigated. A quantitative model has been developed to forecast the thermal runaway conditions and the predictions are in excellent agreements with the observed onset flash temperatures, attesting that the flash starts as a thermal runaway in at least these ZnO based systems. This model can also successfully predict the onset flash temperatures of six sets of different anatase and rutile based TiO_2 specimens with different doping as well as 8YSZ. Using ZnO as a model system, a strong dependence of the onset flash sintering temperature on the atmosphere has been discovered. In the best cases, ZnO specimens have been sintered to >97% relative densities in 30 s at furnace temperatures of <120 °C in Ar + 5 mol.% H_2. A range of other new phenomena of electric field/current effects on sintering and microstructural evolution have also been discovered and explained.

2:30 PM

(ICACC-FS5-003-2016) Spark plasma sintering: from evidence of specific effects to the elaboration of complex architectures and shapes (Invited)

C. Estournes*[1]; R. Marder[2]; R. Chaim[2]; R. Epherre[1]; C. Elissalde[3]; M. Maglione[3]; G. Chevallier[1]; C. Maniere[1]; L. Durand[4]; 1. CIRIMAT, France; 2. Technion Israel Institute of Technology, Israel; 3. ICMCB-CNRS, France; 4. CEMES, France

Pulsed Electric Current Sintering techniques have known a huge development over the last two decades. In recent investigations on different ceramic powders local melting of the particle and nano-particle surfaces have been clearly shown, confirming the formation of spark and plasma during the SPS. The different behavior of various oxide systems depend on the material properties, and the pressure and its application regime. These features also determine the nano-micro-structure evolution during the sintering. The potentialities of SPS to design new materials or architectures will be illustrated through few examples. In particular emphasis will be placed on the large flexibility of experimental SPS parameters which allow to control the morphology and the anisotropy of dielectric inclusions into a ferroelectric matrix which significantly the properties of these multimaterials. The modeling of SPS by finite element method has known drastic development. Coupling three main physics, Electric Thermal and Mechanic (ETM) allows now to predict the temperature, grain size and porosity during the process up to the densification of parts. Considering the great effect of contact resistances between the different parts, Olevsky and/ot Abouaf models, allowed us to define the optimized SPS parameters and tool geometry in order to minimize the porosity gradient in a complex shape part.

3:20 PM

(ICACC-FS5-004-2016) Flash Sintering of Alumina: Phenomenological and Mechanisms Analysis

M. Biesuz*[1]; V. M. Sglavo[1]; 1. University of Trento, Italy

Reduction of energetic, environmental and economic costs is one of the most important issue for the ceramic industry of the 21th century. Many works showed the application of an E-Field during the sintering process (FAS techniques) is very effective in reducing sintering time and temperature. Several authors focused their research on semi conductive or conductive materials demonstrating the presence of a non-linear increase in the conductivity of ceramics at an onset field and temperature. This abrupt increase in conductivity is accompanied by a very quick sintering event (it happens in just few seconds) called Flash Sintering. The reasons and the mechanisms at the base of this process are actually not completely clear, even if many theories have been developed. The main goal of the present work is to provide a deep analysis of the FAS behavior of reactive alumina (99.8% pure) by a phenomenological point of view, then some hypothesis explaining the mechanisms are proposed. The effect of the E-Field and of the current density was investigated by changing these parameters respectively in the range of 250-1500 V/cm and 2-6 mA/mm^2. Moreover two different electrode materials were tested. The sintered samples were analyzed by Archimede's method and SEM micrographs were taken. The mechanisms were investigated by Impedance Spectroscopy and measuring the optical emission during Flash Sintering.

3:40 PM

(ICACC-FS5-005-2016) Effect of Electric Field/Current on Liquid Phase Sintering

J. Gonzalez-Julian[1]; O. Guillon*[1]; 1. Forschungszentrum Juelich, Germany

The sintering behavior of alumina containing different amounts of calcium–aluminum–silicate glass as sintering aid was analyzed under AC electric fields between 0 and 150 V/cm. Liquid phase sintering was enhanced by the electric field, and "flash sintering" behavior depending on the current density and power dissipation within the specimen could be observed. Current flowed only through the liquid phase at high temperature and enhanced the densification process by two effects: Joule heating and athermal response of the viscous liquid under the electric field. Joule heating increased the temperature within the specimen, whereas the applied electric field reduced the viscosity of the liquid phase promoting a more effective matter transport.

FS6: Hybrid Materials and Processing Technologies

Hybrid Materials and Processing Technologies II

Room: Coquina Salon H

Session Chairs: Hyungjun Kim, Korea Advanced Institute of Science and Engineering (KAIST); Byungchan Han, Yonsei University

1:30 PM

(ICACC-FS6-009-2016) Design of Model Experiments for Stress-induced Nanoscale Phenomena (Invited)

S. Hong*[1]; J. Kim[1]; Y. Choi[1]; 1. Argonne Nat Lab, USA

Nanotechnology enabled scientists and engineers to visualize the configuration and kinetics of domains in oxide and polymer materials with the same physical and chemical properties at room temperature. With the improved capability to image and map those domains in-situ using scanning probe microscopy, we are able to study stress-induced phenomena useful to design better functional materials that have enhanced performance and improved reliability. Two examples will be introduced in the talk: one covers the stress-induced enhancement of the piezoelectric properties of polymer ferroelectrics, whereas the other covers the stress-induced corrosion phenomena occurring at the interface between Pb-containing water and a NiO layer. Our model experiments are designed to tackle two of the most important challenges for Internet of Things (IoT) and clean energy future, which lead to the improvement of material properties and reliability via control of nanoscale morphology and chemical phase.

2:00 PM

(ICACC-FS6-010-2016) Graphene Based Hybrid Nanostructures: Nanoscale Assembly & Chemical Modification (Invited)

S. Kim*[1]; 1. Korea Advanced Institute of Science and Engineering (KAIST), The Republic of Korea

Graphene based nanomaterials, including carbon nanotubes and graphene, attract enormous research attention for their outstanding properties along with molecular scale dimension. Optimized utilization of those carbon nanomaterials requires the subtle controllability of the structures and properties. In this presentation, our research progress on the nanoscale assembly of heteroatom-doped carbon nanomaterials will be overviewed. Carbon nanomaterials can be processed into various three-dimensional structures by self-assembly principles. The resultant structures with large surface and electrical conductivity are potentially useful for catalysis, energy storage and so on. Aqueous dispersion of graphene oxide shows liquid crystallinity, whose spontaneous molecular ordering is useful for display or fiber spinning. Additionally, substitutional heteroatom doping of the carbon nanomaterials was achieved for the effective modulation of physical properties. The chemically modified carbon nanomaterials with tunable workfunction and remarkably enhanced surface activity are generally useful for energy storage, environment remediation, nanocomposites for improved material and device performances.

2:20 PM

(ICACC-FS6-011-2016) Assessment of strain-generated oxygen vacancies using $SrTiO_3$ bicrystals (Invited)

S. Choi*[1]; 1. Korea Institute of Materials Science, The Republic of Korea

Control of atomic-scale defects has attracted attentions in materials community due to the amphoteric characteristic of defects. Defects deteriorate the desired properties of materials but also often improve them, and their effects are even more pronounced in the localized dimensions. Here we propose and demonstrate that defects formation can be manually controlled by strain in complex oxides, by combining experiments and calculations. The correlation between strain and oxygen vacancies, the representative defects in the oxides, is investigated using SrTiO3 bicrystals. Through high resolution transmission electron microscopy and electron energy loss spectroscopy, we directly observe the strengthened strain along the grain boundary with the larger tilt angle; and the confined oxygen vacancies at the strain-imposed regions. First-principles calculations support that oxygen vacancies are likely to form under strain, and are further stabilized as the strain becomes stronger. These results indicate that oxygen vacancies could be concentrated not only at the grain boundaries but also in ion-bombarded films and at heterogeneous interfaces where strains accumulate. Our findings open the way to materialize functional devices of which atomic-scale defects can impact on the performance through strain-mediated control and confinement of defects.

2:40 PM

(ICACC-FS6-012-2016) Interfacial Bonding of Multi-Materials Joined with Polymer Derived Ceramics (Invited)

H. M. Chaput*[1]; T. Pruyn[1]; J. Baur[1]; 1. Air Force Research Lab, USA

A fundamental understanding of the bonding between multi-material systems could benefit many aerospace applications. Polymer derived ceramics such as poly(silazane) provide a viable route for joining dissimilar substrates. Combination of these inorganic polymers with organic resins such as epoxy could potentially lead to enhanced hybrid adhesives. For improved interfacial interactions between bonded substrates of ceramic, metal, and polymer, various cross-linking mechanisms (i.e., radical initiator, poly(isocyanate) chemistry) of these blends has been explored. Also to provide more insight into the curing process, different ratios of epoxy to poly(silazane) were investigated. These studies revealed the importance of optimizing adhesion strength and thermal stability. *This abstract is pending public release approval from the United States Air Force. We reserve the right to retract this abstract at any point.*

3:20 PM

(ICACC-FS6-013-2016) Property and application of conductive ceramics prepared by the combination of gelcasting and reductive sintering (Invited)

T. Shirai*[1]; M. Fuji[1]; 1. Nagoya Institute of Technology, Japan

Electrically conductive dense and porous ceramics have been used in diverse fields of industry encompassing various disciplines including electronics, electrical power generation, and many others. To provide such numerous electrical applications, the electrically insulating ceramics are mechanically mixed with electrically conductive fillers, in the form of powders such as metal, metal oxides, and others, to build electrical conduction path. Through this method, however, the composites are prone to suffer segregation of conductive phase that leads to nonuniformity in electrical conductivity and undesirable physical properties. Hence, this dissertation describes a simple and direct approach for introducing a homogeneous electrically conductive phase into insulating dense alumina and porous alumina ceramics by combination of gelcasting and reduction sintering. This study is particularly taking advantage of a gelcast-derived binder network responsible for the strength of green ceramics as a precursor for the in-situ formation of nano-carbon network in alumina matrix, which acts as homogenous electrical conduction path.

3:50 PM

(ICACC-FS6-014-2016) Design of Exceptionally Strong and Conductive Cu Alloys Beyond the Cconventional Speculation via the Interfacial Energy-controlled Dispersion of γ-Al_2O_3 Nanoparticles (Invited)

B. Han*[1]; S. Han[3]; K. Kim[2]; J. Kang[4]; 1. Yonsei University, The Republic of Korea; 2. Pusan National University, The Republic of Korea; 3. Korea Institute of Materials Science, The Republic of Korea; 4. DGIST, The Republic of Korea

In this presentation it is demonstrated that the contradictory material properties of electric conduction and mechanical strength can be

improved simultaneously if the interfacial energies of heterogeneous interfaces are carefully controlled. We uniformly disperse γ-Al_2O_3 nanoparticles over Cu matrix, and then we controlled atomic level morphology of the interface γ-Al_2O_3//Cu by adding Ti solutes. It is shown that the Ti dramatically drive the interfacial phase transformation from very irregular to homogeneous spherical morphologies resulting in substantial enhancement of the mechanical property of Cu matrix. Furthermore, the Ti removes impurities (O and Al) in the Cu matrix by forming oxides leading to recovery of the electrical conductivity of pure Cu. Our experimental measurements demonstrate that the mechanical strength and electrical conductivity of the γ-Al_2O_3//Cu are 300 % beyond the conventional upper limits. We validate experimental results using HRTEM and EDX combined with first-principles density functional theory (DFT) calculations, which all consistently poise that our materials are suitable for industrial applications.

4:10 PM

(ICACC-FS6-015-2016) Polymer/carbon nano-materials composite fibers and films (Invited)

H. Chae*[1]; 1. Ulsan National Institute of Science and Technology, The Republic of Korea

Carbon nano-materials such as carbon nanotube and graphene, have exceptional mechanical, electrical, and thermal properties, which are strongly anisotropic. In order to fully utilize these anisotropic properties, 1D or 2D form of nanocomposites are often considered to be ideal, leading to the investigation of numerous carbon nano-materials/polymer nanocomposite fibers and films. In many cases, the addition of carbon nano-material results in increased tensile and compressive properties, enhanced fatigue resistance, increased solvent resistance, as well as increased glass transition temperature. The property enhancement has been attributed not only to the addition of carbon nano-material, but also attributed to the ability of carbon nano-material to form highly ordered polymer interphase in the vicinity of carbon nano-materials. For example, carbon nanotubes act as a template for polymer orientation and a nucleating agent for polymer crystallization. This ability of carbon nanotubes is expected to have profound impact on polymer and fiber processing, as well as on the resulting morphology and properties. The results of studies carried out to date will be presented.

4:30 PM

(ICACC-FS6-016-2016) Gas Phase Deposition for Direct Integration of Functional Oxides on Microrelectronic Substrates for Gas Sensing Appications (Invited)

T. Fischer*[1]; S. Mathur[1]; 1. University of Cologne, Germany

The direct integration of nanostructures materials in microelectronic devices is still hampered due to separate synthesis and integration proceedures. Especially for one dimensional nanowires high temperature synthesis using chemical vapor deposition (CVD) is mostly incompatible with present microelectronic devices. The availability of micro hotplates using MEMS technology with integrated heaters and readout electrodes and integarted temperature sensors allows the direct growth of nanostructures materials on the functional unit using a CVD approach employing metal organic precursors. By operating the hotplate above 500 °C thermal CVD processes take place and crystalline thin-films or nanostructures can be obtained on electrode structures, which allow the direct contact of the formed functional oxide. By sequential CVD or post processing methods complex device architecturs of hybrid composite materials can be manufactured on the device level, thus facilitating the application of these materials in real life devices. This presentation will examine the reactor as well as substrate requirements for direct on-chip integration of nanomaterials for a one step fabrication of resistive metal oxide gas sensors via metal organic chemical vapor deposition using a dedicated reactor design.

Friday, January 29, 2016

S1: Mechanical Behavior and Performance of Ceramics & Composites

Environmental Effects

Room: Coquina Salon D
Session Chair: Randall Hay, Air Force Research Laboratory

8:30 AM

(ICACC-S1-068-2016) Modeling Environmental Degradation of SiC-Fiber reinforced CMCs (Invited)

T. Parthasarathy*[2]; C. Przybyla[1]; R. Hay[1]; M. Cinibulk[1]; 1. Air Force Research Laboratory, USA; 2. UES, USA

The various mechanisms that are involved in environmental degradation of SiC fiber reinforced ceramics are catalogued and modeled. The key mechanisms that were analytically modeled include oxygen depletion from matrix crack face oxidation, recession of BN interphase from oxidation and volatilization in the presence of moist air, the oxidation of the fibers, the loss of strength from fiber oxidation, and the closure in the matrix crack opening from scale formation. The details of the models are presented along with parametric studies. The possibility of integrating them using a numerical code is suggested and explored. Preliminary results are presented.

9:00 AM

(ICACC-S1-069-2016) Fiber Strength of Hi-Nicalon™-S after Oxidation and Scale Crystallization in $Si(OH)_4$ Saturated Steam

R. Hay*[1]; R. Corns[1]; A. Ross[1]; B. Larson[1]; 1. Air Force Research Laboratory, USA

Hi-Nicalon™-S SiC fiber was oxidized in $Si(OH)_4$ saturated steam for 1 to 100 hours at 500 to 1500°C. Scale thickness and crystallization extent were measured by transmission electron microscopy of fiber cross-sections. Oxidation kinetics for glass and crystalline scales were determined. Crystallization kinetics were determined for glass scales. Oxidized fiber strength was measured using 30 single filament tensile tests with 2.54 cm gauge length. Measured fibers strengths were compared to calculated strengths determined by a model using oxidation and scale crystallization kinetics, change in load-bearing area, thermal and growth residual stress in the scale, and the method of superimposition for crack tip stress intensity factors. Results are discussed and compared with previous results for oxidation in dry and wet air.

9:20 AM

(ICACC-S1-070-2016) Oxidation behavior of SiC fiber-reinforced composites fabricated by melt infiltration using Si-Hf and Si-Ti alloys

T. Tsunoura*[2]; Y. Okubo[2]; K. Yoshida[2]; T. Yano[2]; T. Aoki[1]; T. Ogasawara[1]; 1. Japan Aerospace Exploration Agency, Japan; 2. Tokyo Institute of Technology, Japan

SiC fiber-reinforced composites have received attention for thermal protection system of hypersonic aircraft and jet engine components due to their excellent properties under extreme condition. In our previous work, SiC fiber-reinforced composites were successfully fabricated by melt-infiltration method using Si-8.5at%Hf and Si-16at%Ti eutectic alloy below 1400. In this study, their oxidation behavior was evaluated. Three-dimensional preforms consisting of amorphous SiC fibers were used as the reinforcement, and the fibers were coated with CVI-C as an interphase and CVI-SiC for protecting the CVI-C and the matrix. Then, the preform covered with Si-8.5at%Hf or Si-16at%Ti alloy was heated up to 1375-1390, and the SiC fiber-reinforced composites were obtained. Oxidation tests were carried out at 800-1200 for 100 hours in gas-flow condition, dry-air or gas mixed air with steam. The composites using Si-Hf alloy had

thick oxidation layers with the thickness of about 150-200 μm after dry oxidation test at 1200, and catastrophic oxidation behavior after wet oxidation test at 800-1000 they showed. On the other hand, in the composites using Si-Ti alloy, thin oxidation layer with the thickness of about 30 μm was formed after dry oxidation test at 1200, and catastrophic oxidation behavior did not occur in any condition.

9:40 AM

(ICACC-S1-071-2016) Crack-resistant ceramic matrix composite materials

S. S. Solntsev*[1]; V. A. Rozenenkova[1]; N. A. Mironova[1]; V. Denisova[1]; 1. Federal State Unitary Enterprise All-Russian Institute of Aviation Materials, Russian Federation

The mail principles of crack-resistant ceramic SiC-matrix composite materials (CMC) synthesis are reported. These CMCs are based on polysiloxanes with higher ceramic recovery and high-tensile reinforcing fillers. The influence of technological parameters of CMCs synthesis to thermophysical and mechanical properties is shown.

10:20 AM

(ICACC-S1-072-2016) Slow Crack Growth of Glass in Salt Water

B. Hausmann*[1]; J. Salem[1]; 1. NASA Glenn Research Center, USA

The slow crack growth parameters of soda-lime silicate were measured in distilled and salt water of various concentrations in order to determine if stress corrosion susceptibility is affect by the presence of salt and the contaminate formation of a weak sodium film. Past research indicate that solvents effect the rate of crack growth, however, the effects of salt have not been studied. The results indicate a small but statistically significant effect on the slow crack growth parameters *A* and *n*. However, for typical engineering purposes, the effect can be ignored.

10:40 AM

(ICACC-S1-073-2016) Slow Crack Growth of Germanium

J. Salem*[1]; 1. NASA Glenn Research Center, USA

The fracture toughness and slow crack growth parameters of germanium supplied as single crystal beams and coarse grain disks were measured. Although germanium is anisotropic (A = 1.7), it is not as anisotropic as SiC, NiAl, or Cu, as evidence by consistent fracture toughness on the <100>, <110>, and <111> planes. Germanium does not exhibit significant slow crack growth in distilled water. (n > 100). Practical values for engineering design are a fracture toughness of ~0.7 MPam^0.5 and a Weibull modulus of m = 6 ± 2. For well ground and reasonable handled coupons, fracture strength should be greater than 30 MPa.

11:00 AM

(ICACC-S1-074-2016) A comparison of natural and synthetic sand effects on thermal barrier coatings for gas turbine engines

M. J. Walock*[1]; B. Barnett[1]; A. Ghoshal[1]; M. Murugan[1]; J. Swab[1]; M. S. Pepi[1]; D. A. Hopkins[1]; G. A. Gazonas[1]; K. A. Kerner[2]; 1. US Army Research Laboratory, USA; 2. Aviation and Missile Research, Development, and Engineering Center, USA

Accumulation and infiltration of molten/ semi-molten sand and subsequent formation of calcia-magnesia-alumina-silicate (CMAS) deposits in gas turbine engines continues to be a significant problem for aviation assets. This complex problem is compounded by the large variations in the composition, size, and topology of natural sands, gas generator turbine temperatures, thermal barrier coating properties, and the incoming particulate's momentum. In order to simplify the materials testing process, significant time and resources have been spent in the development of synthetic sand mixtures, such as AFRL 02 and AFRL 03. However, there is debate whether these mixtures accurately mimic the damage observed infield-returned engines. With this study, we provide a direct comparison of CMAS deposits from both natural and synthetic sands. Using air plasma spray and solution precursor plasma spray, 7% yttria-stabilized zirconia coatings are deposited onto bond-coated, Ni-superalloy discs. After determining their as-deposited characteristics, each sample is coated with a slurry mixture of sand, either natural or synthetic, and exposed to a high temperature flame (in a newly developed test rig) for 1 hour. The resultant CMAS deposits, and the underlying coatings are also characterized. In addition to comparison with each other, the test samples will be compared to field-returned equipment.

11:20 AM

(ICACC-S1-075-2016) High Temperature Oxidation Resistance of BN Particle Dispersion SiC Composites

T. Hinoki*[1]; S. Yanagawa[1]; K. Shimoda[2]; 1. Kyoto University, Japan; 2. National Institute for Materials Science (NIMS), Japan

Silicon carbide (SiC) composites are expected to be stable in harsh environments for aerospace and nuclear applications. Silicon carbide composites basically require weak fiber/matrix interphase like carbon or boron nitride (BN). The interphase material and its thickness are keys to determine mechanical properties. However precise control is the critical issue in particular for large scale production. The interphase is the weakest link for the environmental effects. The objective of this work is to develop the novel SiC composites without the interphase by applying BN particle dispersion in SiC matrix and understand the high temperature oxidation resistance. Silicon carbide composites were fabricated by liquid phase sintering method. Silicon carbide with BN matrix was formed by mixture of SiC and BN powder in which BN volume fraction was controlled within the range of 20~70%. Mechanical properties were characterized by tensile test before and after exposure in air up to 1750C. Microstructures and fracture surfaces were characterized by FE-SEM. The BN particle dispersion SiC composites have uniform microstructure through thickness. They showed ductile fracture behavior with fiber pullouts. No significant degradation of tensile strength wasn't observed following exposure up to 1500C in air. Oxidation of the composites were limited to near surface in particular for the fiber bundle region up to 1500C.

11:40 AM

(ICACC-S1-076-2016) Application of Fe-NbC as a hardfacing material using laser cladding

E. Tavares Galvani[3]; S. Simoes[2]; C. Novaes Banov[2]; H. L. Rosa[1]; E. Cannizza*[1]; E. Burgos Cruz[1]; 1. Companhia Brasileria de Metalurgia e Mineracao, Brazil; 2. HRC Metalização, Brazil; 3. Höganäs Brazil, Brazil

The sugarcane and mining sectors experience substantial losses due to shut-downs and repair or replacement of worn out or obsolete components. Surface engineering studies have been widely developed aiming at optimizing the coating processes and, mainly, increasing the portfolio of higher wear resistant materials. HRC Metalização® (a joint venture between Höganäs and Oxipira), in partnership with CBMM, has been working on the development of niobium carbide in iron matrix (Fe-NbC) hardfacing coatings applied by laser cladding on wear components for mining. Field trials were conducted on the coated teeth of a Volvo wheel loader operating at CBMM's mine in Araxá, Brazil. The metallographic analysis of the coated teeth showed an excellent adhesion of the Fe-NbC coating layer, as well as a homogeneous dispersion of the hard niobium carbides. The loader's coated teeth achieved in severe mining operation an increase of approximately 100% in service life above best performance, and 115% above the average service life of the regular uncoated, low alloy carbon steel teeth, demonstrating the significant potential of Fe-NbC as a hardfacing coating applied by laser cladding. The wear resistance is attributed to the intermetallic phase $FeAl_3C$ formed between NbC and the $FeAl_3$ matrix, which withstood the tribological shear, as well as to the fact that the NbC did not fragment.

S3: 13th International Symposium on Solid Oxide Fuel Cells (SOFC): Materials, Science and Technology

Novel Processing and Design

Room: Tomoka C

Session Chairs: Ruey-yi Lee, Institute of Nuclear Energy Research; Mihails Kusnezoff, Fraunhofer IKTS

8:30 AM

(ICACC-S3-060-2016) Saint-Gobain's All Ceramic SOFC Stack: Advances in Design and Performance (Invited)

A. Sarikaya*[1]; A. Mohanram[1]; G. Lin[1]; Y. Takagi[1]; J. Pietras[1]; 1. Saint-Gobain Corporation, USA

Energy generation using solid oxide fuel cells (SOFCs) is a strategic project for Saint-Gobain, a global leader in ceramic materials and components. Our novel all-ceramic SOFC stacks are developed and manufactured to meet and exceed the reliability and durability targets for residential and commercial distributed power generation markets. Substantial improvement in the operational reliability and reduction in manufacturing cost were achieved with the combination of ultra-thin ceramic interconnects, simplified stack-supported design and multi-cell co-firing. Unique design features of the stack modules such as integrated current collection and gas delivery manifolds are presented along with other aspects for future performance improvements. Updates to the proven performance of Saint-Gobain's stacks, including stable operation for extended hours are reported in this paper. Saint-Gobain's stack is shown to withstand thermal cycles over long-term operation, hundreds of power cycles and realistic redox cycling. Response of the stack to fuels simulating internal and external reforming as well as high fuel utilizations is also reported.

9:00 AM

(ICACC-S3-061-2016) CFY-Stack Technology for SOEC applications (Invited)

C. Bienert*[2]; M. Brandner[2]; S. Skrabs[2]; A. Venskutonis[2]; L. S. Sigl[2]; S. Megel[1]; M. Kusnezoff[1]; V. Sauchuk[1]; N. Trofimenko[1]; A. Michaelis[1]; 1. Fraunhofer IKTS, Germany; 2. Plansee SE, Austria

The highly robust stack concept MK351 uses Cr-based CFY interconnects and 10ScCeSZ electrolytes to build an ESC-stack feasible for both, SOFC and SOEC applications. Focusing on long-term stability, the MK351 stack concept was tested for high temperature corrosion under electrical load as well as thermal cycling, both in SOFC and SOEC mode. Stack data of more than 20,000 h of a single stack in SOFC mode is presented. Stack operation in SOEC mode in a test bench for more than 3,000 h indicate similar degradation rates of less than 1%/1,000 h. Special test procedures were developed for a better understanding of degradation mechanisms. A screening of different SOE-cells on 10Sc1CeSZ electrolytes was performed using the MK351-stack design to evaluate different electrode materials. The influence of SOEC-conditions of increased moisture and oxygen concentration was tested for both, the base material CFY as well as the air-side Cr-retention coating, respectively. Enhanced stack performance, especially in regard to thermal cycling, could be achieved with the design follow-up MK352, which enables lower pressure drops through minor changes of the interconnect layout. A symmetrical design and improved tolerance chains for stack setup and system integration make the MK352-desgin even more attractive for modular assembly for systems > 1 kW.

9:30 AM

(ICACC-S3-062-2016) Ceramic Multilayers for Solid Oxide Fuel Cells (Invited)

A. Sanson*[1]; 1. CNR-ISTEC, Italy

A Solid Oxide Fuel Cell (SOFC) is a complex ceramic multilayer in which each element must be carefully designed and produced in order to assure a reliable and cost effective final generator with superior properties. In order to do so, tape casting and screen printing are commonly chosen as the most economical and reliable shaping routes. Several variables however must be taken in account in order to assure the production of a crack free, perfectly planar final device. The work presents an overview of the main issues connected to the production of large area (100x100 mm) SOFC and some unconventional strategies adopted to overcome them. A specific attention will be dedicated to the role of pore formers and additives and to more straightforward process able to shorten the production steps (i.e. reactive sintering approach).

10:20 AM

(ICACC-S3-063-2016) Tailoring the Materials Chemical Stability and Nanostructure to Improve the Performance of Protonic Ceramic Cells (Invited)

E. Traversa*[1]; 1. King Abdullah University of Science and Technology, Saudi Arabia

The high cost of solid oxide fuel cells (SOFCs), associated with their high operating temperatures, hampers their broad use and causes long-term stability problems. A step forward towards reducing the SOFC working temperature at 600°C or below can be the use of high temperature proton conductor (HTPC) oxides as electrolytes, due to their lower activation energy for proton conduction (0.3-0.6 eV), with respect to oxygen-ion conducting electrolytes. We have recently made significant progresses in the development of chemically-stable HTPC electrolytes by improving the sinterability of Y-doped barium zirconate (BZY), which offers excellent chemical stability against CO_2 and H_2O reaction and high bulk conductivity, but low conductivity values for sintered pellets due to the presence of blocking grain boundaries. Co-doping BZY with Pr allowed obtaining a chemically stable, sinterable electrolyte that showed a conductivity of 0.01 S/cm at 600°C. However, efficient cathodes need to be developed to avoid polarization losses at such a low temperatures. In this work, the recent work on improving the SOFC performance will be presented. Power output larger than 300 mW/cm2 at 600°C were obtained by nanostructuring the cathode materials using inkjet impregnation and by carefully processing the electrolyte materials.

10:50 AM

(ICACC-S3-064-2016) Fabrication and Characterization of Freeze Cast Tubular Solid Oxide Fuel Cells

J. Persky[2]; Y. Du*[1]; K. Zhao[1]; 1. Kent State University, USA; 2. Protonex Technology Corp., USA

NASA and others have shown improved power density of planar solid oxide fuel cells (SOFCs) fabricated via a freeze casting route. Freeze casting is capable to produce parts with unique microstructural feature that enhances the SOFC performance. However, due to the low cyclic durability and slow start time planar SOFCs are limited in scope. Tubular SOFCs have demonstrated many hundreds of thermal cycles and have very fast start time; although they have lower power density than freeze cast planar stacks. The adaption of a freeze casting process to the fabrication of a tubular geometry is proposed as a solution to increase the cell level and hot zone level volumetric power density of tubular SOFCs. This paper reports the fabrication and characterization of freeze casting tubular anode and the performance of freeze cast tubular SOFCs. NiO-8YSZ (yttria-stabilized zirconia) anode supported SOFCs were fabricated using five different methods. Slurry rheology was modified for dip vertical coating, and a dual purpose freezing and drying chamber was designed and manufactured. The preferred fabrication method was

a freeze and drain approach. The effects of process and slurry properties are related to the resulting microstructure. The use of gelling agents allows for tailored structures between equiaxed and lamella. Cell performance using methane fuel was also examined.

11:10 AM

(ICACC-S3-065-2016) Fabrication of thin electrolyte for solid oxide fuel cell by inexpensive ink jet printing method

C. Gadea*[1]; D. Marani[1]; Q. Hu[1]; J. Hjelm[1]; K. Agersted[1]; S. Hojgaard[1]; S. Ramousse[1]; V. Esposito[1]; 1. Technical University of Denmark, Denmark

Low thickness and high density at the electrolyte are crucial factors in SOFC to reduce ohmic resistance and increase the performances. Common fabrication methods for the electrolyte are cheap but allow reaching minimum thicknesses of 10 µm. Other advanced methods such as PLD, CVD, can reach nanometric thickness. However, these are also costly and difficult to upscale. In this study, a few micron-thick (1-3 um) dense electrolyte and multilayers components have been fabricated by inexpensive inkjet printing. The resulting cells were tested and compared to those obtained by tape casting, showing superior performances.

11:30 AM

(ICACC-S3-066-2016) Interface-matching for Barium Strontium Ferrate–Ceria by Drop-coating Buffer Layer

Y. Wang*[1]; T. C. Chen[2]; H. Y. Chang[1]; 1. National Taiwan Ocean University, Taiwan; 2. Institute of Nuclear Energy Research, Taiwan

Barium Strontium Ferrate(BSF) is an excellent cathode material for IT-SOFCs. It is difficult to co-fire ceria-based electrolyte with BSF due to the thermal expansion coefficient (TEC) mismatching for both materials. The ceria was mixed with BSF to be a composite cathode. The 70 wt% BSF, termed as 70BSF, did not form $BaCeO_3$ phase until 1200 °C sintering. The ceria could play the roles of electrocatalyst and sintering densification inhibitor in composite cathode. The BSF nitrate solution was drop–coated on sintered ceria-based electrolyte to improve the adhesion of 70BSF on it. The dispersive and discontinuous BSF layer was obtained after 6 times of drop-coating. It behaved a good buffer layer to adhere the 70BSF with ceria-based electrolyte. The AC impedance showed that the diffusion impedance reduced largely for 70BSF-ceria half-cell compared to that without BSF buffer layer. Thus, the drop-coating buffer layer of BSF solved the TEC mismatching issue. The composite cathode provided porosity and extended triple phase boundaries effectively. The half-cell performance was improved due to the interface and diffusion polarization reduction. The power density of the obtained half-cell was achieved to 110mW/cm^2 at 750°C.

S5: Next Generation Bioceramics and Biocomposites

Bioceramics V

Room: Coquina Salon F

Session Chairs: Kohei Soga, Tokyo Univ. of Science; Masamoto Tafu, National Institute of Technology, Toyama College; Fiorenzo Vetrone, INRS

8:30 AM

(ICACC-S5-036-2016) Development of calcium phosphate hybrid for catching fluoride ion (Invited)

M. Tafu*[1]; 1. National Institute of Technology, Toyama College, Japan

Calcium phosphate have been widely used for bioceramics such as artificial bone and bio devices. We have attempted to apply various achievements of calcium phosphate in bioceramics to another fields such as the environmental engineering. We have focused dicalcium phosphate dihydrate (DCPD) and studied reaction between DCPD and fluoride ion in an aqueous solution. DCPD reacts with fluoride ion and forms stable fluorapatite (FAp). This reaction was appeared in treatment of dental enamel with acidic fluoride solution. We have investigated reaction DCPD with a small amounts of fluoride ion. We appeared that DCPD did not react with fluoride ion directly but form nano-scaled precursor particle on DCPD particle in first stage, and transform to FAp in short time after induction of the nano-scaled precursor. Induction of the nano-scaled precursor on DCPD particle was obtained easily by mix DCPD with water. By reaction with fluoride ion, the nano-scaled precursor transformed to FAp and formed FAp growth using calcium and phosphate ions in DCPD. We have investigated hybridization of the DCPD with another calcium phosphate such as HA.The DCPD hybrid shown good property for catching fluoride ion, and some achievements have carried out with various companies and distributed into market. In this presentation, I summarized recently achievements concerning development and applications of DCPD hybrid.

8:50 AM

(ICACC-S5-034-2016) Near-Infrared Nanothermometers: Using Light to Detect Temperature (Invited)

F. Vetrone*[1]; 1. INRS, Canada

Rare Earth (RE)-doped nanoparticles have recently emerged as versatile luminescent probes for a number of biological applications resulting from their interesting photophysical properties. These nanoparticles can be excited with near-infrared (NIR) light, which is a strict requirement for biomedical applications due its light penetration capabilities. Furthermore, rare earth doped nanoparticles possess a multitude of 4*f* electronic energy states and excitation with NIR light can therefore lead to different excitation mechanisms. For example, following NIR excitation, the nanoparticles can undergo upconversion where multiple emissions are observed with energies higher than the excitation wavelength. Also, they can undergo conventional luminescence where emission at lower energies than the excitation wavelength can be observed. Here, we show that it is possible to harness these various emissions (upconverted and luminescence) to design optical nanothermometers capable of detecting temperature in living organisms.

9:20 AM

(ICACC-S5-035-2016) In vivo performance of additive manufactured bioceramics based on TCP

M. Schwentenwein*[1]; F. E. Weber[2]; J. Homa[1]; 1. Lithoz GmbH, Austria; 2. University Hospital and University of Zurich, Switzerland

As a very capable and straight-forward approach, additive manufacturing (AM) technologies based on photopolymerization have gained increasing interest for the application in tissue engineering. Due to the similarity to native bone tissue, compounds based on bioresorbable ceramic materials such as tricalcium phosphate (TCP) would be ideal candidates for temporary bone substitute materials. In this respect the recently introduced Lithography-based Ceramic Manufacturing (LCM) process offers a new approach for the AM of such scaffolds. This work presents the results regarding the shaping of TCP by means of LCM. The layer-by-layer principle of this method enables the fabrication of highly intricate structures with virtually no limitations regarding geometrical complexity. Scaffolds, cellular structures or parts with defined macroporosity can be shaped using LCM to provide environments for cells to adhere, migrate and proliferate throughout the structure. In a first round of in vivo experiments printed TCP scaffolds were placed on top of the calvarial bone of rats and bone ingrowth was assessed 2 and 4 weeks after implantation. The results based on histological sections showed that after 4 weeks bone from the calvarium has extended into the scaffold. In presence of bone morphogenetic protein-2 the bone even extended throughout the implant indicating the suitability of printed scaffolds for bone substitute material.

9:40 AM

(ICACC-S5-033-2016) Ceramic Near Infrared Phosphors for Nanothemometry in the Second Biological Window

K. Soga*[1]; M. Kamimura[1]; 1. Tokyo Univ. of Science, Japan

Some of the wavelength ranges around the visible region are known as biological windows with low optical losses. An near infrared range between 800 and 1000 nm has been known as the "first biological window" for the fluorescence bioimaging by using quantum dots or optical dyes. Recently, the "second biological window," which is located between 1000 and 1700 nm, is attracting interests for more transparent fluorescence observation for biological tissues. The authors has been developed both of the fluorescent probe materials and the imaging systems in the past decade. One of the candidate fluorescent agents is rare-earth doped ceramic nanophosphors (RED-CNP). In the past few years, nanothermometry by using the upconversion fluorescence of the RED-CNP has been reported. In the present paper, we will report the nanothermometry by using the RED-CNP in the second biological window for ten times more observation depth in comparison to the upconversion one.

10:20 AM

(ICACC-S5-037-2016) Easy-to-use Torsion Test Method for Bioceramics

K. Yasuda*[2]; S. Tsutsumi[1]; 1. Kanazawa Institute of Technology, Japan; 2. Tokyo Institute of Technology, Japan

Bioceramics technology have been considered to be a promising application because quality of life becomes important more and more in our societies and can be improved by substitution and restoration of damaged natural bones into artificial bioceramics. However, there were reports that artificial bones were sometimes broken in bending or torsion in clinical courses. So, in this presentation, we propose an easy-to-use torsion test method in order to estimate durability of bioceramics in service. The dimensions of torsion specimen were 8 mm in diameter, 20 mm in gage and 10 mm square in grip part. The specimen was set in an opening torque testing machine for PET bottles, attached with cylindrical jigs for gripping. By this method, a chalk and 4 types of bioceramics were tested at room temperature in air. Except for dense bioceramics, consistent test data were obtained. This work was supported in part by METI, Japan.

10:40 AM

(ICACC-S5-038-2016) *In vitro* properties of Ag-containing calcium phosphates

O. Gokcekaya*[1]; K. Ueda[1]; T. Narushima[1]; K. Ogasawara[2]; H. Kanetaka[3]; 1. Tohoku University, Japan; 2. Department of Immunobiology, Institute of Development, Aging and Cancer, Tohoku University, Japan; 3. Liaison Center for Innovative Dentistry, Graduate School of Dentistry, Tohoku University, Japan

The success of an implantation strongly depends on avoiding infections in the presence of body fluid. The use of Ag is favored because of its antibacterial activity. In this study, Ag-containing calcium phosphate (CaP) powders and sintered compacts with different CaP phases and chemical states of Ag were evaluated for their *in vitro* dissolution behaviors, antibacterial activities, and cytotoxicities. Ag-containing CaP powders were synthesized by using a precipitation method and sintered. The *in vitro* dissolution tests for CaPs were conducted in Tris-HCl solution at pH 7.4. An *Escherichia coli* suspension was used for antibacterial tests. The cytotoxicity of the sintered compacts on V79 fibroblasts was evaluated. The amounts of Ag ions increased during the initial stage with the dissolution Ag-containing as-precipitated CaP powders and decreased during the later stage with an increase in AgCl precipitation *in vitro*. The antibacterial activity of Ag-containing as-precipitated CaP powders improved with increasing Ag content. After sintering of the as-precipitated CaP powders, β-tricalcium phosphate (β-TCP) contained Ag as a solute and hydroxyapatite (HA) contained Ag as a metallic phase. Ag-incorporated β-TCP exhibited high antibacterial activity as compared to HA with metallic Ag because of the high dissolution rate of β-TCP in Tris-HCl. No cytotoxic effect on V79 fibroblasts was detected for Ag-containing sintered compacts.

11:00 AM

(ICACC-S5-039-2016) Effects of Incorporation of Partially Crystallized 45S5 Bioglass® on Glass-ionomer Cements (GIC)

A. Zandi Karimi*[1]; R. A. Drew[1]; 1. Concordia University, Canada

Partially crystallized 45S5 Bioglass® (PCB) was studied as a potentially constructive additive agent in GICs. PCB powder containing 0-100% crystallinity was produced via controlled heat treatment. Thermal analysis was carried out using XRD and DSC. Doped GICs were made by adding 2, 5, 7, 10 and 15wt% of PCB to a commercial GIC. Compressive strength (CS) test was performed on disk-shaped samples which had been immersed in water at 37°C for 1, 3, 7, 14, 30 and 45d prior to CS test. FT-IR was accomplished on ground GIC to study the setting reactions. Microstructure, phase morphology and fracture surface, were studied using SEM and EDS. XRD results showed Combeite was obtained in 45S5 microstructure with various degrees of crystallinity. Highest CS was achieved with 2wt% PCB after 30 days immersion in water. CS improved by increasing the degree of crystallinity of PCB up to 24%, maximum CS being 182MPa (CS of control sample being 188MPa). FT-IR spectra approved the development of acid–base reaction between Ca^{2+} in PCB and COOH in PAA forming a chemical bond between PCB and matrix. PCB map analysis showed the presence of Combeite and an amorphous phosphate-rich phase on the surface. Formation of strong bonding between PCB and matrix was confirmed by SEM. Despite other bioactive additives, addition of 2wt% of PCB did not decrease CS of GIC introducing PCB as a promising additive.

S9: Porous Ceramics: Novel Developments and Applications

Mechanical Properties of Porous Ceramics I

Room: Coquina Salon G

Session Chair: Tobias Fey, Friedrich-Alexander-Universität Erlangen-Nürnberg

8:30 AM

(ICACC-S9-024-2016) Experimental Reliability on Bending Strength Test of Porous Ceramics

S. Honda*[1]; K. Yasuda[2]; H. Kita[3]; M. Takahashi[4]; Y. Takahashi[5]; S. Tanaka[6]; T. Mitsuoka[7]; H. Muto[8]; S. Yamamoto[9]; Y. Yoshizawa[10]; 1. Nagoya Institute of Technology, Japan; 2. Tokyo Institute of Technology, Japan; 3. Nagoya University, Japan; 4. Ehime University, Japan; 5. Noritake Company Limited, Japan; 6. Nagaoka University of Technology, Japan; 7. NGK Spark Plug Co., Ltd., Japan; 8. Toyohashi University of Technology, Japan; 9. Asuzac, Japan; 10. AIST, Japan

Recently, porous ceramic materials are used as SOFC, support material of ceramic separated system, etc. Development of porous material tended to focus on the functional properties, for example, reactivity of surface at pores and permeability. So the measurement and analysis method of fracture strength of porous ceramics are not so much pay attention. In this presentation, we report the bending test data obtained from the round robin tests in Japan, and discuss how to measure the strength distribution of porous ceramics. Samples are porous Al_2O_3, and NiO/8mol%YSZ electrode material. The number of specimens is 30 for both materials in each organization. The stiffness of testing machine and symmetry of applied loading was checked each testing. The average bending strength and fracture location among the organization were almost same. There is no difference between average fracture strength of three and four point bending test. Both samples showed elastic deformation and followed by brittle fracture. At the first onset, we try to apply

2-parameter Weibull distribution, bending strength data of electrode material with smaller pore size can be expressed by 2-parameter Weibull distribution, however, that of porous Al_2O_3 with lager pore size cannot be expressed. This work was supported in part by METI, Japan.

8:50 AM

(ICACC-S9-025-2016) Statistical Analysis on Strength Data of Porous Ceramics

K. Yasuda*[2]; H. Kita[4]; M. Takahashi[5]; Y. Takahashi[6]; S. Tanaka[7]; S. Honda[1]; T. Mitsuoka[8]; H. Muto[3]; S. Yamamoto[9]; Y. Yoshizawa[10]; 1. Nagoya Institute of Technology, Japan; 2. Tokyo Institute of Technology, Japan; 3. Toyohashi University of Technology, Japan; 4. Nagoya Univ., Japan; 5. Ehime Univ., Japan; 6. Noritake Company Limited, Japan; 7. Nagaoka Univ. Tech., Japan; 8. NGK Spark Plug Co., Ltd., Japan; 9. Asuzac, Japan; 10. AIST, Japan

Recently, much attention has been paid to strength reliability of porous ceramics, because porous ceramics are frequently used as key materials in the advanced systems and/or components as SOFC, high capacity batteries, filters, sensors, and bioceramics etc. To attain high reliability of the porous ceramics, their strength distributions must be well-characterized. In this presentation, we statistically analyze the bending test data obtained from the round robin tests in Japan, and discuss how to characterize the strength distribution of porous ceramics. Samples are porous Al2O3, and NiO/8mol%YSZ electrode material. The number of specimens is 30 for both materials. So, we apply 2-parameter Weibull distribution, Double exponential distribution, Normal distribution, Log normal distribution, Composite-mode Weibull distribution, and 3-parameter Weibull distribution to the data, and discuss which type of distribution function is appropriate to express the data. Strength data of NiO/8mol%YSZ electrode material can be expressed by 2-parameter Weibull distribution, however, that of porous Al2O3 composite-mode Weibull distribution or 3-parameter Weibull distribution. This work was supported in part by METI, Japan.

9:10 AM

(ICACC-S9-026-2016) Effect of Grain Necking on the Properties of Porous Alumina

S. Honda*[1]; Y. Daiko[1]; S. Hashimoto[1]; Y. Iwamoto[1]; 1. Nagoya Institute of Technology, Japan

Porous alumina has been investigated as support material for the ceramic permselective membranes. There is a fundamental trade-off between the mechanical properties and the permeation property, and the fluid permeability through the porous support decreases consistently with the decrease in the porosity or pore size. To apply porous alumina as a porous support for microporous ceramic membranes, it is important to establish a novel porous structure design concept to harmonize the simultaneous and sufficient fracture resistance and permeability of the porous alumina. In this research, a series of macroporous alumina with different pore size, porosity and grain necking were fabricated by change of sintering apparatus and conditions. The permeability of the macroporous alumina was characterized by measuring nitrogen gas permeance, while the mechanical and thermal properties were evaluated by conventional and well-established methods. The gain necking of porous alumina with higher fracture resistance properties was larger than that of the others. In order to estimate the effect of grain size and grain necking on thermal conductivity of porous alumina, the numerical analysis was performed using inverse of thermal conductivity. This research clarified quantitatively to the relation between properties of porous alumina and grain necking size.

9:30 AM

(ICACC-S9-027-2016) Mechanical Properties of Porous TiB_2 Produced by Foam Replication

C. Wittmaier*[1]; W. Fahrenholtz[1]; 1. Missouri University of Science & Technology, USA

This study examined the mechanical properties of titanium diboride (TiB_2) reticulated foams. TiB_2 powder was dispersed in organic solvents to form stable slurries. Dispersion was accomplished through ball milling and adding an organic dispersant. Reticulated foams were formed by the replication method using polyurethane sponges with an average pore diameter of ~2.5 mm (10 pores per inch). Green bodies underwent binder burnout and then pressureless sintering for densification. For comparison of properties, dense TiB_2 billets were produced by slip casting the same slurry (without binder) as was used for foam preparation. In addition, alumina foams were produced using aqueous alumina slurries and the same polyurethane preforms. Elastic moduli were measured using impulse excitation and strengths were determined using four point bending. In addition, foam strengths were also measured using crush testing. The influence of slurry processing and sintering conditions on the mechanical properties of TiB_2 foams will be discussed.

9:50 AM

(ICACC-S9-028-2016) Double Torsion Analysis of Microcracked Porous Ceramics – Integrating Digital Image Analysis (DIC), Finite Element Analysis (FEA) and Cohesive Zone Modeling To Understand Fracture

J. Zimmermann*[1]; J. Harris[1]; A. Shamkin[1]; M. Black[1]; J. Markley[1]; 1. Corning, USA

Fracture toughness values obtained by double torsion methods of ceramic have recently been reported in literature. These values were calculated based on historical methods, which require dense samples that behave linear elastically and without large deformations. Ceramic filters are porous and often have engineered microcracks that can result in bulk nonlinear elastic behavior. This work reports the results of an experiment where a research filter material was tested in the double torsion configuration. The study included measures the displacement response directly using DIC and linking the material property data to the test load by matching compliance data using FEA and determining the energy absorbed by the microcracks and macrocrack. Based on the study, it was concluded that the historical double torsion method is not suitable to characterize the material fracture behavior and that probabilitistic failure criteria are currently the most appropriate tools for predicting failure.

Mechanical Properties of Porous Ceramics II

Room: Coquina Salon G

Session Chair: James Zimmermann, Corning

10:30 AM

(ICACC-S9-029-2016) Enforcing of mechanical properties of alumina foams

B. Zierath[1]; P. Greil[1]; T. Fey*[1]; 1. Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany

Cellular materials offer a wide spectrum of applications such as catalyst support structures, lightweight materials, energy adsorption, band gap material or energy storage materials. Due to several ways of processing and a wide range of material properties e.g. thermal conductivity, mechanical strength or damping can be adjusted, measured and verified. Especially in heterogeneous structures, only global effective material properties can be easily measured and influence of microstructure on these properties is hard to determine. Common open cell ceramic foams produced by the replica technic invented by Schwarzwalder provide a high porosity > 70 % but low mechanical compressive strength of 0,5 MPa to 10 MPa depending on porosity and the hollow struts. Due to these weak mechanical

properties of Al_2O_3 replica foams, a novel way of strength enhancement by inducing intrinsic residual stresses were shown. The residual stress was induced by different thermal expansion coefficients of mullite ($5{,}5*10^{-6}$ K^{-1}) and alumina ($8{,}0*10^{-6}$ K^{-1}). The intrinsic mullite layer of 2-6 μm thickness was formed during sintering at 1700 °C. The residual stress increased the characteristic compressive strength by 100% to 217% depending on pore size and grain size of the silica particles with nearly no decrease of the porosity.

10:50 AM

(ICACC-S9-030-2016) Waste heat reduction on sintering furnaces with highly porous ceramic thermal insulators prepared by gelation freezing method

Y. Tanaka*[1]; S. Sasaki[1]; A. Matsuyama[1]; F. Ozeki[1]; T. Kato[1]; M. Fukushima[2]; Y. Yoshizawa[2]; 1. Mino ceramic Co., Ltd., Japan; 2. National Institute of Advanced Industrial Science and Technology (AIST), Japan

Recently, there has been increasing demand for improved energy efficiency of industrial furnaces such as ceramic sintering at elevated temperatures. In order to enhance the energy efficiency, it is necessary to reduce waste heat toward the outside of furnaces. Here, we have developed highly porous ceramic thermal insulators fabricated by the novel gelation freezing method; gelation of ceramic raw powder dispersed slurry, the freezing, drying under vacuum to cause the sublimation of ice crystals and then sintering. The energy efficiency of prototype furnaces using highly porous ceramic thermal insulators we developed is higher than that of commercial furnaces with conventional insulators.

11:10 AM

(ICACC-S9-031-2016) Porous Ceramic Backing Elements for High Temperature Ultrasonic Transducer

M. H. Amini[1]; T. W. Coyle*[1]; A. N. Sinclair[1]; 1. University of Toronto, Canada

Conventional ultrasonic transducers are generally composed of several components: An active element (piezoelectric disc), a backing element, and a quarter-wave matching layer. The backing element is made of an acoustically attenuating material that dampens the vibration of the piezoelement. This broadens the bandwidth of the signal and improves the timing resolution of the reflected echoes. Backing elements are typically made from epoxy resins filled with metal powder, which provide the desired acoustic properties. However the epoxy resins are not suitable for use above 3000C. As part of the design and development of an ultrasonic transducer capable of operating at temperatures up to 800 0C, porous mullite and yttria partially stabilized zirconia (PSZ) backing elements have been produced and tested. Acoustic impedance and attenuation can be regulated through control of porosity and pore size in the ceramic, using scattering from the micropores as the attenuation mechanism. An effective field model was employed to guide material selection and design of the pores size and porosity level. Poly(methylmethacrylate) spheres were used as a fugitive element to control the pore size and porosity in the sintered mullite and PSZ materials. Acoustic measurements showed that the acoustic impedance and attenuation of the porous ceramic backing elements matched well with the predicted values.

S11: Advanced Materials and Innovative Processing Ideas for the Production Root Technology

Innovative Process Technology with Enhanced Performance I

Room: Tomoka B

Session Chair: Sungwook Mhin, Korea Institute of Industrial Technology

8:20 AM

(ICACC-S11-015-2016) Processing for Forming Biofunctional Surfaces on Ceramic Nanoparticles for Biophotnics (Invited)

K. Soga*[1]; M. Kamimura[2]; 1. Tokyo Univ. of Science, Japan; 2. Tokyo University of Science, Japan

Rare-earth doped ceramics nanoparticles (RED-CNPs) has been used as phosphors for biophotonics. Namely, since the RED-CNPs can emit efficient near infrared emission, they are candidate as fluorescent agents for the biophotonics in so-called "second biological window (SBW)." Not only as fluorescent phosphor, but recently the use of them as a temperature reporter for nanothermometry in the SBW. The RED-CNPs must be kept monodispersed in a live body for the circulation and delivery. The CNPs are normally monodispersed in pure water because of their surface charge. However, once introduced into biological conditions with high iconicity as well as the existence of proteins, they are easily aggregated to form agglomerate with the size of several hundreds nm. For avoiding it, it is inevitable to introduce steric repulsion of hydrophilic and nontoxic polymer on the surface of the RED-CNPs to be used for the boiphotonics. This paper will review the various route to introduce biofunctional polymers on the surface of the RED-CNPs.

8:50 AM

(ICACC-S11-016-2016) Fabrication of the Electrochromic Smart Window via Nano Particle Deposition System (Invited)

C. Lee*[1]; H. Kim[1]; D. Choi[1]; K. Kim[1]; W. Chu[2]; S. Ahn[2]; D. Chun[3]; 1. Hanyang University ERICA campus, The Republic of Korea; 2. Seoul National University, The Republic of Korea; 3. University of Ulsan, The Republic of Korea

Electrochromism (EC) is the reversible change in optical properties, when a material is electrochemically oxidized or reduced. Moreover, Transparent Conductive Electrode (TCE) is an transparent and conductive electrode. TCE usually can be fabricated using transparent conducting oxide, metal nanowire and etc. In this research, nanoparticle deposition system (NPDS) which is one of the dry deposition method, was used to fabricate an electrochromic and transparent conductive layer. NPDS is a recently developed dry-deposition technique based on low vacuum air-spray. It is capable of depositing nano- to sub-micron-sized metal and ceramic particles at room temperature under low vacuum using compressed air. Since the deposition does not involve solvent without pre- or post-processing, the fabrication process is simple and eco-friendly. To fabricate electrochromic smart window, an ion storage layer, and a EC supporting layer were deposited on FTO glass, along with PEDOT:PSS as an electrochromic layer, was coated to form composite layer with TiO_2. Its device exhibited its transmittance change greater than 40% at 630nm wave length. Moreover, TCE which consisted of composites of AgNW and FTO, showed 77% of visible transmittance which has similar property of commercial FTO glass. Therefore, we have confirmed this new dry deposition method to be capable of fabricating electrochromic smart window and TCE.

9:20 AM

(ICACC-S11-017-2016) 3D Design of Ceramics Nanoparticle in Polymer Nano Hybrid Films

T. Nakayama*[1]; H. Cho[2]; H. Suematsu[1]; T. Suzuki[1]; 1. Nagaoka Univ of Tech, Japan; 2. Hanyang University, The Republic of Korea

Linear bundles of boron nitride (BN) nanosheets were fabricated in polysiloxane/BN nanosheets hybride film by electrophoresis under alternating DC electric fiels with no modification of BN surface. BN nanosheets were homogeneously dispersed into a pre-polymer polysiloxane mixture by sonication and by mixing with high-speed mixer. The homogeneous suspension was cast on a polyimid spacer (120 mm in thickness) and subjected to DC electric field of 2.3 kV before the mixture was cured through polymerization. The direction of electric flux was shifted according to time interval from 1h to 16h during electric field application. Scanning electron microscope, X-ray diffraction, UV-vis light transmission and digital microscope were used for analys of surface morphology and anisotropic arrangement of BN nanosheets in polymer matrix. BN nanosheets were assembled into inear bundles extending across the space between two ITO coated electrodes and some of them formed brides connecting the electrodes. We could confirm that each BN nanosheet composing the linear bundles show the high anisotropic alignment which is aligned parallel to electric flux and perpendicular to the electrode surface. The mechanism of relocation and anisotropic alignment of BN nanosheets will be explained by electrostatic energy, coulomb attraction and dipole moment.

9:40 AM

(ICACC-S11-018-2016) Nano particulate SiO_2 based inorganic binder for low-temperature processing of functional layers

T. Hwang*[1]; 1. Korea Institute of Industrial Technology, The Republic of Korea

In many of the flexible device fabrication, low-temperature or non-thermal processing is employed for the inorganic layer (such as photoanode of DSSCs) preparation, since the flexible plastic substrates can hardly endure the high-temperature treatment. However, the low-temperature consolidation of the inorganic layer would easily sacrifice the overall performance of flexible device, mainly due to the poor structural integration. Therefore, one of the general targets in the flexible device fabrication where the inorganic layers are frequently used would be to find high performance low-temperature binder materials and the corresponding processing condition. When it comes to the inorganic binder for ceramic particles, SiO_2 nanoparticles (SNP) have been frequently employed to produce films or bulks of various ceramics due to its superior binding performance. The high surface activity of SNP is the main driving force for the superior binding for the constituent particles even at low temperatures. In this paper, some noticeable examples of low-temperature processed inorganic functional films employing SNP based inorganic binder will be presented and discussed.

Innovative Process Technologies with Enhanced Performances II

Room: Tomoka B

Session Chair: Kyoung Il Moon, KITECH

10:20 AM

(ICACC-S11-019-2016) Chemical solution deposition of oxides for energy applications (Invited)

M. K. Van Bael*[1]; A. Hardy[1]; 1. Hasselt University & imec, Belgium

Immense research efforts are devoted to renewable energy generation and storage devices. Key is the search for device structures and materials that generate improved performance and efficiency. At least as important is that materials consist of abundantly available elements and their synthesis and device assembly should be ecologically and economically justifiable. We investigate, preferably aqueous, solution based routes for the synthesis and deposition of materials for energy generation and storage. Although these routes have important advantages over e.g. vacuum based routes, some crucial challenges jeopardize their success in energy applications. We present how we cope with these challenges in two of our recent research topics: Challenges in solution deposition of electrode and solid electrolyte materials for thin film Lithium Ion Batteries are being discussed, whereby we demonstrate how spraycoating brings us a step closer to solution-based coating of 3D structured substrates. Secondly, through in depth characterisation we correlate synthesis conditions to the functional properties of Indium-free TCO's (transparent conductive oxides), and come to functional printed TCO layers competitive with sputtered coatings.

10:50 AM

(ICACC-S11-020-2016) Surface Roughness Reduction and Porosity Elimination of Alumina by Ultrasonic Nanocrystallline Surface Modification Technique

A. Amanov*[1]; Y. Pyun[1]; 1. Sun Moon University, The Republic of Korea

This study reports the improvement in microstructural and tribological characteristics of sintered alumina (Al_2O_3) ceramic subjected to ultrasonic nanocrystalline surface modification (UNSM) technique. The surface microstructure of the untreated and UNSM-treated specimens was examined by SEM and XRD techniques. The tribological properties of the specimens were assessed using a ball-on-disk tribometer against a bearing steel (SAE52100) ball. It was confirmed by SEM that the UNSM-treated specimen had much denser microstructure than that of the untreated specimen. The surface roughness of the UNSM-treated specimen obtained by AFM was found to be smoother compared to that of the untreated specimen, which may be attributed to the decrease in porosity. The tribological test results showed that the UNSM-treated specimens exhibited better tribological properties compared to those of the untreated specimens. It was also found that the UNSM technique was able to modify the surface in the topmost surface layer. The results of this study are expected to make sintered Al_2O_3 ceramic more attractive for numerous applications in various industries.

11:10 AM

(ICACC-S11-021-2016) The Change in Stress Filed in Ceramic Powder Compact during Cold Isostatic Pressing

K. Yasuda*[3]; S. Tanaka[2]; M. Naito[1]; 1. JWRI, Osaka University, Japan; 2. Nagaoka University of Technology, Japan; 3. Tokyo Institute of Technology, Japan

It is well known that cold isostatic pressing (CIP) is very effective to obtain dense and homogeneous powder compacts and is widely used to ceramics production for high-performance applications. During CIP, the stress field in the compact is the fundamental information to optimize CIP operation, however, it is difficult to estimate such the stress filed because the density and related Young's modulus are instantaneously changed depending on local packing process. Theoretically, uniform biaxial stress filed is generated when Young's modulus is constant throughout the compact; however, the real stress filed is not always uniform even if we apply a fixed CIP pressure. In this presentation, Young's modulus is given as a function of radial coordinate of a spherical compact, and elastic stress analysis is carried out for various CIP pressures in quasi-static and dynamic conditions. Actually, an ordinary differential equation for the radial displacement is solved numerically, and the change in the stress filed in the spherical compact is discussed as the CIP pressure is increased. This research was partly supported by Grant-in-Aid for Scientific Researches (C) (25420706) and (B)(15H04129) from Japan Society for the Promotion of Science.

11:30 AM

(ICACC-S11-022-2016) The Effect of Thickness on Flexible, Electrical and Optical properties of Ti- ZnO films on Flexible Glass by Atomic Layer Deposition

W. Lee*[1]; G. Park[1]; J. Anh[2]; S. Kwon[1]; 1. Pusan National University, The Republic of Korea; 2. Korea Maritime and Ocean University, The Republic of Korea

TCO (Transparent Conducting Oxide) on flat glass is used in thin-film photovoltaic cell, flat-panel display. Nowadays, Corning® Willow Glass®, known as flexible substrate, has attracted much attention due to its many advantages such as reliable roll-to-roll glass processing, high-quality flexible electronic devices, high temperature process. Also, it can be an alternative to flexible polymer substrates which have their poor stability and degradation of electrical and optical qualities. For application on willow glass, the flexibility, electrical, optical properties can be greatly influenced by the TCO thin film thickness due to the inherent characterization of thin film in nanoscale. It can be expected that while thick TCO layer causes poor transparency, its sheet resistance become low. Also, rarely reports were focusing on the influence of flexible properties by varying TCO thickness on flexible glass. Therefore, it is very important to optimize TCO thickness on flexible Willow glass. In this study, Ti-ZnO thin films, with different thickness varied from 0 nm to 50 nm, were deposited on the flexible willow glass by atomic layer deposition (ALD). The flexible, electrical and optical properties were investigated, respectively. Also, these properties of Ti-doped ZnO thin films were compared with un-doped ZnO thin film.

11:50 AM

(ICACC-S11-023-2016) Properties of the metallic glass thin films synthesized with multi-component alloyed single target for bipolar plate in PEM fuel cell

K. Moon*[1]; H. Lee[1]; S. Shin[1]; 1. KITECH, The Republic of Korea

Materials for bipolar plate have been changed from graphite to metal to get the appropriate properties. Metallic materials for bipolar plates of proton exchange membrane (PEM) fuel cell have advantages over graphite-based ones because of their higher mechanical strength and better electrical conductivity. However, their low corrosion resistivity in the fuel cell atmosphere could decrease the power output of the fuel cell. Many studies have been reported to enhance their corrosion resistance by using corrosion protected thin film process. Metallic glass thin films are one of the promising materials for the bipolar plate with respect to the corrosion properties because they are well known to provide complete corrosion protection because there is no corrosion channel such as permeable defect. The purpose of this study is to investigate the corrosion and electrical properties of the Zr-based metallic glass thin films synthesized on 316L stainless steel by using DC magnetron sputtering process. The metallic glass thin films were characterized by using SEM, EPMA, TEM, XRD and GDOES methods. The corrosion properties were investigated by using potentiodynamic test at 80;C in 1M H2SO4 + 2ppm F- solution bubbled thoroughly with either hydrogen gas (for simulating a PEMFC anodic environment) or pressured air (for simulating a PEMFC cathodic environment).

FS5: Field Assisted Sintering and Related Phenomena at High Temperatures

Sintering II

Room: Ponce DeLeon
Session Chair: Rishi Raj, University of Colorado

8:30 AM

(ICACC-FS5-007-2016) Developments in Flash Spark Plasma Sintering and Contactless Flash Sintering

B. Milsom*[1]; S. Grasso[1]; T. Saunders[1]; M. Reece[1]; 1. Queen Mary University of London, United Kingdom

Spark Plasma Sintering (SPS) gives several advantages over more traditional techniques such as hot pressing, namely reduced processing time, energy savings and the ability to prepare novel composites. We have developed an evolution of this technique, Flash Spark Plasma Sintering (FSPS) that allows densification of ZrB_2 to 95% in a discharge time as short as 35 seconds. This process can be applied to a wide range of electrically conductive materials. When combined with a preheating process it can also be used to consolidate semiconducting materials. We have demonstrated that through this process a 20mm SiC carbide disc can be sintered from an initial density of 53% to 96% with a discharge time as short as 17 seconds. We have also successfully scaled up this process to prepare 60mm disks of both α and β SiC with a final density of >90%. The second technique we have developed is Contactless Flash Sintering (CFS) which applies a heating rate of 10^5 °C/min to a B_4C:SiC composite sample.

8:50 AM

(ICACC-FS5-008-2016) High temperature phase transformation of alumina under applied magnetic field and its influences on sintering

V. L. Blair*[1]; N. Ku[1]; R. E. Brennan[1]; O. Rios[2]; G. M. Ludtka[2]; 1. US Army Research Laboratory, USA; 2. Oak Ridge National Lab, USA

Alumina is an excellent candidate as an optical material for laser gain media due to its high thermal conductivity. We are tackling two challenges to achieve transparency: 1) alumina is anisotropic, and 2) a rare earth cation dopant is necessary to lase. To combat the dopant issue, we synthesized nanosized alumina via co-precipitation to trap RE ions in the alumina lattice before calcination. To combat the anisotropy, we magnetically aligned the particles such that the change in index of refraction is minimized from grain to grain thus reducing light scattering. Finally, to assist in transparency, we used dual phase, transitional alumina structures to keep the grain size small. It is challenging to obtain the correct ratio of phases, and so this study will explain how high magnetic field influences the transformation temperatures of the transitional alumina. We will present DSC data on precursor alumina under an applied high magnetic field, which shows clear changes in phase transformation temperature under high field application.

9:10 AM

(ICACC-FS5-009-2016) The Influence of Pulsed vs. Non-Pulsed DC in Direct Current/Spark Plasma Sintering

L. S. Walker*[1]; 1. Thermal Technology, USA

The nature of the electric field during Direct Current Sintering (DCS) also known as Spark Plasma Sintering (SPS) and Field Assisted Sintering (FAS) has stirred much debate in the years since the technologies introduction. Initial theories proposed the pulsing of the DC induced sparks and plasma between particles to enhance diffusion and densification while systematic studies have failed to find direct evidence of either. Even with no direct evidence researchers continue to claim indirect evidence of current induced phenomena by relating sintering behavior changes and post processing microstructural features to a specific mechanism. In this

study we will investigate the influence of the current/voltage waveform to determine if it has any impact on densification using several material systems and techniques to isolate the electrical effects. The influence of pulse on:off times and their respective durations will be investigated for their role, if any, during sintering. A combination of in-situ run data, physical sample measurements and microstructure will be presented to determine if pulsing the electrical field has any impact on the material being processed.

9:30 AM

(ICACC-FS5-010-2016) Enhancements on FAST Sintering Systems Promote Transfer from the Lab to Industrial Applications

J. Hennicke*[1]; T. Kessel[1]; J. Raethel[2]; 1. FCT Systeme GmbH, Germany; 2. Fraunhofer IKTS, Germany

In the last decade many laboratories dealing with the development of powder metallic materials as well as engineering and functional ceramics worked on field assisted rapid sintering methods, in particular FAST/SPS. This resulted in a huge number of scientific papers, describing a wide range of innovative materials and production concepts. But now it becomes more and more important to exploit these achievements by applying it for the industrial manufacturing of real parts. In many cases this requires new and extended performance features of the FAST/SPS technology as well as an application-oriented tailoring of the respective sintering systems in opposite to the classical all-purpose lab systems. The presentation will show a short overview of this evolution as well as examples of current applications in the field of material development and industrial production. It will also be demonstrated, how new extensions, e.g. hybrid technology or flash sintering, can lead to essential progress in the development of innovative materials and thereby enable a wide spectrum of new industrial applications. An outlook of future hardware developments will complete the overview.

9:50 AM

(ICACC-FS5-011-2016) Fabrication of transparent polycrystalline ceramics by high pressure spark plasma sintering (HPSPS)

M. Sokol*[1]; S. Kalabukhov[1]; N. Frage[1]; 1. Ben-Gurion University of the Negev, Israel

HPSPS (up to 450MPa) technique was applied for fabricating polycrystalline magnesium aluminate spinel (MAS) and neodymium doped yttrium aluminum garnet (Nd:YAG) at relatively low temperatures with short sintering time. The experimental results on densification of MAS and YAG indicate a strong effect of the applied pressure on the microstructure and allows fabrication of nanostructured ceramics. Densification by SPS under high uniaxial pressure has raised some fundamental questions related to the microstructure evolution, densification and grain growth kinetics. The present work focuses on the understanding of sintering behavior during HPSPS process, mainly on the stress induced grain growth mechanism. The MAS specimens fabricated by this technique display a good combination of optical and mechanical properties, comparable with the best results reported in literature for conventional fabrication processes. Effective laser oscillation of the HPSPS-processed Nd:YAG sample, comparable to that of the specimen fabricated by conventional sintering, was successfully achieved for the first time using a low cost and time-saving approach.

10:30 AM

(ICACC-FS5-012-2016) Microstructure and mechanical properties of graphene/SiC-TiB_2 composites

O. Kaya*[1]; F. Sahin[1]; O. Yucel[1]; G. Goller[1]; I. Akin[1]; 1. Istanbul Technical University, Turkey

Titanium diboride (TiB_2) is a candidate material in many applications such as cutting tools, armour materials, advanced ultra-high temperature devices, and cathode materials. TiB_2 has a good combination of properties, such as low theoretical density (~4.52 g/cm^3), high melting point (~3250°C), high hardness (~25.5 GPa) and high thermal conductivity (~25 W/mK). However, difficulties in densification, low fracture toughness and poor oxidation resistance of TiB_2 limit the use of these materials. A number of studies have shown that addition of SiC improves the oxidation resistance by forming a protective SiO_2-rich layer. Moreover, recent studies have demonstrated that graphene nanoplatelets (GPL) addition can significantly enhance the mechanical properties of ceramic matrices. In this study, graphene nanoplatelets were incorporated into (20-x) SiC-80TiB_2 (vol.%) composite powder with x = 0, 0.5, 3, 5, 7 and 10 vol.% contents. The resulting powder mixtures were sintered by spark plasma sintering (SPS) at 1700°C under 40 MPa with a 5 min holding time. The prepared composites were then characterized in terms of their densification, microstructure, oxidation behavior and mechanical properties. Improvement in oxidation resistance as a result of formation of protective layers and fracture mode change with the incorporation of SiC and graphene nanoplatelets will be discussed in this presentation.

10:50 AM

(ICACC-FS5-013-2016) Flash sintering of TCP bioceramics: effect of particle size and influence on β→α transition

M. Frasnelli*[1]; V. M. Sglavo[1]; 1. University of Trento, Italy

In this work, sintering behavior of tricalcium phosphate ceramics under the effect of an external electrical field (in Flash sintering configuration) was analyzed to obtain dense bio-resorbable components. The aim was to understand whether the application of the external E-field, which allows to reduce drastically sintering time and temperature, limits also the undesired β→α-TCP phase transition. TCP powders were synthesized by solid state reaction and by wet synthesis though precipitation from aqueous solutions, this allowing to obtain amorphous calcium phosphate nano-particles, which were crystallized into nano β-TCP by thermal treatment. Then, cold-pressed green pellets were prepared and their sintering behavior was studied by dilatometry under different E-field at constant rate heating. The presence of α-TCP and the microstructure were investigated by XRD and SEM techniques. It is shown that a Flash phenomenon takes place for both TCP powders morphology below 1000°C it being more evident at higher E-fields and when smaller particles were used. Moreover, although β→α transition occurs at ~1150°C for pure TCP, the detection of both polymorphs indicates a local higher temperature, which could be correlated to Joule effect induced by the current flow along the material.

11:10 AM

(ICACC-FS5-014-2016) Impedance Spectroscopy of Flash Sintered 3YSZ with Different Electrical Field

J. Liu*[1]; D. Liu[2]; Y. Wang[2]; L. An[3]; 1. Southwest Jiaotong University, China; 2. Science and Technology on Thermostructural Composite Materials Laboratory, Northwestern Polytechnical University, China; 3. University of Central Florida, USA

The electrical properties of ytrria doped zirconia, which were sintered via flash sintering with different applied field, were invesitaged by impedance spectroscopy. There are no obvious changes of the bulk and grain boundary in the sintered 3YSZ with different applied field, including conductivity, permittivity and relaxation frequency, hence the concentration of oxygen vacancies was independent on the applied field during sintering. However, the results indicated the grain boundary thicknesses were varied as the applied field. It suggested the space-charge layer on the grain boundary was related to the applied field during flash sintering. The higher applied filed result in wide space-charge layer, then a thicker grain boundary was gained in the sintered 3YSZ.

11:30 AM

(ICACC-FS5-015-2016) Electrical measurements in electric field-assisted ionic and protonic conductors

R. Muccillo*[1]; E. N. Muccillo[1]; 1. Energy and Nuclear Research Institute, Brazil

Impedance spectroscopy measurements were carried out in yttria-stabilized zirconia (tetragonal - 3 mol% and cubic - 8 mol% yttria) oxide ion conductors and in yttrium- (and gadolinium-) doped barium cerate proton conductors. The measurements were performed under three experimental conditions: conventionally sintered samples, green compacts submitted to electric field-assisted sintering, sintered compacts submitted to electric field-assisted sintering. Electric field -assisted sintering consisted in applying an ac electric field (10-200 V cm^{-1} at a temperature T_s (800-1200ºC) for a time t_s (2 s to 5 min), limiting the current pulse amplitude to I_s (0.1-10 A). Conventional sintering consisted in heating the sample up to T_s for a dwelling time t_s. The impedance spectroscopy diagrams show that the blocking of charge carriers at the grain boundaries is strongly reduced in green compacts submitted to electric field-assisted sintering. This result suggests that Joule heating due to electric current flow through the sample, provoked by application of the electric field, might be wiping out the space charge region, decreasing substantially the mismatch at the grain boundaries. Charge and mass transport would increase, promoting sintering without noticeable grain growth.

11:50 AM

(ICACC-FS5-016-2016) Beyond Flash Sintering

R. Raj*[1]; J. Lebrun[1]; S. Jha[1]; 1. University of Colorado, USA

We show two new effects that are related to experiments on flash sintering: (i) the emission of a "green glow", and (ii) changes in structure including phase transformations in polycrystalline materials that turn on and off with the applied field. The latter measurements were made during live experiments at the Advanced Photon Source at the Argonne National Laboratory. The electroluminescence is ascribed to the generation and recombination of electron-hole pairs.

FS6: Hybrid Materials and Processing Technologies

Hybrid Materials and Processing Technologies III

Room: Coquina Salon H

Session Chair: Qimin Wang, Guangdong University of Technology

8:30 AM

(ICACC-FS6-017-2016) Developing Multi-component and Multi-layer Nanocomposite Coatings for High-speed Milling Tools (Invited)

Q. Wang*[1]; 1. Guangdong University of Technology, China

To increase the lifetime and performance of high speed cutting tools, there are increasing demands for coatings. Coatings for cutting applications require combinations of properties such as a relatively high hardness, good adhesion, wear and oxidation resistance. To fulfill these requirements, new coating materials are needed to be developed. Due to the excellent mechanical and physical properties, coatings with nanocomposite microstructure are attracting much attention for application on structural applications. Various ternary, quaternary and quinary nano-structured coatings were fabricated for obtaining not only superhardness, but also improved oxidation resistance, thermal stability, wear resistance, etc. To obtain the better performance as hard coatings on cutting tools, the multi-component and multi-layer nanocomposite coatings were investigated. In this presentation, some multi-component and multi-layer coatings, were fabricated to improve the cutting performance of high-speed milling tools. The related coating microstructure, mechanical properties, and cutting performances will be presented.

9:00 AM

(ICACC-FS6-018-2016) Synthesis of $Ni(OH)_2$ @ ZnO for High Performance Supercapacitor Electrode Materials by Combining Hydrothermal Method and ALD Process

Z. Wan*[1]; Y. Byun[1]; S. Kwon[1]; 1. Pusan National University, The Republic of Korea

$Ni(OH)_2$ is a good promising cathode material for supercapacitors due to its excellent theoretical capacitance. However, its wide applications are limited by the poor conductivity. Inspired by the recent researches, ZnO can be a good candidate to improve the electrochemical activity and electron conducting pathway of the $Ni(OH)_2$ material. Herein, nanoporous $Ni(OH)_2$@ZnO core-shell architectures were synthesized on the surface of Ni foam via hydrothermal reaction and ALD. The results showed that both $Ni(OH)_2$ and ZnO were HCP crystal structures with good crystallinity, and the ZnO thin film was uniformly covered on the surface of $Ni(OH)_2$ nanostructure. The specific capacitance was indeed improved after 5 nm and 10 nm ZnO deposition, however, the capacitance started to decrease with the thickness further increasing, which could be contributed to that the increased ZnO material didn't act as the active materials to provide the capacitance because of low theoretial capacitance of ZnO. Based on the analysis, the resistance of the electrode materials was effectively decreased with increasing ZnO thickness. Moreover, a good rate capability at high current densities and an excellent long-term cycling stability was also examined. Therefore, this kind of 3D $Ni(OH)_2$@ZnO mesoporous hybrid materials can be a promising system for supercapacitor application.

9:20 AM

(ICACC-FS6-019-2016) Atomic Layer Deposition and Role of Precursor Chemistry

S. Wang*[1]; T. Singh[1]; S. Hoffmann-Eifert[2]; N. Aslam[2]; S. Mathur[1]; 1. University of Cologne, Germany; 2. Forschungszentrum Juelich, Germany

Atomic layer deposition (ALD) offers nearly pin hole free, conformality and good thickness control metal oxide nanometric thin films required for next-generation memory devices. Here we report ALD of VO_x thin films grown at about 100 °C from vanadium tri-isopropoxide (VTIP) precursor and water as the co-reactant followed by their post-growth treatments for potential applications in resistive switching (RS) devices. As grown VO_x films were amorphousand transformed into polycrystalline layers upon annealing. Capacitor structures fabricated from amorphous VO_x films showed *I-V* characteristics interesting for the resistive switching applications. Depending on the electroforming conditions, bipolar-type memory switching with a resistance ratio $R_{OFF}/R_{ON} > 10^3$ was obtained, and also a combination of memory and threshold switching. The later is attractive for its highly non-linear *I-V* characteristic and it is attributed to the temperature-induced insulator to metal transition (IMT) in vanadium dioxide.

9:40 AM

(ICACC-FS6-020-2016) Nitrogen-Incorporated Hydrogenated Amorphous Carbon Film Electrodes on Ti Substrates by Hybrid Deposition Technique and Annealing

T. Zhang*[1]; K. Kim[2]; K. Kim[1]; 1. Pusan National University, The Republic of Korea; 2. Korea Atomic Energy Research Institute, The Republic of Korea

A new method was adopted to fabricate the nitrogen-incorporated hydrogenated diamond-like carbon (DLC) film electrodes with TiN/TiCN/DLC multilayers on Ti substrates by a hybrid deposition technique and post annealing. The TiN and TiCN sublayers acted as adhesive layers and a nitrogen donor source for the DLC layer. Solid diffusion of nitrogen from these sublayers to the DLC layer occurred during annealing to form the N-incorporated DLC films. The electrical resistivity of the DLC films was significantly reduced by annealing process due to the graphitization and incorporation of N. The potential window of the DLC/Ti electrodes slightly decreased after annealing, while the electrochemical activity and catalytic

ability of the electrodes for the redox of $Fe(CN)_6^{3-/4-}$ were significantly improved, which was attributed to the decreased resistivity and the active C-N function group on the electrode surface. The optimized annealing temperature was 800 °C and the DLC/$Ti_{800°C}$ electrode exhibited comparable electrochemical characteristics with the boron-doped diamond electrode and superior properties than the Pt/Ti and glassy carbon electrodes. The correlations between the microstructure evolution and the electrochemical properties of the DLC films at various annealing temperatures were also systematically investigated.

10:20 AM

(ICACC-FS6-021-2016) p- and n-Doping Graphene Tuned by Simple Polymer Coating for Electronic Device Application

J. Yun*[1]; W. Park[1]; K. Kim[1]; 1. Global Frontier for Hybrid Interface Materials, The Republic of Korea

Due to inherent limitation of simple dimensional downscaling in silicon electronics, graphene is emerging as an alternative or complementary electronic material. In recent years, there has been noticeable progress toward the realization of integrated circuits based on graphene, including integrated ring oscillators and nonvolatile switching devices. A controllable p- and n-doping method to the graphene sheet without any defect is useful for the ultimate realization of graphene-based electronics. To date, considerable research efforts have been devoted to p- and n-doping of graphene as a fundamental requirement for graphene-based electronics. Unfortunately, previous efforts suffer from undesired defect formation, poor controllability of doping level, and subtle environmental sensitivity. Here we present that graphene can be tuned as p- and n-doping by simple polymer coating with different dipolar characteristics. Significantly, spontaneous vertical ordering of dipolar pyridine side groups of poly(4-vinylpyridine) at graphene surface can stabilize n-type doping effect at room temperature ambient condition. The dipole field also enhances and balances the charge mobility by screening the impurity charge effect from the bottom substrate. We successfully demonstrate ambient stable inverters by integrating p- and n-type graphene transistors, using different dipolar polymers.

10:40 AM

(ICACC-FS6-022-2016) Self-assembled hybrid nanostructures with multi-functionality for nonvolatile memory device applications

W. Park*[2]; J. Shin[1]; J. Yun[1]; K. Kim[1]; 1. Global Frontier for Hybrid Interface Interface, The Republic of Korea; 2. Global Frontier for Hybrid Interface Materials, The Republic of Korea

The self-assembly of block copolymers (BCPs) has attracted much attention due to its excellent ability to overcome the challenges of conventional nanofabrication technologies. The BCP which consists of two or more incompatible blocks can generate periodic patterns with sub-20 nm such as dot, line, hole and ring patterns. However, the self-assembled BCP nanostructures are non-functional in general; therefore, they are used mainly as etch-masks or lift-off templates to produce functional nanostructures. In this study, we introduce the functional/performance-enhancing SiO_x nanostructures which can be applicable to nonvolatile memory devices by employing the self-assembly of Si-containing BCPs. The directly formed SiO_x film and nanodot memristors clearly showed unipolar resistive switching behaviors through the precise surface modification of bottom electrodes. Moreover, for phase change memory device, the thin nanostructured SiO_x layer which locally blocks the contact between a phase change material ($Ge_2Sb_2Te_5$) and a heater electrode (TiN), showing reduction of writing current by 5 folds. This novel and useful approach may be extendable to other device applications such as flash memory and magnetic storage devices without using high-cost photolithography or pattern transfer processes.

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