The American Ceramic Society

39th 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 26, 2015

Plenary Session

Plenary Session

Room: Coquina Salon D
Session Chairs: Michael Halbig, NASA Glenn Research Center; Soshu Kirihara, Osaka University

9:00 AM

(ICACC-PL-001-2015) Materials Selection for the Next Generation Thermal Barrier Coatings

D. R. Clarke*[1]; 1. Harvard University, USA

One of the major successes of engineered ceramics has been the development of the thermal protection system for high-temperature gas turbines. For the last twenty-five years, the ceramic material of choice as a thermal barrier coating has, and continues to be, yttria-stabilized zirconia containing 8 weight percent yttria (8YSZ). As the development of more efficient gas turbines proceeds there is a need for an oxide coating that can sustain higher operating temperatures than 8YSZ. However, no existing oxide has the required combination of low thermal conductivity, adequate fracture toughness, low optical absorption in the infra-red and high temperature stability as well as compatibility with alumina that forms on superalloys at high temperatures. In this presentation, I will discuss the design requirements for the next generation gas turbines as well as a number of approaches being taken to identify suitable oxide systems. As part of the presentation, I will also describe our recent work on the basis for selecting oxides with exceptionally low thermal conductivity at high temperatures as well as studies of the YTaO4-ZrO2 system which we believe has particular promise for future coatings.

9:40 AM

(ICACC-PL-002-2015) Chemically Processed Nanostructured Ceramics: Opportunities for Energy and Health Applications

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

Chemical nanotechnologies play a key role in converging physical and life sciences and engineering ceramics. Chemical processing enables facile and efficient synthesis and assembly of nanocrystals of precisely defined chemical compositions that can be engineered for energy and health applications. Metal oxide nanostructures inherit promises for substantial improvements in materials engineering mainly due to improved physical and mechanical properties resulting from the reduction of microstructural features by two to three orders of magnitude, when compared to current engineering materials. This talk will present how chemically grown nanoparticles, nanowires and nanocomposites of different metal oxides open up new vistas of material properties, which can be transformed into advanced material technologies. The examples will include application of superparamagnetic iron oxide nanoparticles for magnetic resonance imaging (MRI) and drug delivery applications, electrospinning of nanowires for application as electrode materials and vapour phase synthesis of nanolaminates for solar hydrogen production. Finally, the current challenges of integration of nanomaterials in existing device concepts will be discussed.

10:40 AM

(ICACC-PL-003-2015) Regenerative Engineering: The Theory and Practice of a Next Generation Field

C. T. Laurencin*[1]; 1. University of Connecticut Health Center, USA

The next ten years will see unprecedented strides in regenerating musculoskeletal tissues. We are moving from an era of advanced prosthetics, to what I term regenerative engineering. In doing so, we have the capability to begin to address grand challenges in musculoskeletal regeneration. Tissues such as bone, ligament, and cartilage can now be understood from the cellular level to the tissue level. We now have the capability to produce these tissues in clinically relevant forms through tissue engineering techniques. Our improved ability to optimize engineered tissues has occurred in part due to an increased appreciation for stem cell technology and nanotechnology, two relatively new tools for the tissue engineer. Critical parameters impact the design of novel scaffolds for tissue regeneration. Cellular and intact tissue behavior can be modulated by these designs. Design of systems for regeneration must take place with a holistic and comprehensive approach, understanding the contributions of cells, biological factors, scaffolds and morphogenesis.

11:20 AM

(ICACC-PL-004-2015) Next Generation Diesel Particulate Filter (DPF) Development and Implementation Strategy

K. Ohno*[1]; 1. IBIDEN, Japan

Recently emission regulation has become stringent more and more regarding both particulate matter (PM) and NOx worldwide. For diesel passenger car (PC), SCR coated DPF system is considered as one of the promising options for future emission after-treatment system by the benefit of downsizing. To integrate the SCR catalyst into DPF, it is necessary to design the DPF substrate so as to have higher porosity and larger pore size compared with the conventional DPF. However it leads to loss of robustness, so by the oxidation layer formed on the SiC particle that composes DPF, we succeeded to improve the strength of DPF substrate. For diesel heavy duty (HD), PM regulation became tighter and DPF has come to be used in EU and Japan. In diesel HD the fuel consumption is emphasized but a demand of robustness is comparatively low. So the effort to realize the low pressure loss substrate has been made with thin wall DPF for future system. In both PC and HD, the roadmap of the exhaust gas after-treatment system can be estimated from the engine characteristics and the regulations. To meet the roadmap, development goals of the substrate and the catalyst are set and the development has been promoted. We studied DPF substrates and SCR solutions that can be leading this field.

S1: Mechanical Behavior and Performance of Ceramics & Composites

Mechanics, Characterization Techniques, and Equipment

Room: Coquina Salon D
Session Chairs: Rajan Tandon, Sandia National Laboratories; George Quinn, American Dental Association Foundation

1:30 PM

(ICACC-S1-001-2015) Fracture Toughness of Advanced Structural Ceramics: Applying ASTM C1421

J. Swab*[1]; J. Tice[1]; A. Wereszczak[2]; R. Kraft[3]; 1. Weapons & Materials Research Directorate, USA; 2. Oak Ridge National Laboratory, USA; 3. Pennsylvania State University, USA

The three methods of determining the quasi-static Mode I fracture toughness (K_{Ic}) (surface crack in flexure – SC, single-edge precracked beam – PB, and chevron notched beam – VB) found in ASTM C1421 were applied to a variety of advanced ceramic materials. All three methods produced valid and comparable KIc values for the Al_2O_3, SiC, Si_3N_4 and SiAlON ceramics examined. However, not all methods could successfully be applied to B_4C, ZrO_2 and WC ceramics due to a variety of material factors. The coarse-grained microstructure of one B_4C hindered the ability to observe and measure the precracks generated in the SC and PB methods while the transformation toughening in the ZrO_2 prevented the formation of the SC and PB precracks and thus made it impossible to use either method on this ceramic. The high strength and elastic modulus of the WC made it impossible to achieve stable crack growth using the VB method because the specimen stored a tremendous amount of energy prior to fracture. Even though these methods have passed the rigors of the standardization process there are still some issues to be resolved when the methods are applied to certain classes of ceramics. It is recommended that at least two of these methods be employed to determine the K_{Ic} especially when a new or unfamiliar ceramic is being evaluated.

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(ICACC-S1-002-2015) Estimation of Stress Intensity Factors associated with Hypervelocity Impact Damage

J. Salem*[1]; 1. NASA GRC, USA

Windows in the International Space Station are subjected to on-going micrometeorite damage (MMOD). The reliability of the windows is being ensured by monitoring of damage, life prediction, and measurement of the residual strength of man-made and natural hypervelocity impact damage. Life estimates benefit from representative stress intensity factor coefficients (Y's), which are not explicitly known for impact craters. Effective stress intensity factor coefficients were estimated with various models and used to estimate the residual strength of man-made craters and MMOD craters harvested from space shuttle windows. Results indicate that craters act as blunt flaws when the overall dimensions are used to estimate the residual strength. When the dimensions associated with the crater interior are used, better comparisons results.

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(ICACC-S1-003-2015) Shear tests on joined materials: a comparison between torsion and ISO 13124

M. Ferraris*[1]; M. Salvo[1]; A. Ventrella[1]; F. Smeacetto[1]; S. Rizzo[1]; V. Casalegno[1]; S. T. Gonczy[5]; C. H. Henager[3]; T. Hinoki[4]; Y. Katoh[2]; 1. Politecnico di Torino, Italy; 2. ORNL, USA; 3. PNNL, USA; 4. IAE, Kyoto University, Japan; 5. Gateway Materials Technology, USA

Results of an experimental investigation on 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 joining at ambient temperature by compression tests on cross-bonded test pieces. Advantages and disadvantages of these tests are discussed and compared, with particular focus on the measurement of pure or apparent shear strength. Torsion test was found suitable to measure the pure shear strength of joined samples, provided that the fracture occurs in the joined area.

2:30 PM

(ICACC-S1-004-2015) Fatigue Crack Growth Characterization of Structural Ceramics using Engineered Crack Arrays

A. Bujanda[2]; J. Collins[1]; C. L. Muhlstein*[1]; 1. Georgia Tech, USA; 2. Penn State, USA

Quantifying the fatigue resistance of structural ceramics is experimentally challenging because of the narrow range of stable crack growth that is typically observed. In this work we present a general methodology where engineered defect arrays are used to establish the fatigue susceptibility of two silicon nitride materials (GS-44CL from Allied Signal and NT551 from Norton). A series of four-point flexure experiments, microscopy, and weakest link (Weibull) statistical analyses established the characteristics of the intrinsic flaw population. The characteristic flexure strengths of the GS-44CL and NT551 were 805 and 957 MPa, and their Weibull moduli were 32 and 15, respectively. Additional parameters were then determined from a series of standard hardness (~ 14 GPa for both materials) and indentation fracture toughness experiments (~12 MPa m^0.5 and ~9 MPa m^0.5 for the GS-44CL and NT551, respectively). Finally, arrays of cracks were fabricated and fatigued in four-point flexure until catastrophic failure occurred. The failed specimens were then analyzed to determine the fatigue crack growth resistance of the silicon nitride ceramics. This methodology allows for the rapid screening of fatigue susceptibility and can be used to assess the importance of small crack effects in extrinsically toughened structural ceramics.

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(ICACC-S1-005-2015) Measurement of fracture toughness of single grain boundary of c-axis oriented Si3N4 ceramics using single edge notched microcantilever beam specimens

T. Takahashi*[1]; T. Yahagi[1]; J. Tatami[2]; S. Tanaka[3]; 1. Kanagawa Academy of Science and Technology, Japan; 2. Yokohama National University, Japan; 3. Nagaoka University of Technology, Japan

Fracture toughness of single grain boundary, especially almost <001> tilt boundary, of c-axis oriented Si3N4 ceramics was measured using single edge notched microcantilever beam specimens prepared by focused ion beam technique. The c-axis oriented Si3N4 ceramics were fabricated using Y2O3-HfO2-SiO2 by molding in magnetic field. The measured fracture toughness of the grain boundary was 1.82±0.22 MPam1/2. This average value was slightly higher than the fracture toughness of grain boundary of Si3N4 ceramics prepared using Y2O3-Al2O3 as sintering aids. However, the validation is smaller than the previous study because of single grain boundary.

3:30 PM

(ICACC-S1-006-2015) Anisotropic fracture toughness quantitative analysis of elephant dentin based on digital image correlation technique

X. Lu*[1]; J. Walsh[1]; P. Withers[1]; 1. University of Manchester, United Kingdom

Although anisotropic fracture toughness has been studied as a function of dentinal tubule orientations in elephant tusk, so far, however, there has been no controlled study which compares differences of crack tip elastic strain fields in different crack growth directions : in-plane perpendicular (sample 3), out-plane perpendicular (sample 1) and in-plane parallel (sample 2) to the tubule orientation. The objectives of this paper are to address the following questions: (1) compare the experimental extracted stress intensity factor K_{eff} with the nominal K_n as a function of applied load to validate the crack closure effect in three types of samples with different crack growth direction; (2) compare the critical strain fields around the crack tip of three types of samples to evaluate the anisotropic fracture properties. Digital Image Correlation (DIC) technique was used to measure the crack tip displacement fields, from which the crack tip strain field can be obtained. Sample 3 exhibited mixed-mode K (KI+KII) and the critical effective K (K_{eff}) was equal to 1.93 MPa√m, but for sample 2 and sample 1, mode-I loading condition was dominant and the K_{IC} was equal to 1.01 MPa√m and 0.88 MPa√m respectively. Obvious crack closure effect was observed in sample 2 only.

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(ICACC-S1-007-2015) On the Applicability of ASTM Standard C 1421 for Fracture Toughness, KIc, to Glasses and Dental Restorative Materials

G. D. Quinn*[1]; 1. 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 used as dental restorative materials. Many researchers in the dental community are finally moving away from crude Vickers indentation crack length procedures. However, many are gravitating to simple single edged V-notched beam (SEVNB) procedures and the quality of the results is variable. The rigorous test methods in ASTM C 1421 ought to be adaptable to ceramic and composite dental restorative materials, but researchers are unfamiliar with the methods, or worried about how difficult they may be compared to simple notched beam methods. This presentation will show new surface crack in flexure (SCF) and single-edged precracked beam (SEPB) (bridge precracked) data for dental glass ceramic and ceramic-resin composite materials. New SCF results for glass are also presented. The latter results raise a question that has lingered for many years: Just what is the KIc of glass? The standardized advanced ceramic test methods can be readily adapted to dental materials.

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(ICACC-S1-008-2015) The effect of machining on the mechanical properties of porous microcracked cordierite

R. C. Cooper*[1]; A. Pandey[2]; R. J. Parten[1]; E. Lara-Curzio[1]; G. Bruno[3]; A. Shyam[1]; T. R. Watkins[1]; 1. Oak Ridge National Laboratory, USA; 2. LG Fuel Cell Systems, USA; 3. Federal Institute for Materials Research and Testing (BAM), Germany

Synthetic cordierite is commonly used as a diesel particulate filter substrate material. The reliability of these filters is determined by the mechanical properties of the material i.e. Young's modulus, Poisson's ratio, and fracture toughness. Determination of these mechanical properties often necessitates machining of the as-produced filters to tight dimensional tolerances. Machining can, however, induce additional damage to the material's microstructure, owing to the fragile nature of this material. The microstructure is investigated with microcomputed tomography, x-ray refraction and scanning electron microscopy. Mechanical properties of specimens with different thickness values are determined through double-torsion testing and digital image correlation of uniaxial microtension tests. The combined results of these tests provide insights into the nature of microcrack networks in a porous medium allowing identification of proper testing techniques and machining conditions.

4:30 PM

(ICACC-S1-009-2015) Improved Adhesive Characterization and Selection Using High Throughput Testing and Materials Informatics

M. Bratcher*[1]; M. C. Golt[1]; R. Jensen[1]; W. Kosik[1]; 1. U.S. Army Research Laboratory, USA

Composite armor on Army ground vehicles requires adhesives which are selected based on multiple criteria. To some extent, much like aerospace applications, high strength adhesives are highly desirable, but at the same time, highly damage-tolerant adhesives efficiently absorb impact energy and perform well in ballistic events. Current work at the Army Research Laboratory addresses the challenge of adhesive selection through the development of a Material Selection Analysis Tool (MSAT) which is an interactive database for storing comprehensive sample attributes, raw test data and experimental procedures and test methods. Recent work includes an exhaustive study of over 1000 samples of two adhesives, an epoxy and an acrylate, using the single lap joint test with varied experimental parameters. Given the complexity of the entire data set, a materials informatics approach was required and developed to identify the adhesive properties and experimental conditions that correlate most directly to maximum strength and maximum elongation help map the high-strength/damage-tolerance performance trade-space for these adhesives.

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(ICACC-S1-010-2015) Measurement of Adhesion in Alumina/Glass-Epoxy System Using Spherical Indentation

R. Tandon*[1]; 1. Sandia National Lab, USA

Bonded systems between different material families (metals, ceramics, and polymers), and within each family are widely used, e.g., polymer coated dielectrics, encapsulated electronic packages, brazed and soldered assemblies, glass to metal seals, plated and coated electrical contacts, coatings on tribological materials, and arc-sprayed components. The performance of such systems is often limited by the adhesion between the layers. Experimental observations and measurements of interfacial properties in glass-epoxy and alumina-epoxy system are described. Spherical indenters were used to induce delaminations at the interface. The load for initial delamination was used to measure the interfacial strength, while the load-crack length relationships are used to estimate interfacial toughness. Surface modifications of the alumina and glass surfaces and their effects on interface adhesion are also described. Fracture surface observations and cross-sectional views of the delaminated regions were used to understand the physical processes occurring at the delamination site. 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-AC04-94AL8500

5:10 PM

(ICACC-S1-011-2015) Simplifying the thermal conductivity and thermal expansion characterization of advanced ceramic brake pads

J. Nickerson*[1]; M. Ouellette[1]; 1. C-Therm Technologies Ltd., Canada

Accurate measurement of the thermophysical properties of brake pad materials is critical in assessing their performance. Intense heat is created during braking; therefore thermal conductivity must be optimized for effective heat dissipation. Low thermal expansion is similarly an essential attribute in brake system design, preventing thermal shock and stresses. With new ceramic composites now available, accurate measurement of these critical performance attributes is necessary in qualifying performance. This work investigates the thermal conductivity and thermal expansion measurements of high-performance ceramic braking materials. Thermal conductivity is measured via the modified transient plane source (MTPS) technique. Thermal expansion is measured with a horizontal push rod dilatometer. The accuracy of both methods is verified in testing certified reference materials. Ranking of three advanced ceramic brake pads and a traditional semi-metallic composite are presented. Thermal conductivity is measured over a temperature range of 25 to 200°C, and thermal expansion from room temperature to 1000°C. Results highlight the appropriate means for characterizing key performance properties of break pad materials.

S3: 12th International Symposium on Solid Oxide Fuel Cells (SOFC): Materials, Science and Technology

Status and Perspectives of SOFC and SOEC

Room: Crystal

Session Chairs: Mihails Kusnezoff, Fraunhofer IKTS; Narottam Bansal, NASA Glenn Research Center

1:30 PM

(ICACC-S3-001-2015) SECA Program Status - 2015 (Invited)

B. White*[1]; 1. Dept. of Energy, USA

Development of electric power generation technology that efficiently and cost-effectively utilizes coal and natural gas while meeting environmental requirements is of crucial importance to the United States. The U.S. Department of Energy (DOE) Office of Fossil Energy (FE), through the National Energy Technology Laboratory (NETL), is leading the research and development of advanced Solid Oxide Fuel Cells (SOFC) as a key enabling technology. This work is being done in partnership with industry, academia, and national laboratories. The systems being developed, for central-station (>100 MW) application must provide for effective CO2 capture, restrict the emissions of other pollutants (eg, NOx, SOx), and conserve water. While coal continues to be a focus of the SECA program, the SOFC technology developed could provide the basis for advanced power generation systems fueled with natural gas. Thus, there could be strong synergy between efforts to develop advanced coal-fueled power generation, as in the SECA program, 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 could be first to the marketplace, which would provide early manufacturing and operational experience on large commercial scale that would benefit SOFC power system developments with both fuels. Progress and recent developments in the SECA program will be presented.

2:00 PM

(ICACC-S3-002-2015) Recent Development of Micro CHP Systems for Household (ENE-FARM) in Japan (Invited)

Y. Mizutani*[1]; 1. Toho Gas Co., Ltd., Japan

Micro CHP systems are effective solution to reduce CO2 emission from residential sector, and SOFCs are promising technology because their high generating efficiency and simple system configuration. Household fuel cell systems "ENE-FARM" have been developed by based on PEFC technology and commercialized from 2009 in Japan. They have ten years field testing experiences, and their R&D, demonstration, standardization are supported by government and energy utilities. Also, SOFC systems was commercialized from 2011 as ENE-FARM family after four years field testing program. In this presentation, state of the art SOFC technologies for CHP application in Japan will be reviewed. Ceramic manufacturers are challenging different types of cell stacks as flat-plate tubular, micro-tubular, monolithic and planar type with thin film electrolytes. All of SOFC-CHP systems have advantage of compactness and better energy saving ratio compare with PEFC systems. They performed high generating efficiency of over 45% (LHV), and perfectly controlled with load following operation against fluctuating electricity demand in actual households. Cost reduction of systems have been progressed, and newly models for complex housing, uninterruptible power, connectivity with home energy management systems, etc. are ready for commercialization. Also, future challenges and topics for fuel cell systems in Japan will be introduced.

2:30 PM

(ICACC-S3-003-2015) AVL SOFC Systems for Stationary and Mobile Applications (Invited)

J. Rechberger*[1]; M. Hauth[1]; M. Reissig[1]; 1. AVL List GmbH, Austria

AVL is developing stationary combined cooling, heat and power products based on SOFC technology in a power range from 5kW to 100kW. This technology offers significant advantages compared to (gas or diesel) engines, like higher efficiency and lower noise & emissions. Together with Plansee and IKTS, AVL has developed a 5-10kW CHP system with an electrical efficiency above 50% and an extremely low degradation rate. The presentation will show the actual development status of SOFC CHP & CCHP products in the power range from 5 to 20kW and will give an outlook towards product introduction. In 2002 AVL has started the development of a portable power generator based on SOFC technology. This product is developed for various markets including military, marine, leisure, trucks and also stationary power generation. Especially in this low power range the SOFC technology has significant advantages compared to small diesel gen-sets. In 2013 AVL has presented the 2nd generation with a power output of 3kW and above 30% efficiency. This generation has already been integrated into demonstration vehicles. The presentation will show the actual development status and the benefits of this product in various applications.

3:20 PM

(ICACC-S3-004-2015) Solid Oxide Fuel Cell Materials Development at PNNL (Invited)

J. Stevenson*[1]; Y. Chou[1]; J. Hardy[1]; O. Marina[1]; J. Choi[1]; 1. Pacific Northwest National Laboratory, USA

Pacific Northwest National Laboratory (PNNL), a U.S. Department of Energy (DOE) laboratory, is working with government agencies and industrial collaborators to accelerate the commercialization of SOFC-based power systems in the kWe to MWe power range. This presentation will highlight recent progress in SOFC materials development, with an emphasis on work being performed for the DOE Office of Fossil Energy's Solid-state Energy Conversion Alliance (SECA) program. Specific topics to be covered will include interconnect alloys, protective coatings and surface treatments, compliant glass-based seals, and electrode materials and interactions.

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(ICACC-S3-005-2015) High Efficiency Electrical Energy Storage Using Reversible Solid Oxide Cells (Invited)

S. Barnett*[1]; 1. Northwestern Univ, USA

Long-term storage of electrical energy is becoming an increasingly important problem as the utilization of intermittent renewable electricity sources increases. This talk describes a new storage chemistry for reversible solid oxide cells (ReSOCs) where the fuel cycles between H2O-CO2-rich and CH4-rich gases. Decreasing the ReSOC operating temperature from 800°C to 600°C, or increasing the operating pressure to ~ 10 atm, makes the electrolysis reaction less endothermic by increasing CH4 production. This in turn reduces the thermally neutral electrolysis potential, allowing much-improved round-trip efficiency. The attributes of SOCs needed for this application are also discussed. An example of a novel SOC with thin strontium- and magnesium-doped lanthanum gallate (LSGM) electrolytes is presented. These cells have area specific resistance < 0.2 Ωcm2 at 600-650oC. Another critical question is the stability of the SOC under thousands of current-switching cycles. Our results on conventional SOC air electrodes indicate that current switching can actually decrease electrode degradation compared to DC electrolysis operation. Furthermore, little or no degradation is observed for operation at low overpotentials and current densities < 0.9 A/cm2.

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(ICACC-S3-006-2015) CFY-Stack operation and degradation in fuel cell and electrolysis mode

M. Kusnezoff*[1]; S. Megel[1]; N. Trofimenko[1]; V. Sauchuk[1]; A. Michaelis[1]; 1. Fraunhofer IKTS, Germany

Solid electrolyte cell can be successfully operated in fuel cell and electrolysis mode, however the cell resistance and long-term stability during operation in both modes can be different and is strongly influenced by used materials and their interfaces. Electrolyte supported cell is the most robust technology, which has been demonstrated for operation in both modes with very low degradation rates on single cell level. In current study the operation and degradation of single cells on basis of 10Sc1CeSZ electrolyte in ceramic housing under fuel cell and electrolysis conditions has been studied and compared to their performance and degradation in planar stacks with metallic chromium-iron (CFY) interconnects. It was found that in SOEC mode the degradation at thermally neutral voltage can be even lower compared to the fuel cell mode which is in contradiction with results of single cell experiments. Comparison of stack ASR in fuel cell mode after changing the operation mode from electrolysis to fuel cell conditions showed strong deterioration of resistance. The observed effects have been explained by different electrode activation during SOEC operation mode and creation of asymmetry in the overpotential for oxidation/reduction reaction in the electrodes (or in one electrode) during long-term operation. The differences in observed degradation of single cells in ceramic housing and in stacks are discussed.

4:40 PM

(ICACC-S3-007-2015) Highly Efficient Solid Oxide Electrolyzer & Sabatier System

J. A. Olenick*[1]; V. Venkateswaran[1]; C. Iacomini[2]; T. Curry[1]; 1. ENrG Incorporated, USA; 2. Paragon Space Corporation, USA

Paragon Space Development Corporation® (Paragon) and ENrG Incorporated (ENrG) are teaming to provide a highly efficient reactor for carbon monoxide/carbon dioxide (CO/CO2) and water (H2O) conversion into oxygen (O2) and methane (CH4). The fully developed Solid Oxide Electrolyzer (SOE) system with embedded Sabatier reactors (ESR) will be gravity-independent, compact, and leak-tight. Utilizing Corning Incorporated Intellectual Property, Paragon and ENrG will attempt to leverage an all-ceramic, efficient, and low mass solid oxide fuel cell design that remains leak-tight after over a hundred thermal cycles. Paragon plans to incorporate this all-ceramic technology into their SOE/ESR system which is expected to result in a robust design solution that will: 1) be thermally shock-tolerant and capable of hundreds of on/off cycles at faster cycles than compared to the metal-to-ceramic SOE designs, 2) be lighter, smaller, and require less power than existing designs, 3) allow for high (>90%) single pass utilization of feedstock, and 4) achieve a thermodynamic efficiency of up to 80%.

S4: Armor Ceramics: Challenges and New Developments

Materials Characterization

Room: Coquina Salon E
Session Chair: Vlad Domnich, Rutgers University; Jerry LaSalvia, ARL

1:30 PM

(ICACC-S4-001-2015) Atomic structure and deformation behaviour of boron-rich solids (Invited)

K. Reddy*[1]; P. Liu[1]; A. Hirata[1]; T. Fujita[1]; T. Goto[3]; J. W. McCauley[4]; K. J. Hemker[2]; M. W. Chen[1]; 1. Tohoku University, Japan; 2. Johns Hopkins University, USA; 3. Tohoku University, Japan; 4. U.S. Army Research Laboratory, USA

Lightweight boron-rich solids such as boron carbide (B4C) and boron suboxide (B6O) have unusual mechanical properties which come from their basic structure, which is composed of icoshedra with a linear chain at the center of the rhombohedral unit cell. However, unlike other high performance ceramics, they often display an anomalous reduction in shear strength under high pressures. The dynamic and quasi-static loading transmission electron microscopy (TEM) observations demonstrated that amorphous bands are the dominant deformation/ failure mode of the borides. Nevertheless, the formation mechanisms of the amorphous bands remains a long-standing scientific curiosity mainly because of the lack of experimental structure information of the disordered shear bands, comprising of light elements. Therefore experimental observations of the atomic structure and their deformation behaviour for these ceramics are of extreme importance in understanding and tailoring the material's properties. In this presentation, we will show the atomic structure and deformation behaviour of B4C and B6O using newly developed annular bright field scanning TEM (ABF-STEM) technique. The results presented in this talk have important implications in designing new boron rich solids materials with improved mechanical properties by reinforcing chemical doping or changing in ratio of these light elements at atomic level.

2:00 PM

(ICACC-S4-002-2015) Adsorption Transitions and Controlling the Microstructural Evolution of Ceramic Systems (Invited)

W. D. Kaplan*[1]; 1. Technion - Israel Institute of Technology, Israel

The role of dopants on grain growth and sintering of ceramics has been an important topic of research for many years, especially given the contradicting reports of retarded or accelerated grain growth by key dopants and impurities. This issue is critical for the design of specific properties. One of the main difficulties has been the experimental measurement of dopant solubility limits at the sintering temperature, such that actual dopant levels could be associated with equilibrium (Gibbsian) grain boundary (GB) segregation (below the solubility limit) or with enrichment effects when doped above the solubility limit. This is especially important given the potential of adsorption (complexion) transitions to affect GB mobility. This problem has recently been overcome, and new analysis has allowed for the measurement of GB mobility of polycrystalline alumina as a function of dopant concentration, showing that some segregating dopants increase the GB mobility at levels significantly below the solubility limit (i.e. the opposite of solute-drag). The segregating dopants are associated with 2-D structural and compositional transitions at the GBs, and possible changes in the mechanism of GB migration. This presentation will review recent GB mobility measurements and the concept of 2-D GB transitions, and their potential use for controlling the microstructural evolution of polycrystalline ceramics.

2:30 PM

(ICACC-S4-003-2015) 'Seeing' the Atoms in Boron Carbide with Atom Probe Tomography (Invited)

K. Y. Xie*[1]; T. Sato[2]; M. F. Toksoy[4]; R. Haber[4]; S. P. Ringer[3]; J. M. Cairney[2]; K. J. Hemker[1]; 1. Johns Hopkins University, USA; 2. The University of Sydney, Australia; 3. The University of Sydney, Australia; 4. Rutgers University, USA

Boron carbide is an attractive engineering material due to its low density and super hardness. At the atomic level, TEM has shown the basic building blocks of boron carbide to consist of 12-atom icosahedra and 3-atom linear chains. However, the exact boron and carbon site occupancies are difficult to obtain with TEM. For example, a boron carbide with B4C stoichiometry can have multiple configurations such as (B12)CCC, (B11C)CBC and (B11C)CCB. Its exact atomic configuration is difficult to identify using most diffraction and imaging techniques. This is because the inter-atomic distances are small, both boron and carbon are light elements and they have similar electronic and nuclear scattering properties. In this work, we employed atom probe tomography, an advanced microstructure characterization technique that simultaneously captures the chemical and spatial information of individual atoms in a material, to gain insight of the atomic configuration in boron carbide. In addition, the characteristics of twin boundary, regular grain boundary and phase boundary in boron carbide were investigated using atom probe to provide information that has not been uncovered by conventional characterization techniques.

3:20 PM

(ICACC-S4-004-2015) Sub-Surface Characterization of the Inelastic Region Underneath Knoop Indents in Boron Carbide

J. LaSalvia*[1]; S. D. Walck[1]; V. Domnich[2]; J. Ligda[2]; B. E. Schuster[1]; 1. Army Research Laboratory, USA; 2. Rutgers University, USA

Since its discovery more than a decade ago, many studies have added to our fundamental understanding of stress-induced amorphization in boron carbide. Unfortunately, this understanding is far from satisfactory and many fundamental questions still remain. In this study, the inelastic deformation region underneath residual surface imprints of Knoop indents is characterized by electron microscopy and Raman spectroscopy to determine how it evolves as a function of load and whether or not stress-induced amorphization contributes to macrocracking (e.g. spallation). Additionally, evidence suggesting stress-induced melting is examined. Procedures and results will be presented and discussed.

3:40 PM

(ICACC-S4-005-2015) Improving Fracture Toughness of Alumina with Multi-walled Carbon Nanotube and Alumina Fiber Reinforcements

J. Lo*[1]; R. Zhang[1]; B. Shalchi-Amirkhiz[1]; D. Walsh[1]; M. Bolduc[2]; S. Lin[3]; B. Simard[3]; K. Bosnick[4]; M. O'Toole[4]; A. Merati[5]; M. Bielawski[5]; 1. Natural Resources Canada, Canada; 2. Department of National defence, Canada; 3. National Research Council, Canada; 4. National Research Council, Canada; 5. National Research Council, Canada

In this work, alumina reinforced with 2D and 3D alumina fiber mats has been successfully developed for evaluation. The 2D alumina

fiber reinforced alumina composite consists of an alumina matrix reinforced with 18 vol.% of alumina fiber mats. And the 3D fiber reinforced alumina composite was made with alumina matrix with a 2D alumina fiber mats along with multi-wall carbon nanotubes vertically grown onto the fiber mats. In comparing with the fracture toughness of commercial alumina of 3.8 MPa.m1/2, the alumina with the 2D and 3D reinforcement offer toughness of 4.4 MPa.m1/2 and 6.6 MPa.m1/2 respectively. The improvement in fracture toughness by the 3D reinforcement in alumina is almost 74%. Detailed examination on fracture surfaces of both 2D and 3D reinforced composites was conducted with scanning electron microscopy to elucidate the contribution of multi-wall carbon nanotubes and alumina fibers in enhancing the fracture toughness of the alumina matrix. Transmission electron microscopy investigation was also conducted on the composite with the 3D reinforcement to provide information on the morphological features at the fiber/matrix regions.

4:00 PM

(ICACC-S4-006-2015) Assessing the Carbon Concentration in Boron Carbide: A Combined X-Ray Diffraction and Chemical Analysis

K. A. Kuwelkar*[1]; V. Domnich[1]; R. Haber[1]; 1. Rutgers University- New Brunswick, 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. Further, literature suggests that boron carbide properties are dependent on its stoichiometry. This work focuses on further refinement of the analytical methods for boron carbide characterization. In particular, a novel approach for the determination of unbound carbon concentration is proposed, and the importance of accounting for soluble boron and oxidation is discussed. Chemical methods were used for the assessment of total boron, carbon, nitrogen and oxygen concentrations in selected commercial boron carbide powders. Soluble boron concentrations were obtained from chemical analysis at an external laboratory. X-Ray diffraction techniques were used to determine the free carbon concentrations using the modified spiking method. A novel approach was used to model the degree of disorder in graphitic carbon. The variations in the stoichiometry of selected commercial boron carbide powders were determined. The results suggested that bound carbon concentrations in boron carbide can exceed 20 at.%.

4:20 PM

(ICACC-S4-007-2015) Determination of Biaxial Residual Stress in Silicon Carbide Using Raman Spectroscopy

G. Subhash*[1]; S. Mohammed[1]; 1. University of Florida, USA

A novel method for determination of unknown bi-axial compressive stresses within a ceramic is developed. First a relationship relating the Raman peak-shift on a confined silicon carbide (SiC) particle to the magnitude of imposed confinement stress was developed utilizing phonon deformation potentials for 3C-SiC structures. Then ceramic matrix composite specimens consisting of SiC particles in a ZrB2 matrix were prepared and subjected to confinement pressure by thermal shrink fitting metal sleeves. The relationship between Raman peak-shift and confinement stress was then verified by comparing the measured stress in this method with that calculated from analytical expressions for thick walled cylinders. The relationship was further validated independently by applying unknown confinement stress and then measuring the displacements on one planar surface using digital image correlation (DIC) and simultaneously measuring the Raman peak-shift on the other planar surface. It was also noted that the Raman peak-shift relation derived for SiC correctly predicted process-induced residual stress in SiC particles. The derived Raman relationship can also be generalized to experimentally measure unknown bi-axial stress in any Raman active materials.

4:40 PM

(ICACC-S4-008-2015) Structural Investigations in the Silicon - Boron Carbide System

V. Domnich*[1]; K. A. Kuwelkar[1]; R. A. Haber[1]; P. G. Karandikar[2]; 1. Rutgers Univ, USA; 2. M Cubed Technologies, Inc., USA

Boron carbide excels in lightweight armor applications due to its exceptional mechanical and physical properties, such as high hardness, high elastic modulus and low specific weight. However, the unexpected loss of strength beyond the Hugoniot elastic limit significantly restricts the use of boron carbide in high-impact applications. It has been shown in the literature that such strength loss in boron carbide might be related to a structural instability under high contact stresses, resulting in the formation of an amorphous phase. Further, some published work suggests that such structural instability could be ameliorated by incorporating silicon atoms into the boron carbide lattice. In this work, we investigate the structure of silicon doped reaction bonded boron carbide by means of Raman spectroscopy, x-ray diffraction, and elemental analysis. The observed changes in the spectral characteristics are correlated with the incorporation of silicon atoms into various sites of boron carbide lattice. This work provides a reference for further investigation of the silicon – boron carbide system.

5:00 PM

(ICACC-S4-009-2015) Recent Developments in Direct Sintered SiC Armor Tiles

J. Funk*[1]; M. Harrison[2]; R. Campos[1]; 1. Superior Graphite, USA; 2. Superior Graphite, USA

Production capability has been developed in terms of shape, size, and volume for direct solid-state sintered SiC armor tiles. Tile production is a continuation from large scale production of submicron alpha SiC and B4C powders. Parallel developments have been in improved quality and material properties based on experimentation in formulation, powder production, forming, and sintering, which have impacted the sintered microstructure, strength, and hardness. Ballistic performance has been measured along the way on both backed single tiles and in composite systems against multiple threats. This paper will discuss some history and correlations and some of the most recent results.

5:20 PM

(ICACC-S4-010-2015) Characterization of lithium fluoride used to process magnesium aluminate spinel for transparent armor applications

J. A. Miller*[1]; M. Dumerac[2]; I. E. Reimanis[1]; 1. Colorado School of Mines, USA; 2. Technische Universitat Darmstadt, Germany

Magnesium-aluminate spinel ($MgO{\bullet}Al_2O_3$) is a material of interest for transparent armor applications because of its optical transparency and mechanical robustness. To improve transparency, lithium fluoride may be added to spinel in order to promote densification via liquid phase sintering, but at the expense of enhancing grain growth and reducing mechanical properties. In this study, 0.75 and 1.0 wt. % LiF was added to stoichiometric spinel powders, and compacts were synthesized via hot pressing. Secondary ion mass spectrometry (SIMS) is used to locate and quantify LiF concentrations as a function of depth from the specimen surface in order to explain the role of LiF during densification. Atom probe tomography (ATP) of grain boundaries is performed to examine the distribution of LiF. The conclusions from both characterization techniques are related to the microstructure of the hot pressed specimens.

5:40 PM

(ICACC-S4-011-2015) Discoloration and light absorption in polycrystalline spinel produced by spark plasma sintering

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

The optical and microstructural properties were evaluated for a polycrystalline spinel produced by spark plasma sintering (SPS). Residual pores, oxygen vacancies, and a non-homogeneous change in the stoichiometry were the primary defects that influenced the optical properties of the material. High SPS heating rate induced a high concentration of oxygen vacancies that discolored the as-sintered spinel. Annealing treatment in air atmosphere could reduce oxygen vacancies, thereby decolorized the sample SPS at a high heating rate.

S6: Advanced Materials and Technologies for Energy Generation, Conversion, and Rechargeable Energy Storage

Li-ion Battery

Room: Tomoka A

Session Chairs: Palani Balaya, National University of Singapore; Valerie Pralong, CNRS CRISMAT

1:30 PM

(ICACC-S6-001-2015) Overlithiated layered oxides for energy storage (Invited)

C. Delmas*[1]; H. Koga[2]; L. Croguennec[1]; M. Ménétrier[1]; S. Belin[3]; C. Genevois[4]; F. Weill[1]; 1. ICMCB -CNRS, France; 2. Toyota Motor Europe, Belgium; 3. Synchrotron Soleil, France; 4. Rouen University, France

The materials belonging to the (1-x)LiMO2,xLi2MnO3 system (M = Ni, Co) exhibit the largest capacity among all other layered oxides. These materials are overlithiated layered oxides (Li1.(LiyMn1-y-u-tCouNitO2) with a significant amount of lithium in the transition metal site. During the first charge, when all cations are oxidized to the tetravalent state, an overcharge of the cell leads to a structural modification that can be schematically described as a Li2O extraction occurs that cannot explain alone the oxidation process. In order to clarify the mechanism which is involved during the overcharge a systematic study has been carried using chemical analysis, X-ray and neutron diffraction, in operando XAS, very high-resolution electron microscopy. During the high voltage plateau in the first cycle, there is a partial densification on the external part of the particles followed by an oxygen oxidation in the bulk of the lattice without oxygen migration. This redox process is completely reversible in discharge. The contribution of nickel and cobalt and oxygen reduction leads to the huge specific capacity of this material family. A general overview of the behavior of this system, with a special focus of the structural modifications induced by the first charge will be presented.

2:00 PM

(ICACC-S6-002-2015) Mechano-Electrochemical Interactions in Intercalation Electrodes (Invited)

P. P. Mukherjee*[1]; C. Chen[1]; P. Barai[1]; 1. Texas A&M University, USA

In recent years, there has been significant research efforts targeted toward achieving improved performance, safety and life of lithium-ion batteries for electric drive vehicles. The intercalation electrodes in these rechargeable batteries are complex, dynamical systems, which include a multitude of coupled physicochemical processes encompassing electronic, ionic, diffusive transport in solid/electrolyte phases, electrochemical and phase change reactions and stress generation in multi-scale porous electrodes. In this regard, the implications of mechano-electrochemical interactions in the electrode degradation e.g. active particle fracture due to intercalation induced stress combined with unstable solid electrolyte interphase formation and resulting performance decay (capacity fade, impedance rise) require better insights. Computational modeling can play an important role in gaining fundamental understanding of the underlying electrochemical and mechanical interactions. In this talk, a systematic investigation of the mechano-electrochemical interactions in intercalation electrodes for lithium-ion batteries will be presented which will consist of a combined fracture and impedance analysis.

2:30 PM

(ICACC-S6-003-2015) Avenue towards the development of new nanostructured composite cathode materials for lithium-ion batteries (Invited)

N. V. Kosova*[1]; 1. Institute of Solid State Chemistry and Mechanochemistry, Russian Federation

There are ever-growing demands for lithium-ion batteries with high energy and power densities for energy storage, electrical vehicles and others.The present work represents a review on nanostructured composite electrode materials prepared by mechanochemically assisted solid-state synthesis using high-energy mechanical activation (MA)l. Structure, morphology and electrochemical properties of as-prepared materials were investigated by a complex of physicochemical methods including XRD and NPD with Rietveld refinement, FTIR, NMR, Mössbauer and XPS spectroscopy, SEM and TEM microscopy, in situ synchrotron diffraction, galvanostatic cycling and GITT, etc. As-developed approaches include: 1) joint MA of two active cathode materials (LiCoO2/LiMn2O4); 2) direct mechanochemically assisted solid-state synthesis from a multicomponent reagent mixture (LiFePO4/Li3V2(PO4)3); 3) formation of the second phase via partial decomposition of pristine material (LiVPO4F/Li3V2(PO4)3); 4) solid-state formation of “core-shell” materials (LiCoO2/MOx and LiMn2O4/LiMO2, M=Co, Ni). It has been shown that due to unique combination of properties, as-prepared composites have advantages over the individual components, including better cycleability and high-rate capability, lower price, more suitable charge-discharge profiles and operating voltage, etc.

3:20 PM

(ICACC-S6-004-2015) In-situ Characterization of Electrode Materials for Lithium Batteries (Invited)

K. Chapman*[1]; P. Chupas[1]; 1. Argonne National Laboratory, USA

Batteries are complex multi-component devices; understanding their operation and the factors that limit performance presents a significant characterization challenge. During operation, or cycling, transformations of the electrode materials are driven electrochemically with charge transfer between cathode and anode via the electrolyte. This involves widespread, coupled changes spanning the electronic oxidation states, atomic structures and particle/grain morphologies. New advanced characterization tools, including the ability to probe the electrode transformation during the electrochemical cycling, are needed to address these complex systems. This presentation will describe recent developments in in-situ hard X-ray methods to study batteries.

3:50 PM

(ICACC-S6-005-2015) Unique Topotactic Reversible Lithium Insertion between a Crystalline Sodium Iron Hydroxysulfate and an Amorphous Phase

V. Pralong*[1]; 1. CNRS, France

Polyanionic frameworks have been the object of numerous studies for the realisation of electrode materials in Li-ions batteries. This is exemplified by the iron compounds, which have been investigated, due to the reasonably high voltage of the Fe2+/Fe3+ redox couple [1-2]. Among these systems, rather few iron sulfates were studied since the discovery of lithium insertion in the NASICON type Fe2(SO4)3 framework [3, 4]. Importantly, the introduction of hydroxyl groups into the sulfate matrix, has opened the route to materials with promising electrode performances, as shown for the tavorite-type hydroxysulphate LixFeSO4OH [5] which exhibits an average potential of 3.6V vs Li+/Li0 and a reversible capacity of 120 mAh/g [5, 6]. In the present study we have shown that insertion of lithium into the jarosite hydroxysulfate phase NaFe3(SO4)2(OH)6 leads to an amorphous phase Li2+xNaFe3(SO4)2(OH)6 (with 0<x<0.5), through a biphasic mechanism. The latter phase exhibits reversible electrochemical lithium intercalation/deintercalation through a solid solution-like process, leading back to the oxidized jarosite LixNaFe3(SO4)2(OH)6 (with 0.3<x<0.6), with redox cycling at 2.82V and a capacity of 100 mAh/g at C/20. This unique topotactic reaction between an amorphous and a well crystallized phase is interpreted on the basis of the formation of an inorganic polymer and will be discuss in the presentation [7].

4:10 PM

(ICACC-S6-006-2015) Variation of iron valence state in lithium iron silicate glasses by annealing in reducing atmosphere and their electrochemical properties

T. Togashi*[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. It is of importance to develop new cathode materials without rare elements. There are only limited reports on glass-based cathodes, e.g., V_2O_5-P_2O_5 glasses. The purpose of this study is to develop new glass-based cathodes in the ternary Li_2O-Fe_2O_3-SiO_2 (LFS) system through the control of iron valence state and to clarify their LIB performance. A quenched glass with the composition of $Li_8Fe_2Si_5O_{17}$ was prepared by a melt-quenching method, and the glass was heat-treated at 300-500ºC in 5%H_2/Ar. The quenched and heat-treated glass samples were examined by using differential thermal analysis, XRD, AC impedance, cell test, and XPS measurements to clarify their thermal stability and iron valence state. It was found that heat treatments at temperatures below 400ºC are effective to control the iron valence state without causing any crystallization. By heat treatments, for example, the ratio of Fe^{2+}/Fe^{3+} increased from 19% to 37%, and the activation energy of electrical conductivity increased. The discharge capacity of the glass increased largely due to the annealing in 5%H_2/Ar, e.g., 1.9 times larger compared with the quenched glass. The present study proposes that LFS based glasses themselves have a high potential for new LIB cathodes.

4:30 PM

(ICACC-S6-007-2015) The γ'- V2O5 polymorph : Electrochemical properties and new insight into the Li intercalation mechanism revealed by Raman spectroscopy

R. Baddour-Hadjean*[1]; M. Smirnov[2]; K. Smirnov[4]; Y. Kazimirov[3]; D. Muller[1]; J. Pereira-Ramos[1]; 1. CNRS, France; 2. Saint Petersburg University, Russian Federation; 3. Frank Laboratory of Neutron Physics, Russian Federation; 4. CNRS, France

The electrochemical properties of γ'-V2O5 toward Li insertion are investigated and new insights into the structural and bonding changes occurring during the γ'-V2O5→γLiV2O5 phase transition are provided through a combined experimental and computational study of the structure and vibrational dynamics of both crystals, studied within DFT and Raman spectroscopy. A complete assignment of peaks in the Raman spectra is provided and characteristic peaks, which can be used as fingerprints of the two structures, are identified and assigned to vibrations of particular structural units. Spectral changes induced by the Li insertion into the γ'-V2O5 lattice are related to particular bonding changes and frequencies of phonon modes related to the vibrations of Li atoms are estimated and discussed. An outstanding result concerns the vibrational modes related to the motion of Li atoms, one of which is clearly discerned. This mode with frequency of ca. 450 cm-1 involves the Li atom vibration only slightly coupled with lattice vibrations. This assignment is strongly corroborated by the fact that the spectral region around 450 cm-1 is empty in the γ'-V2O5 vibrational spectrum. This work highlights the efficiency of Raman spectroscopy as a powerful tool for understanding the structural changes induced by Li insertion into the γ'-V2O5 lattice at the atomic level.

4:50 PM

(ICACC-S6-008-2015) Fabrication and optimization of Li-ion battery using LiNi1/3Mn1/3Co1/3O2 and α-Fe2O3

M. Nagarathinam[1]; E. Teo[2]; S. Muntoha[2]; P. Balaya*[1]; 1. National University of Singapore, Singapore; 2. Republic Polytechnic, Singapore

Extensive research has been carried out to increase the individual performance of various cathode and anode materials to meet the demands of LIBs for modern electronics and transport applications. However, detailed translational research on full cell LIBs is mandatory to bring the success in their commercialization. Herein, we present the cost effective large scale synthesis of mesoporous iron oxide (Fe2O3) and the electrochemical performance of this material against Li metal and in full cell against LiNi1/3Mn1/3Co1/3O2 (NMC). Fe2O3 can efficiently be synthesized by a solution based soft template approach in 100 g scale. The powder X-ray diffraction pattern and FESEM image of the as-synthesized product confirms the formation of pure phase α-Fe2O3 with primary particle size ranging from 30 – 40 nm. The electrochemical performance of α-Fe2O3 against Li provides charge capacity of 1069, 1045, 909, 763, 543 and 436 mAh.g-1 at 0.2, 0.5, 1, 2, 3 and 4C respectively. α-Fe2O3 against NMC as cathode exhibits reversible capacity of 165 mAh. g–1 (estimated using cathode weight) at 0.2C. The role of cathode to anode ratio, suitable binder, electrolyte and voltage window to achieve better performance of the full cell will be discussed in detail.

S8: 9th International Symposium on Advanced Processing and Manufacturing Technologies for Structural and Multifunctional Materials and Systems (APMT9)

Novel Ceramic Processing I

Room: Coquina Salon A

Session Chairs: Surojit Gupta, University of North Dakota; Tohru Sekino, Osaka University

1:30 PM

(ICACC-S8-001-2015) From MAX to MXene - From 3D to 2D (Invited)

M. Ghidiu[1]; M. Naguib[1]; M. Lukatskaya[1]; Y. Gogotsi[1]; M. W. Barsoum*[1]; 1. Drexel University, USA

It is now well-established that the layered, hexagonal carbides and nitrides with the general formula, Mn+1AXn, (MAX) where n = 1 to 3, M is an early transition metal, A is an A-group (mostly IIIA and IVA) element and X is either C and/or N – sometimes referred to as polycrystalline nanolaminates because every basal plane is a potential deformation or delamination plane - combine some of the best attributes of metals and ceramics. Recently we have shown that by placing MAX phase powders at room temperature in HF, the A-layers are selectively etched to produce 2D materials that we labeled MXenes to emphasize the loss of the A-group element and their similarities to graphene. Unlike hydrophobic graphene, MXenes are hydrophilic and behave as "conductive clays", a hitherto unknown combination. MXenes such as Ti2C, V2C, Nb2C and Ti3C2 can be used as electrode materials in lithium-ion batteries (LIBs) and supercapacitors (SCs) with performances that are impressive. In all cases, when used as anodes in LIB, MXenes showed excellent capability to handle high cycling rates. Flexible additive-free electrodes of delaminated Ti3C2 showed reversible capacities of > 400 mAh/g at 1 C and 110 mAh/g at 36 C, the latter for > 700 cycles. SCs with volumetric capacities of > 300 F/cm3 were also demonstrated, and recently volumetric capacitances of > 900 F/cm3 were obtained. The potential of MXenes in energy storage and other applications will be highlighted.

2:00 PM

(ICACC-S8-002-2015) Effect of Nanolaminate (Ti3SiC2) additives on the "Soft" Metals

T. Hammann[1]; R. Johnson[1]; S. Gupta*[1]; 1. University of North Dakota, USA

Mn+1AXn (MAX) phases (over 60+ phases) are thermodynamically stable nanolaminates displaying unusual, and sometimes unique, properties. These phases possess a Mn+1AXn 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 Wd (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-Soft Metals (Zn, Sn etc.) composites will be demonstrated. Preliminary results suggest that the addition of MAX Phases enhance the mechanical behavior of soft metals. Detailed survey about the mechanical and tribological performance will be presented.

2:20 PM

(ICACC-S8-003-2015) Effective nano-infiltration to make fully-densed ceramic composites with a high volume fraction of reinforcements

C. Xu*[1]; J. Yang[1]; 1. Florida State University, USA

Aiming to macroscopically utilize nano materials, Carbon nanotube (CNT) reinforced ceramic matrix composites (CMCs) are quite challenging and prosperous research area nowadays. Different from most CNT reinforced CMCs, we take advantage of the superior electrical, thermal and mechanical properties of CNTs by substantially increasing their volume fraction to up to 60 vol%. We accomplish this through a specially designed synthesis approach — a polymer infiltration and pyrolysis (PIP) process is employed to realize the formation of the matrix ceramics inside the reinforcement. We repeat this process a few cycles to improve the density and thus the conductivity and mechanical properties of the composites. Effective precursor infiltration is critical for the quality of the composites, and Darcy's law is adopted in the process modeling and simulation. We investigate this process quantitatively and obtain threshold pressure for samples with different pore sizes in different stages, which established solid foundations prior to the controlled synthesis of high quality CNT reinforced CMCs.

2:40 PM

(ICACC-S8-004-2015) Flexible ceramic matrix composite with high strength and conductive by aligned CNTs

J. Yang*[1]; C. Xu[1]; 1. Florida State University, USA

Carbon nanotubes (CNTs) is considered as the potential unique reinforcement materials for making super performance nanocomposites due to their superior properties like high strength and modulus and great electrical/thermal conductivity. A novel method was developed to fabricate flexible ceramic matrix nanocomposites with aligned CNTs for obtaining high performance materials and devices. In our research, polymer infiltration and pyrolysis (PIP) process was employed to impregnate liquid ceramic precursor into buckypaper, which are thin preformed sheets consisting of well-controlled and aligned CNTs networks. It is investigated that CNTs buckypaper with stretch alignment reinforced polymer derived ceramics composites can own high tensile strength over 600 MPa, and the resistivity of the final composite is around 4.0×10-5 Ωm, which is almost equal to that of graphite carbon. Such unique integration of high mechanical and electrical properties can promote the development of ceramic matrix composite combining structural and functional performances.

3:20 PM

(ICACC-S8-005-2015) Transparent ceramic chips for solid-state laser applications (Invited)

Y. Wu*[1]; 1. New York State College of Ceramics at Alfred University, USA

Transparent ceramics are emerging as a highly promising alternative to single-crystal materials for laser applications. Bulk laser ceramics have been widely investigated in terms of novel processes, spectroscopic properties, and thermal properties. Meanwhile, research on the processing of transparent ceramic chips is also desired for a wide of applications including microchip lasers and ceramic substrates for solid-state lighting. For instance, Yb-doped YAG is one of the most well-developed thin disk laser ceramics. Ceramic disk laser is therefore high needed to develop high-energy laser systems. In this work, a newly developed gelling system without using toxic organic compounds has been investigated to process transparent ceramic chips. The mechanisms and characteristics of the new gelling system are studied to understand the fundamental rheological behavior of the colloid suspensions. These rare-earth doped YAG transparent ceramic chips are characterized in terms of the microstructures and optical properties.

3:50 PM

(ICACC-S8-006-2015) Photoluminescence study of trivalent ion doped CuAlO2 fibers

Y. Liu*[2]; Y. Wu[1]; 1. Alfred University, USA; 2. New York State College of Ceramics, USA

As a classic p-type transparent conducting oxide, CuAlO2 has gained much attention due to its potential application in building a high efficiency p-n junction in various optoelectronic devices. In the delafossite structure, trivalent ions other than Al can be substituted into the Al site without significantly affecting hole transport along the Cu-O-Cu direction. In this study CuAlO2 is investigated as a promising photoluminescence host, exhibiting both photoluminescence behavior and good electrical conductivity, which would make it a good candidate for display technologies. Trivalent transition metal and rare earth ions (yttrium, europium and ytterbium) were successfully doped into the delafossite structure through a combination of sol-gel and electrospinning methods. Subsequent resistance-temperature measurements confirmed semiconducting behavior and the effect of trivalent dopants on the thermal activation energy of the host material. The delafossite-structured CuAlO2 can be regarded as a promising luminescence host material which also possesses good electrical conductivity.

4:10 PM

(ICACC-S8-007-2015) Reduction mechanism of Eu3+ to Eu2+ in oxide ceramics

Y. Yang*[1]; Y. Wu[2]; 1. Alfred University, USA; 2. Alfred University, USA

Eu2+ is a promising candidate for an activator ion in blue emission phosphors. To tune the valence of En ion, a reduction of Eu3+ to Eu2+ is manipulated favorably to achieve divalent Eu during the sintering. It has been found that both matrix and atmosphere conditions play important roles in the reduction of Eu3+ to Eu2+. In this work, three different host matrices, corundum, yttrium aluminum garnet and yttrium oxide, were investigated as oxide based matrixes compatible with the introduction of the Eu3+ ion into the lattice to understand the formation mechanisms of Eu2+. In addition, the effect of sintering in air and vacuum atmospheres was investigated to further understand the Eu3+ to Eu2+ reduction mechanism. Microstructures were examined by scanning electron microscopy. Phase composition and lattice parameters were determined with

X-ray diffraction. Photoluminescence emission spectroscopy and excitation spectra measurements were performed to investigate the valence state of the dopant europium ion. The luminescence lifetime of the europium doped oxide ceramics was also measured.

4:30 PM

(ICACC-S8-008-2015) Optoelectronic properties of Zn-based transparent conductive oxide films

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

Zn-based conductive thin films were prepared on glass substrates for display panel applications. Critical parameters were studied to prepare high quality thin films by using a versatile process called electrostatic spray deposition. The effect of different annealing schedules was studied in order to enhance the optoelectronic properties of the films. The roughness, topography, crystallinity and lattice parameter variation of ZnO thin films was characterized by AFM and XRD. Hall Effect measurements and UV-VIS spectroscopy were used to evaluate the optoelectronic properties of the ZnO-based TCO films. Statistical analysis, factorial design and ANOVA were used to identify the effect of dopants on the lattice parameters and optoelectronic properties of the ZnO based thin films.

4:50 PM

(ICACC-S8-009-2015) Manufacturing, Sintering and Piezoelectric Properties of Laser-fused K0.5Na0.5NbO3 Glass Granules

F. Hmood*[1]; J. J. Heinrich[1]; 1. Clausthal University of Technology, Germany

Life equirements need advanced materials with more than one property. Low weight noise cancelling windows are one of the anticipated applications for transparent piezoceramics which have acquired considerable attention in recent years. The conventional way to produce transparent ceramics is sintering of nanopowder compacts followed by hot isostatic pressing (HIP). An alternative method to synthesize transparent ceramics is sintering of glass microspheres utilizing the viscous flow of the glass granules. The crystallization process is considered a crucial step to control the final properties of the sintered body. In this study, K0.5Na0.5NbO3 (KNN) glass granules have been sintered using the hot isostatic pressing method. The glass microbeads were prepared by laser fusing with a cooling rate of 10^5 K/s, where 5 kW CO2 laser beam has been used to yield a material with 75% transparent fraction. Considering the DSC measurement, 525 °C has been chosen as sintering temperature which is in the kinetic window of the KNN glass. The sintered body showed a piezoelectric constant d33 of 5 pC/N. Sintering behavior and microstructure of the sintered samples have been investigated and the relationship between the microstructure and the piezoelectric properties will be discussed.

5:10 PM

(ICACC-S8-010-2015) Effect of Dy^{3+} substitution in ferroelectric phase on properties of multiferroic composites

R. P. Tandon*[1]; 1. University of Delhi, India

Multiferroic materials being possess coupling between electrical and magnetic order parameters i.e. Magnetization with electric field and polarization with magnetic field, are the major focus of research due to their multi-functionality and miniaturization of devices they cause. These materials are utilized in potential applications such as magnetic field sensors, microwave devices (filters, actuators, transducers), spintronic devices etc. In the present investigation, Dy substituted Barium strontium titanate ($Ba_{0.95-1.5x}Sr_{0.05}Dy_xTiO_3$) and Nickel cobalt ferrite ($Ni_{0.8}Co_{0.2}Fe_2O_4$) respectively, has been used as ferroelectric and ferrimagnetic phases to prepare multiferroic composites. Dielectric constant of composite samples gets significantly increased on Dy^{3+} substitution in ferroelectric phase. Dy substituted BST possess superior ferroelectric properties in comparison to pure BST resulting into still better ferroelectric properties in composite samples. Advantage of using Dy substituted BST as ferroelectric phase in multiferroic composites is the enhancement of magnetoelectric coefficient of composite samples. The value of magnetoelectric coefficient for composites with BST as ferroelectric phase is 0.08 mV/ cm Oe which gets increased to 0.3 mV/ cm Oe on Dy^{3+} substitution in BST.

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

Materials Design, New Composition and Composite I

Room: Ponce DeLeon

Session Chair: Jochen Schneider, RWTH Aachen Univeristy

1:30 PM

(ICACC-S12-001-2015) Magnetic properties and stability of Mn_2GaC and effects of Cr-Mn alloying (Invited)

M. Dahlqvist*[1]; 1. Linköping University, Sweden

Mn_2GaC is the first MAX phase to include Mn as the sole *M*-element. It was predicted by first-principles calculations and subsequently synthesized as a heteroepitaxial thin film. Using density functional theory (DFT) for a ground state search, several collinear and noncollinear low energy magnetic spin configurations have been identified, each with different out-of-plane lattice parameter *c*. Further, some of these theoretical configurations have different symmetries compared to the non-magnetic crystal structure. X-ray diffraction measurements performed upon sample cooling display a sharp contraction of the lattice in the *c*-direction around ~240 K as well as the appearance of an additional peak. This is consistent with theoretically predicted structural changes between different, close to degenerate, magnetic ground states. The accompanying sharp magnetic transition at 240 K suggests that Mn_2GaC is a new material which undergoes magnetically driven anisotropic structural changes. From vibrating sample magnetometer measurements at 50 K, Mn_2GaC displays a net magnetization with a saturation moment of $m_s = 0.29$ μ_B per Mn atom. *M*-site alloying between Mn and Cr up to a 1:1 ratio results in an increase of the saturation as well as remanent moment by at least 100 %. Furthermore, the transition temperature increases up to around 300 K, suggesting alloying as an approach for tuning the magnetic properties.

2:00 PM

(ICACC-S12-002-2015) Synthesis and characterization of thin films of Mo_2GaC MAX phase

R. Meshkian*[1]; A. Petruhins[1]; ÁRNI. S. Ingason[1]; A. Mockute[1]; M. Dahlqvist[1]; U. B. Arnalds[2]; J. Lu[1]; J. Rosen[1]; 1. Linköping University, Sweden; 2. University of Iceland, Iceland

Predicting and synthesizing unexplored MAX phases is highly motivated, as the number of possible isostructural compositions ensures a wide range of different properties. Mo_2GaC is one such phase, where theory suggests superconducting behavior. Bulk Mo_2GaC was previously synthesized in 1967, with a measured critical temperature of 3.9 K. As phase purity is essential for analysis of transport properties, especially with respect to the superconducting competing phases MoC and Mo_2C, we have explored thin film synthesis of Mo_2GaC and optimization with respect to structure and composition. An initial first principles investigation on phase stability of the MAX phase confirmed a stable phase, though with a formation enthalpy of only - 0.4 meV/atom with respect to the identified most competing phases γ-MoC, Mo_3Ga and Mo_6Ga_{31}. Thin film synthesis of Mo_2GaC was performed by magnetron sputtering from elemental targets onto Al_2O_3 (0001), 6H-SiC (0001) and MgO (111) substrates, at temperatures between 520 and 750 °C. Close to phase pure films, with only trace amount of Mo_3Ga, were identified for synthesis on

MgO (111) substrates at 640 °C. Heteroepitaxial growth to a thickness of approximately 25 nm was evident from transmission electron microscopy. Evaluation of transport properties was also performed on a ~90 nm film, showing common metallic behavior between 10 and 300 K.

2:20 PM

(ICACC-S12-003-2015) New Solid Solution MAX Phases: (Ti0.5,V0.5)3AlC2, (Nb0.5,V0.5)2AlC, (Nb0.5,V0.5)4AlC3 and (Nb0.8,Zr0.2)2AlC

M. Naguib[1]; G. Bentzel*[1]; J. Shah[1]; J. Halim[1]; E. N. Caspi[3]; J. Lu[2]; L. Hultman[2]; M. W. Barsoum[1]; 1. Drexel University, USA; 2. Linköping University, Sweden; 3. cNuclear Research Centre-Negev, Israel

We synthesized the following previously unreported aluminum-containing solid solution Mn+1AXn phases: (Ti0.5,V0.5)3AlC2, (Nb0.5,V0.5)2AlC, (Nb0.5,V0.5)4AlC3 and (Nb0.8,Zr0.2)2AlC. Rietveld analysis of powder X-ray diffraction patterns was used to calculate the lattice parameters and phase fractions. Heating Ti, V, Al and C elemental powders - in the molar ratio of 1.5:1.5:1.3:2 - to 1450 °C for 2 h in flowing argon, resulted in a predominantly phase pure sample of (Ti0.5,V0.5)3AlC2. The others compositions were not as phase pure and further work on optimizing the processing parameters needs to be carried out if phase purity is desired.

2:40 PM

(ICACC-S12-004-2015) $(Cr_xV_{1-x})_{n+1}AlC_n$ MAX phases solid solutions

T. Cabioch*[1]; P. Chartier[1]; J. Halim[2]; E. Caspi[3]; 1. University of Poitiers, France; 2. Drexel University, USA; 3. Nuclear Research Centre, Israel

$(Cr_xV_{1-x})_{n+1}AlC_n$ MAX phases solid solutions with n = 1,2,3 and x=0;0.25;0.5;0.75;1 were synthesized by annealing cold compacted mixtures of Cr, V, Al and C powders at high temperature (1400°C to 1600°C) with or without isostatic pressure. $(Cr_xV_{1-x})_2AlC$ solid solutions were obtained for all the x values whereas the synthesis $(Cr_xV_{1-x})_3AlC_2$ was achieved only for x=0.25,0.5 and 0.75 and that of the $(Cr_xV_{1-x})_4AlC_3$ phase for x=0, 0.25 and 0.5. The structure of the so obtained samples was studied by X-Ray and neutron diffraction experiments at several temperatures allowing to discuss the evolution of the structure as a function of x and n. Interestingly, ordering of the vanadium and the chromium in M layers is evidenced for n=2 and 3. Furthermore, whereas the thermal expansion is isotropic for n=1 and 3 it is not the case for n=2.

Structural-property Relationships of Existing Systems I

Room: Ponce DeLeon
Session Chair: Martin Dahlqvist, Linköping University

3:20 PM

(ICACC-S12-005-2015) The relevance of kinking in the hysteresis of MAX phases (Invited)

W. J. Clegg*[1]; N. G. Jones[1]; F. Giuliani[2]; 1. University of Cambridge, United Kingdom; 2. Imperial College, United Kingdom

This paper examines the accepted idea that the reversible hysteresis in MAX phases is caused by the formation, growth and collapse of unstable, or incipient, kink bands. It is shown that in polycrystalline Ti3SiC2 in compression residual elastic lattice strains are developed during the first loading cycle and remain during subsequent cycles, whereas incipient kink bands would be expected to collapse completely without any residual strains. These lattice strains varied systematically with the Schmid factor, suggesting that plastic flow is important. Furthermore, elasto-plastic self consistent simulations showed that reversible hysteresis is predicted, if some grains yield by slip on the basal plane, while others remain predominantly elastic, giving both the experimentally observed magnitude of the work dissipated and its dependence on the maximum applied stress. These results show that reversible hysteresis can be associated with conventional dislocation flow using existing ideas of the deformation of a polycrystalline aggregate, without the need for unstable kinking.

3:50 PM

(ICACC-S12-006-2015) Plasticity in MAX Phases at low and high temperature: a multiscale experimental approach (Invited)

A. GUITTON[1]; A. Joulain*[1]; L. THILLY[1]; C. TROMAS[1]; 1. Pprime Institute, France

The mechanical properties of MAX phases are intrinsically linked to their nanolayered structure. At room temperature, plastic deformation in MAX phases is governed by basal slip, with dislocations arranging themselves in pile ups or walls. In such configuration, two dislocation walls define a kink band which is thought to be the key mechanism of the plastic deformation of MAX phases at room temperature. Nevertheless, the elementary mechanisms and the exact role of microstructural defects are not fully understood yet. Moreover the origin of the brittle to ductile transition (BDT) remains unclear. We present here a multi-scale experimental study of deformation mechanisms of the Ti_2AlN MAX phase below and above the BDT. Compression tests were performed under confining pressure at room temperature and at 900°C. The deformed surface microstructures were observed by SEM and AFM. These observations associated with nanoindentation tests showed that grain shape and orientation relative to the stress direction control formation of intra- and inter- granular strains and plasticity localization. A detailed dislocation study by TEM revealed the presence of dislocation configurations never observed before in MAX phases: at room temperature, dislocation reactions and dislocation dipoles are observed, in Ti_2AlN deformed at 900°C, cross-slip from basal plane to prismatic or pyramidal planed are evidenced.

4:10 PM

(ICACC-S12-007-2015) Structure evolution during low temperature growth of nanolaminate thin films

L. Shang[1]; A. Al Gaban[1]; M. to Baben[1]; J. M. Schneider*[1]; 1. RWTH Aachen Univeristy, Germany

V–Al–C, Cr-(Si)-Al-C and Mo-B-C and thin films were deposited by magnetron sputtering. The formation temperatures for V2AlC, Cr2AlC and Mo2BC during sputter deposition are compared to the amorphous – crystalline transition temperatures in these material systems. Formation of the crystalline nanolaminate structure during low temperature growth is enabled by surface diffusion. Besides the energetic requirements also the effect of composition on the low temperature synthesis of MAX phase thin films was investigated.

4:30 PM

(ICACC-S12-008-2015) Electronic structure and transport properties of Ti2Al(CxNy) MAX phase solid solution

W. Yu[1]; V. Mauchamp[1]; L. Gence[2]; T. Cabioc'h[1]; L. Piraux[2]; D. Magne[1]; V. Gauthier Brunet[1]; S. Dubois*[1]; 1. Institut PPRIME, France; 2. Institute of Condensed Matter and Nanosciences, Belgium

Ti2AlCxNy solid solutions are synthesized by using Hot Isostatic Pressing. The X site solid solution effects are investigated by focusing on the electronic structure and transport properties of the Ti2AlCxNy MAX phases. Combining electron energy-loss spectroscopy (EELS) and band structure calculations, it is demonstrated that solid solution effects induce weak perturbations on the electronic structure. Solid solution effect thus mainly results in a rigid shift of the Fermi energy in a flat part of the electron density of states of Ti2AlC (or Ti2AlN). From these observations, the variations of two key parameters of the conductivity are rationalized. The relative variations of the residual resistivity in the whole composition range are shown to be rather small which well agrees with the weak disorder evidenced from EELS. However, the values of the slope of the resistivity versus temperature variation are shown to vary quite significantly, evidencing a deviation from Matthiessen's rule in these systems. By comparing the experimental data with calculations based on the semi-classical Boltzmann equation, it is demonstrated that the observed variations are due to a combination of band structure effects and changes in the scattering mechanisms.

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(ICACC-S12-009-2015) Effect of Microstructure on Mechanical Damping in Ti_2AlC

R. Benitez*[1]; H. Gao[1]; I. Karaman[2]; M. Radovic[2]; 1. Texas A&M University, USA; 2. Texas A&M University, USA

The unique mechanical properties of Ti_2AlC, and to the further extent of all other MAX phases, can be attributed to their plastically anisotropic nano-laminated structure. One of the most intriguing properties of MAX phases is their hysteretic stress-strain behavior particularly since the amount of mechanical energy dissipated during each loading-unloading cycle is quite large for stiff solids like MAX phases. Initially incipient kinking was proposed as the primary hysteretic mechanism in MAX phases, but recently alternate and contradicting mechanisms, such as friction of microcracks and dislocation glide and pileups have been proposed. The objective of this work is to investigate the possible contributions that incipient kinking, microcracks, and or dislocation pileup and glide may have on the hysteretic behavior of MAX phases. Through the combination of mechanical cyclic loading of Ti_2AlC with different microstructure in compression with resonant ultrasound spectroscopy (RUS) the evolution of the elastic properties of Ti_2AlC and hysteresis was studied. Results show that Ti_2AlC exhibits distinct regions of hysteresis from which the underlying mechanism can be identified.

5:10 PM

(ICACC-S12-010-2015) Crystallisation and toughness of Cr2AlC and Ti3SiC2 thin films

V. Vishnyakov*[1]; B. Beake[2]; M. Davies[2]; J. Colligon[1]; 1. University of Huddersfield, United Kingdom; 2. Micro Materilas Ltd, United Kingdom

MAX phase compositions and phases of Ti3SiC2 and Cr2AlC were created on nickel superalloy substrates by magnetron deposition and ion sputtering. At the substrate temperature below 400 0C for Cr2AlC and 600 0C for Ti3SiC2 amorphous ceramics were produced, while above those temperatures MAX phases were observed. Amorphous materials were a bit harder than corresponding MAX phases (11.1 against 10.7 GPa for Cr2AlC) and surfaces look much smoother. Ion deposited films were by 3 to 5 GPa harder than magnetron deposited films. During nano-scratching amorphous films have shown brittle behaviour and spallation while MAX phase films were very ductile and cracking was extremely limited to small linear cracks. We speculate that crack propagation in MAX phase is limited by the material plasticity. This shows that for demanding applications careful consideration should be undertaken while choosing amount of ion assistance during deposition and final state of the coating.

S13: International Symposium on Advanced Ceramics and Composites for Sustainable Nuclear Energy and Fusion Energy

Ceramics and Composites Technology for Accident-tolerant LWR Fuels I

Room: Tomoka B

Session Chairs: Yutai Katoh, Oak Ridge National Laboratory; Steven Zinkle, University of Tennessee

1:30 PM

(ICACC-S13-001-2015) Materials Options for Accident Tolerant Fuels in Light Water Reactors (Invited)

S. J. Zinkle*[1]; K. Terrani[2]; L. L. Snead[2]; 1. University of Tennessee, USA; 2. Oak Ridge National Laboratory, USA

Further enhancement of safety margins in current and next generation commercial fission reactors in general requires an integrated engineering systems design approach. However, tangible gains in safety margin (and performance) may be achievable by utilizing one or more materials science modifications to the fuel system in order to achieve improved accident tolerance to loss of coolant or reactivity insertion scenarios. From a materials science perspective, there are four key metrics to be considered for such a fuel under transient accident conditions: reduced enthalpy production, reduced hydrogen production, improved resistance to clad ballooning and rupture (maintaining coolability of the core), and suppressed fission product release. There are a variety of materials science approaches that can be considered to address one or more of these four metrics for accident tolerant fuels, ranging from relatively incremental modifications to the cladding material to dramatic alternatives to the historical monolithic UO2 ceramic fuel pellets surrounded by seamless Zr alloy tubing. This presentation will review several potential accident tolerant fuel system options and outline key feasibility challenges that need to be resolved, along with briefly discussing potential impact on reactor neutronics and overall electricity production costs. Potential roles for ceramics in these new fuel systems will be highlighted.

2:00 PM

(ICACC-S13-002-2015) Mechanical Behavior and Chemical Compatibility of SiC-Based Ceramics and Composites for Nuclear Applications (Invited)

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

We evaluated the corrosion behavior of CVD SiC ceramics and the hoop strength of triplex SiC composite tubes for the application of nuclear fuel cladding. For the fabrication of composite layer, we varied fiber winding patterns and angles as well as the type of fibers. The hoop strength of the composite tubes tended to be proportional to the volume fraction of the reinforced fibers. The hoop strength increased slightly as the winding angle increased. Fracture behavior of the SiC triplex tube was also investigated via the observation of microstructure of the failed samples. In the corrosion test of CVD SiC, analogous to the outermost environmental barrier coating of the triplex composite tube, in 360°C water, the dissolution rate was much higher in the static autoclave, where the dissolved oxygen content was not controlled, than in the PWR-simulating water loops with the dissolved oxygen content less than 5 ppb. Furthermore, the dissolution rate of SiC in the environment with the control of the dissolve hydrogen was extremely low, indicating that the dissolved hydrogen significantly affects the corrosion behavior of SiC under PWR water condition. Surface characteristics of the corroded samples were analyzed using scanning electron microscopy, X-ray photoelectron spectroscopy, and atomic force microscopy.

2:20 PM

(ICACC-S13-003-2015) Chemical compatibility between UO2 fuel and SiC/SiC structural material

C. Sauder[1]; J. Braun*[1]; F. Balbaud[4]; C. Gueneau[2]; S. Chatain[2]; E. Brackx[3]; 1. DEN/SRMA/LTMEX, France; 2. DEN/SCCME/LM2T, France; 3. DEN/SGCS/LMAC, France; 4. DEN/DADN, France

SiC/SiC composites constitute an advanced solution for Fast Neutron Reactors (SFR, GFR …) as core materials regarding their stability under neutron irradiation at high temperature. Recently, they have also been envisaged as cladding materials in Water Pressurized Reactors to overcome Zircaloy drawbacks, such as rapid oxidation at high temperature. That is why the chemical compatibility of the fuel, restricted in this case to UO2, with SiC has to be investigated. On the one hand, Knudsen cell mass spectrometry has been performed to measure the composition of the gas phase along time at temperatures ranging from 1473 to 1923K. This gas phase is mainly composed of CO and, to a lesser extent, of CO2 and SiO. Therefore, uranium silicides and ternary compounds have been formed in the condensed phase. On the other hand, diffusion couples tests in screwed crucibles have been carried out at the same temperatures to evaluate the behaviour in a close system. Both results will be discussed to evaluate the behaviour between the fuel and SiC/SiC composites as core materials.

2:40 PM

(ICACC-S13-004-2015) Effect of thermal shock on microstructure and mechanical properties of SiC triplex tube

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

SiC and its composites have been considered to be used as a nuclear fuel cladding material of pressurized light water reactors because of its superior accident tolerance properties such as excellent high-temperature mechanical strength, low hydrogen liberation rate, and good corrosion resistance under severe accident conditions. In this study, SiC triplex tubes comprising of a CVD SiC inner layer, a SiCf/PyC/CVI-SiC composite intermediate layer, and a CVD SiC outer layer were fabricated through chemical vapor processes and thermal shock behaviors of the SiC triplex tubes were investigated. Tubular samples with dimensions of 30 mm in length, an inner diameter of 8.5 mm, and an outer diameter of 9.6 – 10.1 mm were used for the thermal shock test. Experiments were performed using a drop tube furnace with a vertical quartz tube at 1200oC. After thermal shock tests, changes in hoop strength and microstructural damages such as matrix cracking, debonding between each layer were also investigated. Effects of PyC interphase with about 200 nm in thickness between the SiC inner layer and the SiCf/SiC composite layer on hoop strength were also evaluated.

3:20 PM

(ICACC-S13-005-2015) Development of SiC composite for light-water reactor accident tolerant fuels (Invited)

S. Suyama*[1]; M. Ukai[1]; M. Uchihashi[1]; H. Heki[1]; K. Okonogi[1]; K. Kakiuchi[1]; 1. Toshiba Corporation, Japan

In the accident at Fukushima Daiichi nuclear power plant, oxidation of zirconium alloy with high-temperature steam resulted in generations of hydrogen which caused explosions in the reactor buildings. In order to prevent the hydrogen explosions, accident tolerant fuels (ATF) are expected for nuclear power plants. Silicon carbide (SiC) composite is expected one of the candidates to enhance safety of light water reactor (LWR) core materials instead of zirconium alloy at high temperature. SiC composite is one of the most promising candidates for high-temperature structural materials, because of its stability at high temperature. To protect SiC fibers and the fiber/matrix interface from hydrothermal corrosion and an oxidizing environment, a dense matrix is favorable. Toshiba and the collaborators have started new project of SiC composite process technology for channel box and fuel cladding of LWR core materials.

3:50 PM

(ICACC-S13-006-2015) Effect of sintering additives on the high temperature water vapor oxidation of liquid phase sintered SiC materials for nuclear fuel cladding materials

M. Lee*[1]; S. Kondo[1]; Y. Kawaharada[2]; F. Kano[2]; T. Hinoki[1]; 1. Kyoto university, Japan; 2. Toshiba Corporation, Japan

The oxidation of nuclear fuel cladding materials under high temperature steam has placed importance on the oxidation resistance at loss of coolant accidents in LWRs. To secure safety margins avoiding serious degradation of the cladding by high temperature steam attacks, SiC has been considered as a replaceable candidate to conventional cladding materials. Several types of liquid phase sintered (LPS)-SiC were prepared in which the amount of sintering additives (Y2O3, Al2O3) and dispersion methods were selected. The surface oxidation of LPS-SiC was examined after steam exposure at 1200 and 1400°C for 72h. To investigate the effects of detrimental impurities as yttrium-aluminum garnet (YAG) and Al2O3 on oxidation behaviors of LPS-SiC, underlying mechanism was discussed with the analyses of oxidation rate, microstructure, and X-ray diffraction. The formation of protective silica scales was observed at the surface of LPS-SiC tested at 1400 °C. Note that the thickness and morphology of the scales was strongly dependent on the amount of sintering additives. 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).

4:10 PM

(ICACC-S13-007-2015) Hydrothermal Corrosion of SiC-based Materials in LWR Environments

K. Terrani*[1]; Y. Yang[1]; 1. Oak Ridge National Laboratory, USA

Silicon carbide (SiC) materials have a long history in nuclear applications, particularly in high temperature gas reactor systems and fusion platforms. Emerging in recent years are proposals for extension of their application to light water reactor (LWR) systems. For the latter application, hydrothermal corrosion of these materials needs careful assessment. A review of the current state of knowledge with regards to silica formation and dissolution as a result of oxidation of SiC in aqueous environments is provided. Results from autoclave testing of SiC materials under various LWR water chemistries, comprising of pressurized water reactor as well as normal- and hydrogen-water chemistry for boiling water reactors are discussed. Following these exposures these samples are characterized. All of this information is then used to determine and quantify the rate-limiting step for recession of SiC materials in these environments.

4:30 PM

(ICACC-S13-008-2015) Hydrothermal corrosion of ion irradiated SiC

S. Kondo*[1]; M. Lee[1]; T. Hinoki[1]; Y. Hyodo[2]; F. Kano[2]; 1. Kyoto University, Japan; 2. Toshiba, 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 and beyond design basis accident. Recently we have focused on the effect of irradiation damage on the hydrothermal corrosion of SiC, because the irradiation significantly modified the microstructure in the LWR relevant conditions. 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 at DuET facility, Kyoto University. The irradiated surface subjected to 320 or 360 °C water (20 MPa) was studied by scanning and transmission electron microscopy. 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).

4:50 PM

(ICACC-S13-009-2015) Prototyping a Channel box

M. Tanahashi*[1]; H. Kato[1]; T. Takagi[1]; S. Kubo[1]; 1. IBIDEN CO., LTD, Japan

We will report that we created a prototype of a channel box. Firstly, we used a machined mold set based on a special carbonaceous material in order to form long SiC fiber in the shape of the channel box, and used CVD in order to produce a SiC material with high precision, without compromising density or strength.This technology can be used to create specially shaped items such as thin-wall, long cylinders. It can also be applied to the production of fuel cladding tubes. For example, we could create a prototype, 133mm x 133mm x 800mm.

5:10 PM

(ICACC-S13-010-2015) Hermetic Sealing of Silicon Carbide using Iron, Chromium, and Aluminum Alloys

A. Morgan[1]; G. Vasudevamurthy*[1]; L. L. Snead[2]; 1. Virginia Commonwealth University, USA; 2. Oak Ridge National Laboratory, USA

Silicon Carbide (SiC) is increasingly gaining attention in the nuclear industry as a potentially viable alternative fuel clad due to its great thermo-mechanical and thermo-physical properties. One of the major challenges with employing SiC is its ability to provide hermetic sealing. It is critical to have a hermetically sealed fuel cladding to prevent any fission products and gases from diffusing through, which could ultimately reach the coolant. The High Temperature and Materials Laboratory at Virginia Commonwealth University is currently investigating methods to achieve hermetic sealing of SiC using a special alloy, FeCrAl, developed by our partners at ORNL. Solving the hermetic seal issue requires addressing typical ceramic and metallic components, which are largely dissimilar in both thermal and mechanical properties. Preliminary experiments to bond SiC with FeCrAl resulted in adverse separation partially attributed to the differences in thermal expansion mismatch. To address these issues, compositionally graded interfaces assisted by deposition (thin and thick compositional interlayers) were applied to SiC specimens. SEM and EDS characterization of coated SiC cross-sections subjected to high-temperature diffusion bonding revealed bonding of FeCrAl within the composites.

FS3: Materials Diagnostics and Structural Health Monitoring of Ceramic Components and Systems

Materials Diagnostics and Structural Health Monitoring of Ceramic Components and Systems

Room: Coquina Salon B

Session Chair: Joerg Opitz, Fraunhofer IKTS-MD

1:30 PM

(ICACC-FS3-001-2015) Metal oxide heterogeneous interfaces for robust photocatalysis (Invited)

C. Dinu*[1]; 1. West Virginia University, USA

Active research is focused on identifying technologies capable to increase the energy portfolio while reducing the footprint on the environment. Highly desired is the development of photocatalyst materials that effectively utilizes visible light to form resourceful photo-electro-systems. However, light-absorbance efficiency, high corrosion-resistance properties, as well as low energy levels that do not match material reduction/oxidation half-reactions in dry conditions, remain contemporary challenges in designing and manufacturing the next generation of proficient photocatalysts. Further, fundamental mechanisms, properties and processes need to be understood before increased performance, efficiency, reliability, competitiveness and implementation of such energy conversion systems can be achieved. This presentation will highlight the systematic strategy designed for the formation of user-controlled catalytic interfaces containing carbon- and oxide-based building blocks, as well as their architectural and functional integration in heterostructures with high photocatalytic capability. Photon absorption efficiency relative to the heterostructure composition, morphology, and physico- chemical properties to explain the fundamental mechanisms that drive photocatalysis and their efficiency function of the heterostructure interfaces and their properties are highlighted.

2:00 PM

(ICACC-FS3-002-2015) Ceramic phosphors for process control and quality assurance

M. Reitzig[1]; J. Katzmann[1]; F. Gaska[1]; C. Zeh[1]; J. Opitz[2]; K. Wätzig[3]; T. Härtling*[1]; 1. Fraunhofer IKTS, Germany; 2. Fraunhofer IKTS, Germany; 3. Fraunhofer IKTS, Germany

Ceramic phosphors (CPs) are brightly luminescent, physically and chemically stable in harsh environments, and applicable to any surface if in powder or particle form. The optical luminescence properties of certain CPs change predictably upon exposition to high energy input such as electron beam irradiation or heating above 500 °C. Reading out the optical properties before and after energy exposition allows a unique way of monitoring corresponding processes, e.g. electron beam sterilization or hot forming and heat treatment. In order to transfer this approach to a ready-to-use technology we investigate the response of different ceramic phosphors to high energy irradiation as well as heating. The results of these investigations allow us to properly choose materials which enable a precise evaluation of the applied electron dose in irradiation processes, and also of the oven transit time of metal parts in the 1000 °C regime. Both applications were realized in industrial environment to demonstrate the readiness level of the method. In our contribution we will present the application conditions and the obtained results in detail. It turns out that the approach carries high potential especially for the monitoring of ceramic material processing, e.g. sintering or tempering. Hence, we will deduce the possibilities and benefits the method holds for process control and quality assurance of ceramic materials.

2:20 PM

(ICACC-FS3-003-2015) Nanoparticle-based monitoring of surface status

V. A. Lapina*[1]; P. P. Pershukevich[1]; T. Pavich[1]; J. Opitz[2]; 1. Institute of Physics of NAS Belarus, Belarus; 2. Fraunhofer Institute for Ceramic Technologies and System, Germany

Nanoparticles of detonational diamond are actively used for producing various compose materials and coatings. We developed new very effective luminescence supramolecular complexes based on ND and rare earth elements. These complexes have high quantum output, broad excitation bands, high sensitivity to various types of irradiation, enhanced photo- and radiation stability. Luminescent properties of such nanodiamond complexes was shown to be characterized with high stability and preserved at different forms of including particles in composite matrix. Due to high quantum efficiency, long time luminescence narrow irradiative bands, large Stokes shift, possibilities of simultaneously using the various REE ions, high sensitivity detection method under small complexes concentration can be developed. The combination of optical characteristics of nanodiamonds and their sizing allows observing their homogeneous distribution onto the composite surface as well as local concentration of particles on the interboundaries, cavities and defect points of the matrix. The developed method allows receiving the useful information on the structure and texture of the composite matrix. This nondestructive method of structural health monitoring can be successfully applied for inspection of ceramic components subjected to increasingly extreme conditions in order to assure their functional reliability.

2:40 PM

(ICACC-FS3-004-2015) Thermal Diffusivity Measurement of Ceramic Materials with the Flash Method

M. Thermitus*[1]; 1. Netzsch Instruments, USA

The flash method has become the technique of reference for measuring thermal diffusivity. In this method, a cylindrical specimen is heated on its front face by a short pulse of energy, and the thermal diffusivity is calculated based on the resulting temperature rise of the back face. The original method assumes ideal conditions of uniform and instantaneous pulse, homogeneous, isotropic and opaque material, adiabatic boundaries, 1D heat diffusion, and constant thermophysical properties. Most of these requirements are not met in real experiments, and as a consequence, several calculations methods have been introduced over the years primarily to account for heat losses, 2D heat diffusion and the duration of the pulse. One of the common applications of the flash method is testing ceramic materials. Even at moderate temperatures, the transport properties of such materials are strongly related to their composition. It is in particular very critical to track changes in the thermophysical properties during the firing of the green body, up to and beyond the sintering temperature. Measurement data will be presented, showing the influence of particle size, heating/cooling rate, and chemical components like binders. It will also be demonstrated how important it is to account for the transparency effect of these materials during the measurements.

3:20 PM

(ICACC-FS3-005-2015) Quantitative Thermographic Characterization of Ceramic-Based Coatings and Structures

S. Shepard*[1]; 1. Thermal Wave Imaging, Inc., USA

Thermography provides fast, non-contact inspection of non-planar ceramic-based components and structures. It is widely used for Nondestructive Evaluation (NDE) of thermal barrier coatings and ceramic matrix composites to identify localized flaws such as delamination, lack of bonding to substrate layers or cracking. Often, these types of flaws can be visually identified in the infrared image sequence after the sample has been heated, without the use of extensive signal or image processing. However, quantitative thermographic analysis and characterization, poses several unique challenges. Many ceramic materials are translucent in visible and/or infrared spectra, so the usual simplifying assumptions of heating and emission at the sample surface must be must be discarded. Infrared cameras and excitation sources must be selected to avoid transparency bands in the material. In a flash heating configuration, where the sample is heated by an electronically truncated optical pulse, each pixel is processed using the Thermographic Signal Reconstruction (TSR) technique, and characterized according to the peaks and zero crossings of the first and 2nd logarithmic derivatives of the signal. These are used to generate maps of porosity, thermal diffusivity or thickness, and to confirm the construction of multilayer materials. Examples on ceramic matrix composites and thermal barrier coatings will be presented.

3:40 PM

(ICACC-FS3-006-2015) In situ X-ray diffraction reveals grain size dependence of domain wall motion and relation to macroscopic properties in BaTiO3

D. Ghosh*[1]; J. L. Jones[2]; 1. Old Dominion University, USA; 2. North Carolina State University, USA

Recent developments in diffraction-assisted techniques allow making direct measurements of piezoelectric nonlinearities and separating the contributions from intrinsic lattice strain and ex-trinsic domain wall motion. It is now widely accepted that poly-crystalline barium titanate (Ba-TiO3) exhibits maximum room temperature permittivity at a grain size of approximately 1-2 μm, and permittivity decreases below and above this grain size. Limited studies have also shown analogous behavior of the piezoelectric coefficients with grain size. Two widely accepted theo-ries attribute this behavior to either internal residual stress or non-180° domain wall motion. However, a direct measurement of the exact origin of such grain size effects has, to date, eluci-dated researchers. Using in situ high-energy X-ray measurements during high electric field ap-plication, it is shown that 90° domain wall motion is present across the grain size range of 0.2 μm to 3.5 μm and is maximum at a grain size of approximately 2 μm, where macroscopic proper-ties also peak. This study thus conclusively attributes 90° domain wall motion to the grain size dependence of BaTiO3 ceramics in the 0.2-3.5 μm range.

4:00 PM

(ICACC-FS3-007-2015) Material Diagnostics for New Bio-Ceramics

J. Schreiber*[1]; D. Lee[1]; 1. NUGA LAB GmbH, Germany

For the development of bio-ceramics the characterization of the physical properties and then the test of bio-medical effects are required. Such ceramics like Tourmanium, prepared by a mixture of barley stones, sericites, volcanic stones, and tourmaline, are e.g. used today for thermal cure devices, medical belt, and bracelet by releasing maximized far-infrared radiation. On the basis of Tourmanium attempts were made to improve their functional features by a new technology with nano-diamond addition. Both infiltration of nano-diamond suspension into porous presintered ceramics as well as mixing of nano-diamond suspension with raw Tourmanium powder during spray granulation were tested. For obtaining optimal parameters the manufacturing technology of the new Nano-Diamond-Tourmanium (NDT) ceramics was mainly controlled by infrared emission and thermal diffusivity measurements. Using thermo-gravimetric and dilatometric measurements, X-ray diffraction, light and SEM microscopy as well as toughness and hardness tests the new NDT ceramics were comprehensively characterized. Finally substantial improvement of the infrared emission rate and the heating characteristics were achieved. Moreover, we could prove a significant higher bio-medical effect of NDT ceramics in comparison with Tourmanium one. For that purpose cell tests carried out and blood microcirculation were investigated by Laser Speckle Photometry and dark field microscopy.

4:20 PM

(ICACC-FS3-008-2015) Non-Destructive Testing (NDT) for Ceramics and Ceramics for NDT: A short review

B. Koehler*[1]; 1. Fraunhofer IKTS-MD, Germany

Although nondestructive testing (NDT) plays a role in the ceramic industry already for a long time, most of the NDT and nondestructive material characterization (NCM) methods has traditionally been developed with metallic materials and components in mind. Today, with increased applications of advanced ceramics in modern systems as fuel cells, high temperature electronics and sensors, the needs for NDT and material characterization increase. To fulfil these needs conventional methods are adapted to ceramic materials and very specific methods are developed. The talk will give an overview of the developments and illustrates this with interesting case studies. On the other side, ceramics play a central role in some NDT sensors especially in ultrasonic probes. It will demonstrated that advanced ceramic technologies as the manufacturing of piezoelectric fiber patches enable also new, alternative sensing principles.

4:40 PM

(ICACC-FS3-009-2015) Semi-automated inspection unit for ceramics

C. Wolf*[1]; A. Lehmann[1]; G. Unglaube[1]; 1. Fraunhofer Institute for Ceramic Technologies and Systems - Branch Materials Diagnostics, Germany

A swept source optical coherence tomography system (SS OCT) combined with the convenience of automated scanning capabilities defines an innovative way to inspect large objects three-dimensional in high-resolution. The OCT is an optical, non-destructive and non-contact measurement technology, which generates unique object data with up to 2 μm axial resolution. Our inspection system with a three-axis robotic positioning system is capable of measuring large areas up to 400 mm in square instead of the limited field of view of existent OCT setups. It demonstrates the capability for in-depth and high-speed quality inspections on high performance ceramic electrolytes. This makes it possible to detect flaws, like cracks, pinholes or inclusions in such samples. Pristine used in medical applications, the relevance of OCT for testing of non-biological samples in manufacturing and research is increasing. We presented a combination of SS OCT and a semi-automated scanning robot, which is perfectly suited for high-resolution, in-depth and high-speed acquisition needed for in-line quality management of high-performance ceramics and other materials.

FS4: Additive Manufacturing and 3D Printing Technologies

Additive Manufacturing and 3D Printing Technologies I

Room: Coquina Salon G

Session Chairs: Junichi Tatami, Yokohama National University; Michael Halbig, NASA Glenn Research Center

1:30 PM

(ICACC-FS4-001-2015) A Fully Nonmetallic Turbine Engine by Additive Manufacturing Technologies (Invited)

J. E. Grady*[1]; 1. NASA Glenn Research Center, USA

The Nonmetallic Gas Turbine Engine project, funded by the NASA Aeronautics Research Institute, represents the first comprehensive evaluation of emerging materials and manufacturing technologies that will enable fully nonmetallic gas turbine engines. This will be achieved by assessing the feasibility of using additive manufacturing technologies to fabricate polymer matrix composite and ceramic matrix composite turbine engine components. The benefits include: 50% weight reduction compared to metallic parts, reduced manufacturing costs, reduced part count and rapid design iterations. Two high payoff metallic components have been identified for replacement with PMCs and will be fabricated using fused deposition modeling (FDM) with high temperature polymer filaments. The CMC effort uses a binder jet process to fabricate silicon carbide test coupons and demonstration articles. Microstructural analysis and mechanical testing will be conducted on the PMC and CMC materials. System studies will assess the benefits of fully nonmetallic gas turbine engine in terms of fuel burn, emissions, reduction of part count, and cost. The research project includes a multidisciplinary, NASA - industry team that includes experts in ceramic materials and CMCs, polymers and PMCs, structural engineering, additive manufacturing, engine design and analysis, and system analysis.

2:00 PM

(ICACC-FS4-002-2015) Additive Manufacturing of Silicon Carbide-Based Ceramics by 3-D Printing Technologies

S. X. Zhu*[1]; M. C. Halbig[2]; M. Singh[3]; 1. The Ohio State University, USA; 2. NASA Glenn Research Center, USA; 3. Ohio Aerospace Institute, USA

Silicon carbide (SiC)-based materials are needed for a number of high temperature applications due to their excellent strength, thermal stability, and oxidation resistance. Fabrication of functional SiC ceramics by additive manufacturing technologies greatly reduces production time and cost, particularly for small production quantities necessary for prototype development. Two approaches which utilize 3-D printing technologies to obtain a SiC ceramic were investigated in this study. Various shapes with engineered porosity were printed using a commercially available wood filament which served as a carbonaceous preform. The printed samples were infiltrated with a pre-ceramic polymer containing dip-coat solution then pyrolyzed. The effect of solution composition on structure retention and conversion to SiC were investigated. In the second approach, pre-ceramic pastes comprised of SiC, silicon (Si), and carbon (C) particulates, were evaluated as a potential extruder feedstock. Characteristic decomposition patterns in nitrogen and air were observed using thermogravimetric analysis (TGA) and X-Ray Diffraction (XRD) was used for phase identification. The effect of Si addition, SiC particle size, and pyrolysis conditions on the conversion to SiC has been studied.

2:20 PM

(ICACC-FS4-003-2015) 3-D Printing and Characterization of Polymer Composites with Different Reinforcements

A. Salem*[1]; B. Hausmann[1]; N. Wilmoth[2]; G. L. Piper[3]; M. C. Halbig[4]; B. E. Lerch[4]; J. Salem[4]; J. E. Grady[4]; M. Singh[5]; 1. St. Ignatius High School, USA; 2. Vantage Partners, LLC, USA; 3. Jacobs Technology, USA; 4. NASA Glenn Research Center, USA; 5. Ohio Aerospace Institute, USA

Recently there has been tremendous growth in the additive manufacturing of polymers using 3-D printing technologies. In addition to commercially available high end fused deposition modeling (FDM) machines, desktop 3-D printers and open source printers have facilitated the large scale growth of distributed digital manufacturing. Two types of filaments (ABS and PLA) are used by many of these printers. However, the effect of filament composition, reinforcements (chopped fibers and nanotube), and 3-D printing variables on the microstructure and thermomechanical behavior is not well understood and systematic studies are needed. In this work, different types of ABS and PLA materials with and without carbon fiber and carbon nanotube reinforcements were printed under various processing conditions. Microstructure, elastic behavior, tensile behavior, and fracture toughness of these specimens was characterized. Elastic modulus as measured using impulse excitation was compared with the mechanically measured modulus. The effects of different materials, reinforcements, and printing parameters on the microstructure and mechanical properties will be discussed in detail.

2:40 PM

(ICACC-FS4-004-2015) Rheological properties of aqueous based ZrO2-slurries for Additive Manufacturing

M. D. Araújo*[1]; C. M. Gomes[2]; G. Steinborn[2]; W. Acchar[1]; J. Günster[2]; 1. Federal University of Rio Grande do Norte, Brazil; 2. Federal Institute for Materials Research and Testing, Germany

Additive Manufacturing (AM) is a process for directly producing complex components without tooling where the materials usually are added layer by layer. Several conventional processes have been developed to manufacture ceramics components, such as tape casting, gel casting, etc in which concentrated ceramic slurries in an aqueous or non-aqueous media are used. In AM, the LSD offers also the possibility to process slurries layer-by-layer into a 3D part. In this way, the study of the rheological characteristics and the stabilization of the suspension with high concentration of solids is of

fundamental importance. Aqueous based slurries from commercial yttria stabilized zirconia (3Y-TZP) were produced and characterized, with different solids loading and with and without addition of dispersants. The slurry stability is achieved by utilizing two commercially available dispersants, Disperblast 1142 and Triton X-114. The effects of the dispersants content and the solid loading on the rheological measurements have been performed to investigate the suspensions properties. All the slurries show typical shear-thinning fluid behavior. Rheological measurement confirmed that well dispersed slurries could be obtained with the solid content as high as 79,6 wt%. It was shown that the adsorption of the dispersant Triton X-114 could effectively improve the stability of ZrO2 slurries for the LSD process.

3:20 PM

(ICACC-FS4-005-2015) Controlling the Coffee Stain from Inkjet Printed Drops (Invited)

Y. Liu*[1]; R. Bradley[1]; B. Derby[1]; 1. University of Manchester, United Kingdom

The aim of this study is to improve the quality of 3D inkjet printed ceramic structures by reducing the coffee stain (or coffee ring) that forms during the drying process of inkjet printed drops. ZrO_2 inks have been used to print drops and 3D structures using a laboratory scale inkjet printer. Inks were formulated using a range of solvents and solvent mixtures in order to control the coffee stain that forms and to study the influence of the drying condition. Coffee stains and printed lines were characterized through optical phase contrast microscopy (PCM) and scanning electron microscopy (SEM). The influence of coffee staining on the internal defect population within 3D inkjet printed ZrO_2 structures prior to sintering and after sintering have been studied by characterizing the structures through high-resolution X-ray micro-tomography. The temperature of the substrate during printing has a great influence on almost all the inks studied but at higher temperatures there appears to be less effect of ink composition on the magnitude of the coffee stain. Mechanisms for this observation were presented.

3:50 PM

(ICACC-FS4-006-2015) New water-soluble and water-thinnable organic additives in processing of advanced ceramic materials

M. Szafran[1]; P. Falkowski*[1]; P. Wiecinska[1]; 1. Warsaw University of Technology. Faculty of Chemistry, Poland

The key role in the colloidal processing plays the selection of some suitable polymers or monomers, which are able to provide high mechanical strength of formed elements. The applied monomers must meet some strict requirements: they should be water-soluble and non-toxic, moreover, good mechanical properties of ceramic elements must be achieved by as low as possible addition of polymer or monomer in ceramic slurry. The present work shows selected properties of some new, effectively working compounds based on monosaccharides, which can be used as deflocculants, organic monomers and self cross-linking compounds in colloidal processing of high quality ceramic elements. The synthesis of new acryloyl compounds based on glucose, fructose and galactose is presented as well as application of synthesis products in processing of advanced ceramic materials. The influence of spatial structure of as-obtained monomers on rheological properties of alumina suspensions is widely discussed. Selected properties like density or tensile strength of ceramic green bodies are demonstrated. The multifunctional role of monosaccharides derivatives is pointed out, as well as advantages of their application. This work has been financially supported by the National Centre for Research and Development (Poland) (agreement no PBS1/A5/19/2012) and by the Warsaw University of Technology.

4:10 PM

(ICACC-FS4-007-2015) Contour Crafting (CC) of Advanced Ceramic Materials

M. Shirooyeh*[1]; M. Vali[1]; P. Torabi[1]; P. W. Rehrig[2]; O. Kwon[2]; B. Khoshnevis[1]; 1. University of Southern California, USA; 2. Saint-Gobain, USA

Contour Crafting (CC) is an Additive Manufacturing technology that can fabricate parts with high surface quality and geometric accuracy at relatively high speed out of a variety of materials including ceramics. CC is a layer-by-layer additive manufacturing method empowered by a computer controlled trowel mechanism which produces smooth surfaces with unusually thick layers. This study presents the recent developments in Contour Crafting of functional components from Al_2O_3 and ZrO_2 ceramics. Processing parameters in the CC machine such as extrusion rate, linear speed of the extrusion head, layer thickness, and pivoting and rotation angles of the side trowel about Z-axis, as well as materials parameters such as rheology, powder/water ratio and green density, and also final product parameters including surface finish, density, uniformity and dimensional integrity were studied. It is shown that the dense parts produced by Contour Crafting exhibit promising mechanical properties thereby assuring that the fabrication method has the potential to produce a wide range of high performance ceramic materials.

FS5: Single Crystalline Materials for Electrical, Optical and Medical Applications

Scintillator

Room: Tomoka C

Session Chairs: Kiyoshi Shimamura, National Institute for Materials Science; Robert Feigelson, Stanford University

1:30 PM

(ICACC-FS5-001-2015) Discovery, Growth and Characterization of Scintillators (Invited)

E. Bourret*[1]; G. Bizarri[1]; S. E. Derenzo[1]; 1. Lawrence Berkeley National Laboratory, USA

The ability to make new materials is often key to major progress in fundamental physics and numerous applications. In that context, we will present the versatile materials synthesis and crystal growth facilities developed at Lawrence Berkeley National Laboratory and discuss the impact on science and applications using scintillator materials as example. As there is a strong need for applications-driven new materials, mainly due to the needs for domestic and international security, the pace of discovery of new scintillators has increased dramatically the last few years, The multi-disciplinary approach used at LBNL for discovering scintillators for gamma detection that approach fundamental limits in terms of luminosity, energy resolution, stopping power and response time will be presented. This project has resulted in the discovery of dozens of new scintillators, the best of which have been grown as single crystals and has led to the discovery of some of the brightest known Eu-doped scintillators. In addition to applied research, systematic fundamental studies can be done based on the large amount of data accumulated from characterized samples. This allows for determination of trends in optical properties of classes of compounds that can be used to engineer new materials with tailored properties.

2:00 PM

(ICACC-FS5-002-2015) Co-doping technique in scintillation materials synthesis (Invited)

J. M. Frank*[1]; P. Menge[1]; K. Yang[1]; V. Ouspenski[2]; S. Blahuta[2]; J. Lejay[2]; 1. Saint-Gobain Crystals, USA; 2. Saint-Gobain Recherche, France

The engineering of scintillator material performance is a new area enabled by co-doping. Co-doping demonstrates a significant performance improvement of scintillation materials like LYSO:Ce:Ca or more recently for LaBr3:Ce:Sr/Ba or CeBr3:Sr/Ca. In this report we share an alternative co-doping technique which is applied to the melt for crystal growth. The objective is to reduce the anionic vacancies in crystals under growth. Post growth annealing could be omitted in the case of the use of oxidizing (halogenating) agents added directly into the melt of the grown compound. The cationic presence in crystalline matrix is detected at a trace level only and is not involved in the scintillation process. The scintillation parameters of the compound are improved via vacancy reduction. One example is the crystal LYSO:Ce with the use of SnO2 or ZnO. These compounds reduce the number of oxygen vacancies in the LYSO melt and in the grown crystal. The dopants are effectively segregated during crystal growth without effect of cation co-doping of crystalline matrix. The use of oxidizing agents for LYSO:Ce:Ca compound improves the light yield from standard values 34000 ph/MeV at 662 keV up to 41000 ph/MeV. A similar effect is found for LaBr3 or CeBr3 compounds when the melt is co-doped by ZnBr2, ZrBr4 or HfBr4. Melt treatment by volatile bromine agents is responsible for reduction of Br- vacancies in the relevant crystalline matrix.

2:30 PM

(ICACC-FS5-003-2015) Growth of Halide Single Crystals by the EFG Method (Invited)

R. S. Feigelson*[1]; G. Calvert[1]; A. Yeckel[2]; J. Derby[2]; 1. Stanford University, USA; 2. University of Minnesota, USA

Many halide crystals are excellent scintillators useful as radiation detectors. Some of the newer, more efficient crystals are, however, very expensive and therefore deployment is financially prohibitive. The EFG method permits the growth of shaped crystals at higher growth rates than many other crystal growth methods. This increases production throughput and reduces machining costs. The method involves pulling crystals from shaped dies placed on or in the melt surface. The die not only shapes the crystal cross-section but also provides steeper thermal gradients at the growth interface. The EFG growth of CsI and SrI2, two important scintillator compounds, will be discussed. CsI, is mildly hygroscopic while SrI2 is deliquescent and requires special handling. In these experiments floating graphite or quartz dies were used. Both round and square cross-section crystals of both materials were grown at rates up to 45 mm/hr and 8 cm long. Some bubble tracks found in CsI crystals grown from graphite dies were not present in crystals grown from quartz. Bubble tracks were not present in SrI2 crystals grown from graphite dies but contained scattering centers giving the crystals a milky appearance. The growth system and parameters will be discussed along with examples of the large single crystals produced and thermal modeling studies of the sensitivity of the growth interface and crystal diameter to furnace-scale heat transfer.

3:20 PM

(ICACC-FS5-004-2015) Crystal Growth at Northrop Grumman SYNOPTICS (Invited)

K. T. Stevens*[1]; D. Solodovnikov[1]; M. Randles[1]; G. Foundos[1]; 1. Northrop Grumman SYNOPTICS, USA

Northrop Grumman SYNOPTICS is a leading supplier of single-crystal laser materials grown by the Czochralski technique. Recently, additional crystal materials have been added to the available products offered by SYNOPTICS to serve both the laser and radiation detection industries. Over the past few years, Strontium Iodide has gained attention in the scintillator industry as a gamma radiation detector because of its superb energy resolution and high light-yield values. Recently, new efforts have been undertaken by Northrop Grumman SYNOPTICS to grow Strontium Iodide scintillator crystals via the Vertical Bridgeman growth process. Because of the material's hygroscopic nature, a sealed quartz ampoule was utilized with a two-zone vertical furnace to achieve single-crystal growth. To date, growth of large, crack-free crystals has been accomplished. Test results showed crystals yielding an energy resolution of < 3.0%. However, while exhibiting several superior characteristics as a radiation detector, there are many difficulties with the growth, fabrication, and packaging of strontium iodide for use in commercial detectors. In addition to scintillation products, new laser crystal materials have been added to the product portfolio of Northrop Grumman SYNOPTICS. The growth, characterization, and application of materials for use as laser gain media and Faraday rotators will be presented.

3:50 PM

(ICACC-FS5-005-2015) Densification of Halide Scintillator Ceramics at Low-Temperature and High-Pressure

T. Shoulders*[1]; B. D. Doan[1]; M. Gascon[2]; G. Bizarri[2]; E. Bourret-Courchesne[2]; R. Gaume[1]; 1. University of Central Florida, USA; 2. Lawrence Berkeley National Laboratory, USA

Many novel optical materials, specifically the halides, are difficult to process in polycrystalline form due to their sensitivity to the ambient atmosphere. We present a completely sealed hot pressing system suitable for processing ceramics of air-sensitive materials. A compressible vacuum chamber housing the heating element and die is detachable from the press frame allowing precursor powders to be handled and loaded inside a glove box. The hot press operates at a low temperature (0-500°C) and high pressure (0-20 US tons) compared to many commercial systems. The pressing chamber is capable of holding a vacuum of 5 x 10^{-3} millibar. We present the results of sintering barium chloride scintillator ceramics. These results are analyzed with respect to residual porosity, densification rate, and optical clarity. Results from low temperature, high pressure experiments are compared to results obtained using a commercial hot press to demonstrate the benefit of the different pressing regime.

4:10 PM

(ICACC-FS5-006-2015) Compound Semiconductor X- and Gamma-Ray Radiation Detectors (Invited)

R. B. James*[1]; A. Bolotnikov[1]; G. Camarda[1]; Y. Cui[1]; A. Hossain[1]; U. Roy[1]; G. Yang[1]; W. Lee[2]; K. Kim[2]; 1. Brookhaven National Laboratory, USA; 2. Korea University, Korea (the Republic of)

Compound semiconductors are important for detecting and imaging X- and gamma-ray radiation. Cadmium Zinc Telluride (CZT) is the most extensively studied material today due to its band-gap, high atomic number, availability of large crystals, and good charge-carrier transport properties. We are pursuing a two-pronged approach to advance the technology, (1) Identify and fix defects in the crystals, and (2) Use the best material for fabricating detectors and incorporating them into instruments. We will report on the physical properties of CZT at the micro-scale level, and correlations of the crystal's defects with device performance. We built a set of dedicated tools for this R&D, including automated infrared transmission microscopy, X-ray micro-scale mapping using a synchrotron light source, X-ray transmission / refraction tomography, current deep level transient spectroscopy, and photoluminescence setups. This presentation will report some of our recent findings to improve the crystal growth and fabrication processes, improve the purification methods, distinguish various crystal defects and their effects on carrier trapping, study the internal electrical field in detectors, and clarify the effects of annealing on the material's properties. We will also report progress towards development of new high-granularity detectors that provide high performance using average-grade and relatively low-cost crystals.

4:40 PM

(ICACC-FS5-007-2015) (Cd,Mn)Te as a New Material for X - ray and Gamma – ray Detectors (Invited)

A. Mycielski*[1]; M. Witkowska-Baran[1]; D. Kochanowska[1]; A. Szadkowski[1]; B. Witkowska[1]; R. Jakiela[1]; W. Kaliszek[1]; A. Wittlin[1]; W. Knoff[1]; A. Suchocki[1]; P. Nowakowski[1]; K. Korona[2]; E. Kaminska[4]; M. Juchniewicz[4]; M. Lewandowska[3]; M. Rasinski[3]; 1. Institute of Physics Polish Academy of Sciences, Poland; 2. University of Warsaw, Poland; 3. Warsaw University of Technology, Poland; 4. Institute of Electron Technology, Poland

The semiinsulating (Cd,Mn)Te crystals are believed to be materials suitable for effective manufacturing of large area X- and gamma – ray detectors, instead of commonly used (Cd,Zn)Te and CdTe crystals. The purpose, was to elaborate a technology of the (Cd,Mn) Te crystals plates with high resistivity, uniform in the whole volume of the plate, and with high homogenous $\mu\tau$ product, where μ and τ are drift velocity, and lifetime of carriers, respectively. The semiinsulating (Cd,Mn)Te crystals, doped (for compensation) by vanadium (V) or Cl or In, or Cl together with V, were grown by the Bridgman method. The monocrystalline plates were cut out of the ingot. The plates were annealed in the Cd-vapour. After annealing the resistivity of the plates was around 10^9 Ωcm, and the $\mu\tau$ – product was from10^{-4} to 10^{-3} cm^2 /V. Annealing in the saturated Cd vapours influenced the amount of tellurium inclusions/precipitates. The photoluminescence (PL), time resolved photoluminescence (TRPL), and electron paramagnetic resonance (EPR) measurements indicated that after annealing the concentration of intrinsic acceptors (V_{Cd}) become significantly lower. Density and structure of defects were measured by the etch pit density (EPD) and scanning electron microscopy (SEM). The best electrical contacts to semiinsulating (Cd,Mn)Te crystal plates were made by the amorphous layer of Sb doped ZnTe covered by an Au layer.

5:10 PM

(ICACC-FS5-008-2015) Shaped Scintillating Materials (Invited)

C. Dujardin*[1]; 1. University Lyon1, France

Scintillating materials are widely used in many applications where ionizing radiation detection is needed. Their requirements in terms of performances depend on the final application and on the way they are used . A significant number of parameters are generally checked such as scintillation yield, decay time, density and effective atomic number, chemical and mechanical stability, radiation hardness, index of refraction, industrial capability to produce large quantities, etc... Another crucial point is the shape. Scintillators are thus used as single crystals (high-energy physics, medical imaging, etc.), as powders (X-ray phosphors), needles, organic or inorganic fibers, and even as liquids . The aim of this presentation is to provide a review of this latest aspect, combining illustration of various needs, current capabilities, performences and achievements.

FS6: Field Assisted Sintering and Related Phenomena at High Temperatures

Flash Sintering Phenomena and Mechanisms

Room: Coquina Salon H
Session Chair: Rishi Raj, University of Colorado

1:30 PM

(ICACC-FS6-001-2015) The Phenomenon of Flash Sintering: Scientific and Technological Implications (Invited)

R. Raj*[1]; 1. University of Colorado at Boulder, USA

In flash sintering, ceramics that nominally require several hours at temperatures near 1500 oC, sinter to nearly full density in a matter of seconds at furnace temperatures that may lie below 1000 oC, under modest electrical fields applied directly to the specimen. The "flash" not only produces ultrafast rates of self-diffusion, which is needed for densification, but also a dramatic increase in electrical conductivity, as well as intense electroluminescence in the visible range. Thus, the uncharged (sintering) and charged (conductivity) species, and the production of photons (e-h recombination?) occur all at once. These aspects of this unusual phenomenon will be discussed. The short sintering time and low furnace temperatures may offer new ways of manufacturing ceramics, for example by a continuous rather than a batch process. An example of such a system will be described. Supported by the Basic Energy Sciences Division of the Department of Energy and by the Office of Naval Research.

2:00 PM

(ICACC-FS6-002-2015) Electric field-assisted sintering of zirconia-3 mol% yttria

S. G. Carvalho*[1]; R. Muccillo[1]; E. N. Muccillo[1]; 1. Energy and Nuclear Research Institute, Brazil

Green pellets of ZrO2:3 mol% Y2O3 were sintered by applying ac (60 Hz and 0.5-1.1 MHz) electric fields (typically 100 V.cm-1) during the first stage sintering process (T < 1200oC). The experiments were carried out positioning the specimens inside a vertical dilatometer with platinum disks acting as electrodes in a capacitor-like setup. The shrinkage level was controlled by monitoring the dilatometer gauge, allowing either for stopping the shrinkage at pre-determined shrinkage levels or applying the same voltage at the same temperature during the same period of time. Under the same conditions of temperature and magnitude of the applied ac voltage, the threshold shrinkage level attained for similar green pellets was found to depend on the frequency of the applied field. This result signals to suggest that the amount of Joule heating imparted to the specimen depends on the number of charge carriers (mainly oxide ions) collisions. A phenomenological mechanism taking into account the enhancement on the intrinsic thermodynamic oxide ion vacancy concentration due to localized Joule heating is proposed as the main responsible for sintering.

2:20 PM

(ICACC-FS6-003-2015) Towards the flash sintering of zirconium diboride

W. A. Paxton*[1]; H. Bicer[1]; T. E. Ozdemir[1]; I. Savkliyildiz[1]; E. Akdogan[1]; Z. Zhong[2]; T. Tsakalakos[1]; 1. Rutgers, The State University of New Jersey, USA; 2. Brookhaven National Laboratory, USA

Flash sintering is an exciting development in ceramic processing where densification temperature and time are greatly reduced through the application of an electric field. As a result, flash sintering uses considerably less energy and therefor has the potential to enable new applications for materials where processing is traditionally cost-prohibitive. Zirconium diboride is an ultra-high temperature ceramic (UHTC) for which low-cost processing would be a real boon. Successful flash sintering of zirconium diboride could be transformative for applications in atmospheric re-entry, hypersonic flight, and continuous metallurgical processing. Flash sintering experiments are conducted in a custom-built pressure-less desktop furnace. Three different powders are tested over a range of direct-current voltages and temperatures. Archimedes density measurements, gas pycnometry, scanning electron microscopy, and hardness measurements are used to characterize the processed samples. Additionally, energy-dispersive synchrotron x-ray diffraction (EDXRD) is used to monitor the process in situ with high temporal resolution. Variance of electric field shows little effect on density outcome. Isotropic expansion of lattice parameters is observed with correlation to the current flow in the sample.

2:40 PM

(ICACC-FS6-004-2015) Microstructural coarsening and electrical conductance at nanoscale of Si_3N_4/TiC nanocomposites in spark plasma sintering

C. A. Lee*[1]; H. Lu[2]; H. B. Liu[1]; D. Lii[3]; J. Huang[1]; 1. National Cheng Kung University, Taiwan; 2. National Chin-Yi University of Technology, Taiwan; 3. Cheng Shiu University, Taiwan

A conductive TiC nano powder was incorporated into nanosized β–Si_3N_4 based powder and consolidated by spark plasma sintering. Firstly, the influence of conductive phase on the microstructure development of Si_3N_4 matrix was demonstrated. In the composite containing 5 wt% TiC, microstructural coarsening of Si_3N_4 grains is observed over that of monolithic Si_3N_4, probably owing to higher heating rate or a temporary temperature rise by dielectric breakdown mechanism at a localized region. When the amount of conductive phase is added above 10wt%, the pinning effect results in suppression of grain growth of Si_3N_4. Secondly, the use of localized impedance measurements with a conductive AFM based technique on Si_3N_4 containing 20 wt% TiC allows differentiation among the electrical properties of the isolated Si_3N_4 grains, the connective network of the glassy phase and conductive nano-TiC at nanoscale. TEM provides 2D projections of the microstructure near grain boundaries and EDS line scanning gives the chemical composition profile across the boundaries. It is concluded that the incorporation of nano-TiC in the sintering bulk might provide electro-conductive paths, and thus the field-activated mechanisms could enhance densification during the spark plasma sintering process.

3:20 PM

(ICACC-FS6-005-2015) Towards induced flash sintering in a spark plasma sintering furnace

E. Zapata-Solvas*[1]; D. Gómez-García[2]; A. Domínguez-Rodríguez[2]; R. I. Todd[3]; 1. CSIC-US, Spain; 2. University of Seville, Spain; 3. University of Oxford, United Kingdom

Traditionally, electric current sintering techniques (ECAS) are divided into electric discharge sintering (EDS) and resistive sintering (RS). Both techniques depends on electric nature of die; (i) EDS is carried out with an electric insulator die to sinter electric conductor ceramics, (ii) RS is carried out with an electric conductor die to sinter conductor or non-conductor ceramics, such as spark plasma sintering (SPS). Recently, the design of a new mold, which concentrates the electric current through the specimen bulk (EDS) or throughout specimen surface (RS) depending on electric nature of specimen, has allowed the fabrication of dense ZrB2, MoSi2, ZrB2/MoSi2 composites, Al2O3 and 3Y-TZP among other ceramic systems in less than 1 minute. Energy consumption is from 1 to 7% compared to SPS with heating rates higher than 3000 °C/min and maximum working temperature of ≈2700 °C. Flash sintering could be considered a transition to an EDS process at certain temperature under an electric field intense enough. However, some resistive heating is required to reach the transition temperature. Electric fields during conventional SPS are not high enough to induce flash sintering in ionic-conductor or semiconductor ceramic materials. However, electric fields under this new approach are stronger than in conventional SPS and could be tailored to induce flash sintering in a SPS furnace.

3:40 PM

(ICACC-FS6-006-2015) Flash Sintering Yttria-stablized Zirconia (3Y-TZP) and Zirconia-3mol%Yttria Nanocomposites

J. Liu*[1]; D. Liu[1]; Y. Wang[1]; L. An[2]; 1. Northwestern Polytechnical University, China; 2. University of Central Florida, Orlando, USA

The effects of dc electrical field and current on flash sintering yttria-stablized zirconia (3Y-TZP) and zirconia-3mol%yttria nanocomposites (3Y-N) were studied. We show the 3Y-N required higher onset temperature under the same electrical field compared to 3Y-TZP, which arising from the lower defect concentration in the 3Y-N powders, as well as lower conductivity. The grain size and grain-boundary thickness of the dense sintered bodies were measured by scanning electron microscopy and impedance spectroscopy. We also analyzed the conductivity and permittivity of the bulk and grain boundary. The contribution of Y-dopant/yttria on densification and grain growth for both sets of samples were discussed.

4:00 PM

(ICACC-FS6-007-2015) Abnormal Lattice Expansion in Sintered 8% Y2O3-ZrO2 under Simultaneous Applied Electric and Thermal Fields Using in situ EDXRD Method with an Ultrahigh Energy Synchrotron Probe

I. Savkliyildiz*[1]; E. Akdogan[1]; H. Bicer[1]; E. Ozdemir[1]; R. Raj[2]; Z. Zhong[3]; T. Tsakalakos[1]; 1. Rutgers University, USA; 2. University of Colorado at Boulder, USA; 3. Brookhaven National Lab, USA

Effects of superimposed thermal and electric field on sintered 8% yttria doped zirconia (8YSZ) samples which are flash sintered sample(FSS) at 900 C and sinter forged sample(SFS) at 1400 C, resulted particle size of 250 nm and 1μm, respectively, was studied under 100 V/cm dc electric field and 12 oC/min heating rate, using time-resolved in-situ high temperature energy dispersive x-ray diffractometry with a polychromatic 200 keV synchrotron probe. The maximum 1,5 A current draw observed on FSS at 614 oC,corresponding power dissipation on sample approximately 2.14 kW/cm3with 1.64 % expansion on unit cell volume. However, on SFS two different current draw mechanisms which are 0.6 A and 3.0 A was recorded at two different temperatures which are 630 oC and 643 oC, respectively. The power dissipations on SFS due to current draw is 0.375kW/cm3 at 630 oC and 1.36 kW/cm3 at 643 oC, with 0.53 % and 2.61 % unit cell volume expansions, respectively. The peak width is not affected by the electrical and thermal process on both FSS and SFS which means that there is no changing at crystallite size (coherently diffraction domains) of samples. No local melting at particle-particle contacts was observed in scanning electron micrographs as well as no theoretical density improvement was measured on both samples.

4:20 PM

(ICACC-FS6-008-2015) Fabrication of Al2O3-Hydroxiapatite composites by chemical synthesis and SPS

L. Flores-Esperilla[1]; L. Tellez-Jurado[1]; H. Balmori*[2]; S. Diaz-de-la-Torre[3]; 1. National Polytechnic Institute, Mexico; 2. National Polytechnic Institute, Mexico; 3. National Polytechnic Institute, Mexico

Alumina-Hidroxiapatite (HA) composites are prepared by chemical synthesis, mixing and Spark Plasma Sintering (SPS). HA is obtained by precipitation of calcium hydroxide and phosphoric acid in water. Alumina is synthesized by a sol-gel method. Bohemite precipitates by this method. The bohemite and HA are mixed by high-energy ball milling and densified by SPS at 1100°C at holding times of 0 and 10 min to fabricate Al2O3-(5-90) HA composites. The samples are characterized by XRD, FT-IR and SEM. Nanometric particles of HA and bohemite are obtained by chemical synthesis. A homogeneous powder mixture is obtained by milling. After SPS, the bohemite transforms to α-Al2O3, but the Al2O3-HA composites show the presence of θ-Al2O3 and δ-Al2O3. The HA does not decompose during SPS. The (0-40 %) HA composites show hexagonal prismatic grains of alumina. The Al2O3 grain size and aspect ratio increase with sintering time. The composites that have > 50 % HA show Al2O3 particles dispersed in a matrix of HA equiaxial grains. Regarding porosity, the composites with 0-50 % HA have > 14 % porosity, while the composites with > 50 % HA are almost fully dense. In conclusion, HA delays the formation of α-Al2O3. HA delays densification and promotes the formation of prismatic alumina grains in the composites with < 40 % HA. Composites with > 50 % HA are dense and have Al2O3 particles dispersed in a matrix of equiaxial HA grains.

4:40 PM

(ICACC-FS6-009-2015) Effects of Applied Electric and Thermal Fields on the Oxidation of Titanium Diboride

T. E. Ozdemir*[1]; I. Savkliyildiz[1]; E. Akdogan[1]; H. Bicer[1]; Z. Zhong[2]; T. Tsakalakos[1]; 1. Rutgers University, USA; 2. Brookhaven National Laboratory, USA

TiB2 is a high strength ceramic material which is considered for use in military armors. It is an excellent electrically and thermally conductor. The biggest issues with TiB2 are its poor sinterability and sensitivity to oxidation. In this study, TiB2 pellets of 58 nm average particle size were used. Oxidation process of TiB2 under electric and thermal fields was studied in situ time-resolved, high temperature EDXRD with a polychromatic 200 keV synchrotron probe. Firstly, we report the oxidation process of TiB2 under temperature up to 600 °C with no applied electric field as a reference study. The results showed that no extra peak had occurred. Secondly, we report effects of electric field over the same temperature range. Temperature was increased to 330 °C, and dc electric field of 4.44 V/mm was applied instantaneously at the mentioned temperature. It yielded the sample to become conductive. Current reached 10A and stayed stable. Both experiments were carried out under Argon gas of 4 psi pressure. We observe an electric field facilitated irreversible oxidation of TiB2 under 600 °C that it yielded TiBO3 peaks almost instantaneously. A shift in the peak positions also occurred during current draw as a result of unit cell expansion due to charge transport. Current induced unit cell expansion will be discussed based on tunneling phenomena at particle-particle contacts.

5:00 PM

(ICACC-FS6-010-2015) Flash Sintering of Ultrahigh Melting Temperature Covalent Nonoxide Ceramics at Low Temperatures with Low DC Electric Fields (Invited)

T. Tsakalakos*[1]; H. Bicer[1]; K. Akdogan[1]; I. Savkliyildiz[1]; T. E. Ozdemir[1]; W. Paxton[1]; A. Choksi[1]; J. Zhou[1]; Z. Zhong[2]; 1. Rutgers University, USA; 2. Brookhaven National Laboratory, USA

The fundamental purpose in Functional Ceramics Technology is to obtain 100% dense polycrystalline covalent nonoxide ceramics with grain size <100 nm at lowest temperature and shortest time. We report a new method of utilizing a low applied electric field on nano/micro B4C powder at low temperature <1000 oC so as to obtain a properly sintered ceramics with small grain size . The applied electric field helps to reduce the sintering temperature by at least a factor 0.33. The time frames involved are measured in minutes/seconds and not in tens of hours/days. We will focus on the B4C system. However, other nonoxide ceramics nanocomposites such as ZrB2, TiB2, Si3N4, SiC, BN and their combinations will be reviewed. We will also present results of an in situ time- resolved EDXRD study, using synchrotron radiation of 200 keV photons, as a function of electric field and temperature whereby the flash sintered nano-B4C particulate system shows an anomalous lattice expansion accompanied by a maximum current draw with an increase in density up to 99%. The effectiveness of the sintering method which relies on the understanding of the conductivity mechanism of non-oxide ceramics will be also discussed. Applications of the B4C ceramics in this flash sintering processing exhibiting small grain size including but not limited to ballistic armor will be shown.

2nd European Union - USA Engineering Ceramics Summit

Advanced Ceramic Technologies: Challenges and Future Prospects I

Room: Coquina Salon F
Session Chairs: Mrityunjay Singh, Ohio Aerospace Institute; Gerard Vignoles, University Bordeaux

1:30 PM

(ICACC-PRECS-001-2015) Advanced Ceramic Materials for Future Aerospace Applications (Invited)

A. Misra*[1]; 1. NASA Glenn Research Center, USA

With growing trend toward higher temperature capabilities, light-weight, and multifunctionality, significant advances in ceramic matrix composites (CMCs) will be required for future aerospace applications. The presentation will provide an overview of material requirements for future aerospace missions, and the role of ceramics and CMCs in meeting those requirements. Aerospace applications will include gas turbine engines, aircraft structure, hypersonic and access to space vehicles, space power and propulsion, and space communication. Current NASA research and development activities on advanced ceramic materials for both aeronautics and space missions will be presented. Key challenges for introduction of new ceramic materials, including structural integration and long-term durability, in aerospace applications will be discussed.

2:00 PM

(ICACC-PRECS-002-2015) Status of CMCs and C/Cs in the EU: markets, research & development, perspectives (Invited)

G. L. Vignoles*[1]; F. Teyssandier[2]; E. Bouillon[3]; 1. University Bordeaux, France; 2. CNRS, France; 3. Herakles, Safran Group, France

Since a long time CMCs with long fibers reinforcements have been developed and studied essentially at very low TRL levels in research laboratories. They were first aimed at very specific and dedicated applications requiring very high properties in harsh environments: high temperatures, oxidative ambiance, and high mechanical loads and/or heat fluxes. During the past five to ten years the paradigm has changed because broad market applications are now foreseen, principally in the field of civil aircraft. On the other hand, carbon/carbon composites have gained sooner a larger dissemination because of their use as aircraft brake disks; however, research efforts are still needed in order to provide more economically competitive materials. We will review the current research and development efforts carried out in the EU and discuss some near future perspectives in terms of materials improvement for existing applications and markets and of potentialities for new fields of application, as for an example low cost CMCs and C/Cs competing with CMOs or metallic alloys.

2:30 PM

(ICACC-PRECS-003-2015) Industrialization of Ceramics for Aerospace Applications (Invited)

M. Manoharan*[1]; 1. GE Aviation, USA

The development of aircraft engines with higher efficiencies and performance has often been driven by key innovations in high temperature materials. Ceramic materials provide very high temperature capability and light weight and were first introduced as thermal barrier coatings in aircraft engines. A newer generation of engines will have ceramic composites in the hot sections. A key to successful introduction of these ceramics components in engines is the ability to translate these innovations from laboratory to pilot scale and ultimately to production volumes. This talk will outline some of the key challenges unique to scale up of high performance ceramics.

3:20 PM

(ICACC-PRECS-004-2015) Ceramic Matrix Composites Based on Liquid Phase Routes (Invited)

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

Ceramic engineering materials play a more and more important role in people's everyday lives as part of commodities and luxury products. The biggest barrier we face in the use of these materials is their inherent brittleness and the lack of damage tolerance of ceramic structures. Ceramic matrix composites show considerably higher fracture toughness and have proven their feasibility in space and frictional applications like TPS and brake disks. However, these safety-critical components have to withstand harsh conditions in terms of temperature and corrosion only for short times, accumulated to some hours. Increasing interest in CMCs arise in long-term applications like components for the combustion environment. Oxide as well as non-oxide CMCs are under development to be used for example in future thermal power plants. Liquid phase routes like PIP, MI and slurry impregnation are promising manufacture routes to overcome the still high processing costs. In Germany, different approaches in institutes as well industries are on the way to develop new CMC processes on the basis of prepregs and other preforms with chopped and continuous oxide and non-oxide fibers. The paper reports about the current status of some of these research activities in this field of engineering ceramics.

3:50 PM

(ICACC-PRECS-005-2015) Recent development in joining of CMC (Invited)

M. Ferraris*[1]; 1. Politecnico di Torino, Italy

The introduction of CMC components into the hot section of jet engines represents a significant technology breakthrough for the jet propulsion industry and for CMC. CMC components will be on the LEAP jet engine, which will enter airline service in 2016, is being developed by a joint USA (GE) and EU (SAFRAN) company and will mark the first time CMCs are used for a commercial application. Starting from this technology breakthrough, recent development in joining and integration issues of CMC in EU will be briefly discussed. EU and national projects on these subjects, industrial involvements and research groups working in these areas will be presented, with the aim of strengthening and extending EU-USA cooperation in this field.

4:20 PM

(ICACC-PRECS-006-2015) Cost Effective Ceramics in High Efficiency Microturbines (Invited)

M. J. Vick*[1]; 1. U.S. Naval Research Laboratory, USA

Clean, efficient ceramic microturbines will soon be technologically viable. An exciting frontier for ceramic materials research is to make them economically viable as well. This talk will outline a simple architecture for a high-efficiency ceramic microturbine that could be adapted to fit the needs of various markets, including portable power generation, residential combined heat and power (CHP), quiet power generation for RVs, boats, trucks, and hybrid electric car range extenders. For each ceramic component in the engine, basic performance requirements, material options, cost and life targets, and viable fabrication processes will be reviewed, along with NRL's perspective on where these seem likely to meet near-term needs, or fall short. Objectives are: 1) to seek input from experts on new/emerging technologies that could be relevant to our current endeavors, and 2) to inspire focused R&D in affordable materials and fabrication methods that represent the lowest-hanging fruit, in this potentially very fruitful commercial space.

4:50 PM

(ICACC-PRECS-007-2015) Advanced Si-based Ceramics for Clean Energy Technologies (Invited)

H. Lin*[1]; 1. Guangdong University of Technology, China

Forecasts indicate that the total global energy consumption will increase up to 50% from 2007 to 2035 based on the data analyzed and published by the U.S. Department of Energy's Energy Information Administration. The key driving forces behind the predicted increase in worldwide demand include: 1) industrialization and strong economic growth in emerging markets, especially in China, India, Brazil, Russia, and South Africa, 2) globalization, and 3) concerns over national energy security by reducing energy imports. It is well recognized that the use of natural gas and coal will continue to grow and dominate the energy market, but that in turn causes an increased concerns about greenhouse gas (GHG) emissions and global warming that have caused many to look negatively at long-term use of fossil fuels. Therefore, there is an imminent need for alternative energy resources such as renewable and nuclear energy to meet the worldwide fast-growing demand. This need has now created tremendous new markets for these alternative and nuclear energy technologies. However, most renewable energy technologies still cannot compete economically with fossil fuels. This lecture will review how emerging advanced Si-based ceramic technologies would help to improve manufacturing and energy generation efficiency and bring renewable energy production closer to reality.

4th Global Young Investigator Forum

GYIF Award Lecture

Room: Coquina Salon C

Session Chairs: Thomas Fischer, University of Cologne; Eva Hemmer, INRS

1:30 PM

(ICACC-GYIF-001-2015) Nanocrystalline Ceramics: A Thermodynamic Perspective to Enable Design and Control (Invited)

R. Castro*[1]; 1. University of California, Davis, USA

Nanocrystalline ceramics (nanoceramics) refer to a class of ceramic systems where crystallite sizes are at the nanoscale, such as in nanoparticles, bulk polycrystalline structures, or even composites like metal-ceramics. This class has intrigued the scientific community already for many years due to their unique and unexpected properties that emerge largely from the inherent great interfacial areas in the form of surfaces and grain boundaries. From a thermodynamic perspective, the energetic contribution of interfaces to the total energy of the system is responsible for differences in polymorphisms as compared to bulk microscale, as well as an increased thermo-instability due to elevated driving force for coarsening. Recently, highly sensitive microcalorimetric techniques have been able to depict the energetic contributions from interfaces and enabled quantification of the effects on nanoceramics' behavior. This creates an unprecedented possibility of designing nanoceramics to meet targeted polymorphs and test mechanisms to increase nanostability on a thermodynamics basis.

2:00 PM

(ICACC-GYIF-002-2015) Fabrication, morphology control and engineering characteristics of highly porous ceramics with oriented micrometer sized cylindrical cells by gelation and freezing method

M. Fukushima*[1]; T. Ohji[1]; Y. Yoshizawa[1]; 1. National Institute of Advanced Industrial Science and Technology (AIST), Japan

Porous architectures composed of oriented micrometer sized cylindrical pores, nearly honeycomb-like shape, are of great interest in fundamental research and engineering applications, because they can improve mechanical reliability and provide various functionalities, together with very high potrosities above 90vol%. This report will give a brief introduction to the advanced processing methodology to create oriented micrometer sized cylindrical pore prepared by gelation freezing technique and the engineering characteristics related with the fluid permeability, machinability, compressive strength and thermal conductivity as well as electrochemical performance. Several morphological features in highly porous ceramics, including oritened morphologies interconncected and completely closed porous structures, will be also discussed from the processing factors, microstructural control and functional characteristics.

2:20 PM

(ICACC-GYIF-003-2015) Cermet synthesis under electric field

S. K. Jha*[1]; 1. University of Colorado, Boulder, USA

Cermet have long been proposed to be a next generation material that poses the best properties of both ceramics and metals; namely light weight, high temperature stability, strength and ductility. However, current processing techniques have put a practical limit on cermet manufacturing. Metal particles cannot be sintered with ceramic particles because of their lower melting point and susceptibility to oxidation long before the ceramic fraction starts to bond together. In an earlier study regarding titania/alumina composites (which have a significant gap in their sintering temperature (~ 400 C), we demonstrated a lowering of their sintering temperature and a negation of the constrained sintering effect by sintering under an electric field (flash sintering). In this work, we demonstrate sintering of 3 YSZ (m.p. ~ 2500 C) with 20 vol % aluminum metal (m.p. ~ 660 C) to a solid mass of ~ 90% theoretical density. XRD patterns have confirmed the presence of metallic aluminum as well as some alumina, which is created in-situ during flash sintering. Three point bending flexural test showed a strength of ~ 300 MPa. SEM analysis has shown some porosity at the interfaces, which once removed could allow higher flexure strength and toughness.

2:40 PM

(ICACC-GYIF-004-2015) Atomic arrangement of Polymer-Derived Ceramics studied by Pair Distribution Function from Electron Diffraction in TEM (Invited)

S. Hapis*[1]; H. Kleebe[1]; Y. Gao[2]; R. Riedel[2]; J. Rohrer[2]; X. Mu[4]; P. van Aken[3]; 1. Technical University Darmstadt, Germany; 2. Technical University Darmstadt, Germany; 3. Max Planck Institute, Germany; 4. University of Strasbourg/ CNRS, France

Focus of this study is the sensitivity of the final ceramic microstructure to the molecular structure of the precursor. Bulk ceramics with different polymers were synthesized and annealed at different temperatures. Subsequent examinations were carried out with Transmission Electron Microscopy (TEM), including High Resolution Transmission Electron Microscopy (HRTEM) and the calculation of the Pair Distribution Function (PDF) from electron diffraction patterns of the predominantly amorphous matrix. The Pair Distribution Function is a powerful technique to investigate the short range order in disordered materials like the amorphous Polymer-Derived Ceramics up to ~1400°C. The advantage of PDF from electron diffraction is that a very small sample volume can be analyzed in conjunction with the corresponding image information (HRTEM) compared to the already established X-ray or neutron diffraction techniques. It is known that the onset of crystallization in boron-containing ceramics is shifted towards higher temperatures; however, the resulting, slightly different, atomic arrangement in the amorphous PDCs is investigated and the relationship between molecular architecture and chemistry on the amorphous nature of the pre-ceramic and, in addition, its influence on the resulting crystallization behavior is highlighted.

Novel Concepts for Solar Cells

Room: Coquina Salon C

Session Chairs: Manabu Fukushima, National Institute of Advanced Industrial Science and Technology (AIST); Stefania Hapis, Technical University Darmstadt

3:20 PM

(ICACC-GYIF-005-2015) Perovskite solar cells – a tale of fascination (Invited)

B. Conings*[1]; 1. Hasselt University, Belgium

Organometal trihalide perovskite solar cells represent the fastest developing photovoltaic technology so far, combining an astonishing combination of favorable properties.[1,2] The impressive and rapid advances achieved so far bring forth highly efficient and solution processable solar cells that trump their silicon counterparts in terms of material and production cost, and their performance is forecasted to be equivalent very soon. This contribution aims to highlight several key aspects explaining why perovskite solar cells have become so successful on a short timescale, and at the same time address the challenges that have to be overcome in order to push this technology to a sufficiently mature level for large-scale applications. To that end, different device stacks are discussed, comparing their individual assets and deficiencies. Furthermore, strategies for performance tuning are presented, involving both the perovskite absorber as well as its adjacent hole and electron collecting contacts. Finally, the focus is put on the degradation mechanisms of this type of perovskites. [1] M. M. Lee, J. Teuscher, T. Miyasaka, T. N. Murakami and H. J. Snaith, Science 2012, 338, 643. [2] B. Conings, L. Baeten, C. De Dobbelaere, J. D'Haen, J. Manca and H.-G. Boyen, Adv. Mater. 2014, 26 (13), 2041.

3:40 PM

(ICACC-GYIF-006-2015) Highly efficient hybrid n-silicon/PEDOT:PSS solar cells

S. Jaeckle*[1]; M. Mattiza[1]; M. Goebelt[1]; S. Schmitt[1]; S. Christiansen[2]; 1. Max Planck Institute for the Science of Light, Germany; 2. Helmholtz Center for Materials and Energy, Germany

Hybrid inorganic/organic junction solar cells are promising candidates for highly efficient and cost-effective photovoltaic devices. The solution processed organic polymer serves as transparent front contact and introduces the charge separating interface, while the light is absorbed in the inorganic material with its good charge carrier transport properties. However, silicon (Si) is known for its low performance in majority carrier dominated Schottky junction devices with metals because of large reverse saturation currents and Fermi-level pinning by a high density of surface states. Yet, a junction with the 'metal'-like wide-gap polymer PEDOT:PSS and n-doped silicon shows remarkable characteristics. C-V and I-V measurments proof that at the hybrid n-silicon/PEDOT:PSS junction the Fermi-level is unpinned, an inversion layer is created on the silicon surface and the charge transport is dominated by minority carriers. We present planar n-Si/PEDOT:PSS junctions with open circuit voltages up to 640mV and power conversion efficiencies of 12%. We will also discuss possible degradation mechanisms of the hybrid solar cells under ambient conditions and the effect of encapsulation with low temperature deposited metal oxides. First results and the potential of combining this hybrid solar cell concept with nanostructured thin film silicon will be presented.

4:00 PM

(ICACC-GYIF-007-2015) Atomic layer deposition of metal oxides for nanostructured heterojunction solar cells

M. Goebelt*[1]; M. Latzel[1]; S. Schmitt[1]; S. Christiansen[2]; 1. Max-Planck-Institute for the Science of Light, Germany; 2. Helmholtz Center Berlin for Materials and Energy, Germany

Silicon nanowire (SiNWs) structures are promising a generation of efficient, low-cost thin-film silicon photovoltaics. But the high surface area of the SiNW arrays needs to controlled. Atomic layer deposition (ALD) is a perfect tool to achieve homogenous and conformal coatings on nanostructures with high aspect ratios. By precise deposition of metal oxides a Semiconductor-Insulator-Semiconductor (SIS) heterojuction can be realized as an innovative solar cell concept on SiNWs. Plasma enhanced ALD was used to deposit Al2O3 as tunneling oxide. Since the quality and the thickness (Angstrom-accuracy) of the tunneling oxide have a wide influence on the resulting power conversion efficiency of the proposed solar cell, the layer properties at different deposition conditions were analyzed to find the best process parameters. The combination of Al2O3 and ZnO based thermal ALD processes allows aluminum doped zinc oxide (AZO) films to be deposited, which act as transparent front contacts for the solar cell. The aluminum doping concentration of the AZO layer was controlled by adjusting the ratio of the Al2O3 and ZnO-cycles. For a high optical transparency and a low sheet resistance of the AZO films, a tradeoff between film thickness and Al-concentration has been found. Optimized ALD deposition routines are presented as well as conformal coated SiNWs. First results of SIS solar cells are discussed.

4:20 PM

(ICACC-GYIF-008-2015) Electrochemical Impedance Spectroscopy on Dye Sensitized Solar Cells: characterization case study on Carbon nanotubes / TiO_2 composite systems

D. Benetti*[1]; K. Dembele[1]; C. Trudeau[3]; S. Cloutier[3]; A. Vomiero[2]; F. Rosei[1]; 1. Institut national de la recherche scientifique, Canada; 2. University of Brescia, Italy; 3. École de technologie supérieure, Canada

Dye sensitized solar cells (DSSCs) represent a viable low-cost alternative to conventional photovoltaic devices. An important tool for the interpretation of the different photoelectron transfer processes occurring in a DSSC is the Electrochemical Impedance Spectroscopy (EIS) analysis. Here we present a case study, in which EIS is applied to characterize a DSSC photoanode composed of a mixture of carbon nanotubes (CNTs) and TiO_2 nanoparticles. Introduction of CNTs into TiO_2 mesoporous film increases electron collection and reduces charge recombination. Optimized device increased the short-circuit photocurrent (J_{sc}) and the photoconversion efficiency by 30% and 32%, respectively, compared to bare TiO_2 cell, up to maximum efficiency of 7.95%. We measured the two most relevant parameters describing the photoelectron transfer processes in a photoelectrochemical system, i.e. the chemical capacitance (C_μ) and the recombination resistance (R_{rec}) as a function of the applied bias, to understand the role of CNTs at the different interfaces. The results show a reduced charge recombination in the best cell, clearly identifying the physic-chemical mechanism behind the increase of photoconversion efficiency.

4:40 PM

(ICACC-GYIF-009-2015) TiO2 thick film sensitized with quantum dot through electrophoretic deposition

L. Jin*[1]; H. Zhao[2]; D. Ma[1]; A. Vomiero[2]; F. Rosei[1]; 1. Institut National de la Recherche Scientifique, Canada; 2. CNR-INO SENSOR Lab, Italy

Electrophoretic deposition (EPD) is a technique based on application of an external electric field to colloidal nanoparticles (NPs) suspended in a liquid medium to induce their migration and their final grafting to a desired electrode. It has been demonstrated for preparation of high efficiency photoanodes in which QDs are grafted to a mesoporous TiO2 NP thick film. As the performance of photoanodes is highly dependent on not only the loading amounts, but also the QDs dispersion in TiO2 film, it is very important to control the QDs loading process, while a systematic investigation of the physical chemical QD loading dynamic by EPD is still missing. Here, for the first time, we systematically investigated the dynamics of near infrared QDs loaded into TiO2 mesoporous film via EPD, including the determination of the main parameters regulating the process. In addition, we also demonstrated the increased stability of the core/shell structure compared to PbS QDs after EPD in terms of structure and optical properties. Considering our previous study confirmed a fast charge transfer from PbS/CdS to TiO2, QD sensitized TiO2 can be strong candidates for the development of highly efficient and stable photoanodes in PV devices and H2 generation through water splitting.

5:00 PM

(ICACC-GYIF-010-2015) Combined Semiconductor Nanostructures for Efficient Solar Water Splitting

F. Podjaski*[1]; J. Vukajlovic[2]; G. Tutuncuoglu[2]; F. Matteini[2]; H. Potts[2]; E. Alarcon-Llado[2]; V. Lau[1]; B. V. Lotsch[3]; A. Fontcuberta-i-Morral[2]; 1. Max-Planck-Institute for Solid State Research, Germany; 2. Ecole Polytechnique Fédérale de Lausanne, Switzerland; 3. Ludwig Maximilian University, Germany

Due to the environmental concern and economic dependence on the use of fossil energy carriers, the production of renewable and storable energy carriers has attracted a lot of attention since the past decades. We approach this by direct solar water splitting combining two semiconducting materials in a Z-scheme configuration. Highly textured core-shell (Al)GaAs nanowires grown by molecular beam epitaxy were proven to be very efficient light absorbers. We will show that they can also act as photo-anodes for the oxygen evolution reaction. Coating with thin metal-oxides enhances their stability, while maintaining high photocurrents of these otherwise unstable materials within the electrolyte. The relatively low absorption and high diffusion lengths in silicon suggest the use of p-doped Si-pillars as photocathodes for the hydrogen evolution at the back side of this Z-scheme hybrid system. We will show that metal-oxide coatings and addition of co-catalysts can reduce the high overpotentials at the silicon-electrolyte interface, shifting the onset potentials positive with respect to RHE at 1 sun illumination and improving the hydrogen gas evolution rates.

5:20 PM

(ICACC-GYIF-011-2015) WSi2 in Si/Ge composites: processing and thermoelectric properties

J. Mackey*[1]; A. Sehirlioglu[2]; F. Dynys[3]; 1. University of Akron, USA; 2. Case Western Reserve University, USA; 3. NASA Glenn Research Center, USA

Traditional Si/Ge thermoelectrics have potential for enhanced figure of merit (ZT) via nano-structuring with a silicide phase, such as WSi2. A second phase of nano-sized silicides can theoretically reduce the lattice component of thermal conductivity without significantly reducing the electrical conductivity. However, experimentally achieving such improvements in line with the theory is complicated by factors such as control of silicide size during sintering, dopant segregation, matrix homogeneity, and sintering kinetics. Samples were prepared using powder metallurgy techniques; including mechano-chemical alloying, via ball milling, and spark plasma sintering for densification. Processing, micro-structural development, and thermoelectric properties will be discussed. Additionally, couple and device level characterization will be introduced.

Tuesday, January 27, 2015

S1: Mechanical Behavior and Performance of Ceramics & Composites

Processing - Microstructure - Mechanical Properties Correlation I

Room: Coquina Salon D
Session Chair: Rajesh Kumar, United Technologies Research Center

8:30 AM

(ICACC-S1-012-2015) Functionally Graded Alumina-Silicon Carbide Materials for Robust Joints and Wear Resistant Surfaces

C. E. Dancer*[1]; N. A. Yahya[3]; T. Berndt[4]; C. J. Salter[2]; M. Achintha[5]; J. A. Fernie[6]; G. de Portu[7]; R. I. Todd[2]; 1. University of Warwick, United Kingdom; 2. University of Oxford, United Kingdom; 3. University of Malaya, Malaysia; 4. Otto-von-Guericke-Universität, Germany; 5. University of Oxford, United Kingdom; 6. Ceramics Joining Limited, United Kingdom; 7. ISTEC-CNR, Italy

Functionally graded ceramics are useful in a number of applications as they enable two or more ceramic materials with different properties to be combined in a single structure. In this work alumina and silicon carbide, being materials with very different coefficients of thermal expansion were combined in two types of graded structure which can both be heat-treated in a single hot pressing treatment. Through microstructural and mechanical characterisation, the structures created are shown to have applications as wear resistant surfaces and as robust joints. Residual stresses in the functionally graded structures have been modelled analytically and using finite-element methods, as well as being directly measured using piezospectroscopic microscopy. The consistency of the predictions of these models with the experimental measurements will be discussed for the different structures.

8:50 AM

(ICACC-S1-013-2015) Spatially Tailored Strength and Toughness in Alumina-Based Composites

R. Bermejo*[1]; Y. Chang[2]; Z. Chlup[3]; O. Sevecek[4]; R. Danzer[1]; G. L. Messing[2]; 1. Montanuniversitaet Leoben, Austria; 2. The Pennsylvania State University, USA; 3. Czech Academy of Science, Czech Republic; 4. Brno University of Technology, Czech Republic

The low resistance to crack propagation, variable strength, and poor damage tolerance have limited the use of monolithic ceramics as advanced engineering materials. Much progress has been made to fabricate ceramic composites to improve fracture toughness, such as layered composites of alternate layers of different compositions ordered in a periodic design. In this work, it is shown that the combination of layers in a non-periodic manner can be even more effective in arresting the propagation of cracks than the commonly used periodic designs. The location and thickness of the "embedded" layers designed with compressive stresses can be optimized to maximize the crack growth resistance of the multilayer system. Experimental findings demonstrate that placing the first compressive layer closer to the tensile surface and increasing this layer's thickness yields a significant increase in the threshold strength (~470 MPa) and apparent fracture toughness (~17 MPam1/2). New design concepts using different "connectivity" for tailoring the resistance to crack propagation in laminates are also presented in layered architectures combining different materials within a layer plane. This opens new possibilities for design of multilayer structures with spatially defined strength and toughness by tailoring the location and thickness of the "embedded" compressive layers.

9:10 AM

(ICACC-S1-014-2015) Length Scale Effects on the Toughening of Barium Titanate-Ni Laminate Composites

W. R. Lanning*[1]; C. L. Muhlstein[1]; 1. Georgia Tech, USA

In order to extrinsic toughening mechanisms in ceramics to be effective, they must be designed with the length scales and locations of the intrinsic flaw populations in mind. In this work, we examine why the dielectric and bending strengths of barium titanate-based (X7R) multilayer ceramic capacitors (MLCCs) scale with the metal electrode array density and intrinsic flaw population. We compared externally identical MLCCs with different electrode configurations and our Weibull analysis gave characteristic strengths of 236 MPa vs. 190 MPa for 19- and 3-electrode MLCCs, respectively. We then deduced the length scale characteristic of the crack tip – electrode array interaction using fractographic analysis, in-situ electrical measurements, and force-displacement curves. We were then able to identify which intrinsic flaws initiated failure and the dominant toughening mechanism. Dielectric breakdown and fracture in bending initiate at different intrinsic flaws and the common assumption that electrical and mechanical failure share the same failure-initiating flaw populations is incorrect. The toughening effect of the metal electrode array on MLCCs is due to both the presence of the electrodes and the thermal processing used to manufacture the devices.

9:30 AM

(ICACC-S1-015-2015) Application of computational thermodynamics in LSM pervoskite thermal cycle shrinkage

A. Karbasi[1]; S. Darvish[1]; M. Mora[1]; Y. Zhong*[1]; 1. Florida International University, USA

Computational thermodynamics has been widely used in the prediction of phase equilibria of multi-component systems. However, very limited work has been done on the application of computational thermodynamics in thermo-mechanical properties and electrical properties. In the current work, we will use the thermodynamic database of La-Sr-Mn-O system to predict the defect chemistry during the thermal cycles of LSM perovskite. It will also be used to explain the weight changes and CTE change during the thermal cycles. Experiments on TGA and in-situ XRD will be adopted to verify the thermodynamic predictions.

9:50 AM

(ICACC-S1-016-2015) Mechanical Properties, Deformation Mechanisms, and Crystallography of Directionally Solidified WC-W_2C Eutectoids

W. Chen*[1]; C. Meredith[1]; E. Dickey[1]; 1. North Carolina State University, USA

WC-based metal-carbide composites are of interest for use in ceramic cutting tools, which require high hardness. Cobalt is usually added to WC as the second phase to improve sintering kinetics and fracture toughness of the resulting composites. However, the use of cobalt decreases the oxidation resistance and hardness relative to monolithic WC. A study of indentation mechanical properties, deformation, and crystallography of laser-processed directionally solidified WC-W_2C eutectoids is presented, illustrating the advantages of composite microstructure without sacrificing hardness. The interlamellar spacing (λ) of WC-W_2C eutectoids followed the relationship $V\lambda^{3.8}$ = constant, where V is the laser velocity. The highest indentation hardness (28.5 GPa) was measured in the samples with the smallest interlamellar spacing (331 nm), an 28% improvement over the highest reported WC-Co composites (12 wt% Co). Indentation fracture toughness ranged between 4.7 - 5.4 $MPa.m^{1/2}$. Further study investigated the deformation mechanisms of WC-W_2C eutectoids, which was different from monolithic WC and W_2C. Crystallographic orientations along solidification direction were characterized by electron backscatter diffraction. Image of Interface between WC and W_2C were performed by scanning

transmission electron microscopy and the accommodation of lattice mismatch at interface was investigated.

10:30 AM

(ICACC-S1-017-2015) Bio-Inspired Al/Al2O3 Micro-Layered Composites from Anodized Aluminum Foils

G. R. Villalobos*[1]; S. S. Bayya[1]; W. Kim[1]; C. Baker[1]; R. Goswami[1]; M. P. Hunt[3]; B. M. Sadowski[2]; J. S. Sanghera[1]; 1. US Naval Research Lab, USA; 2. Sotera Defense Solutions, USA; 3. University Research Foundation, USA

This work was inspired by the alternating plastic and elastic layers found in nature in biological composites such as nacre and fish scales, and their measured high strength and fracture toughness. There has been a great push in replicating that alternating structure by other researchers using naturally layered clays, fractured ceramics infiltrated with polymers, and layered polymer composites. We have developed similar structure of alternating elastic (Al2O3) and plastic (Al) layers by anodizing aluminum foils, stacking and pressing to form Al/Al2O3 layered composite disks. Mechanical testing shows a 50% increase in strength over a monolithic aluminum sample while maintaining graceful failure. Degree of bonding between the layers has a direct impact on the strength and failure mode of the composite. SEM, TEM and XRD characterization of the layered composite will also be presented.

10:50 AM

(ICACC-S1-018-2015) Towards Mussels under Stress: A Novel Path to Flaw Tolerant Materials with Enhanced Fracture Resistance

Y. Chang[1]; G. L. Messing[1]; R. Bermejo*[2]; 1. The Pennsylvania State University, USA; 2. Montanuniversitaet Leoben, Austria

The design of ceramic layered composites with weak or strong interfaces can affect the propagation of surface cracks during external loading. The former approach aims to induce crack deflection, i.e. higher failure resistance. The latter uses residual compressive stresses to arrest the propagation of cracks. In this work, alumina-based microstructural composites combining equiaxed and textured layers were fabricated in one architecture to examine how cracks propagate and the mechanical properties are affected as a function of the residual stress and volume fraction of textured material. The embedded textured layers were placed under compressive residual stresses as high as –670 MPa. Composites with a near constant maximum failure stress of up to 300 MPa were shown to be almost independent of the initial defect size, with an apparent fracture toughness of up to 10 MPam1/2. The high compressive stress in the textured layers arrested cracks whereas the weak bonding parallel to the basal surfaces of the textured alumina grains caused cracks to deflect within the textured layers. The coupling of these two mechanisms resulted in crack arrest and a maximum work of fracture of ca. 1200 J/m2. We believe that embedding textured layers having compressive stresses below the surface is an important strategy for designing flaw-tolerant materials.

11:10 AM

(ICACC-S1-019-2015) Understanding Microstructure-Mechanical Properties Relations in Ceramic/Carbon Nanotubes Nanocomposites

W. Wu*[1]; L. Zhang[1]; Y. Liu[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 a debate on the validity of different techniques used to measure the toughness of CNTs/ceramic nanocomposites exist among the published studies. In this work, a systematic study has been carried out to understand better the mechanical properties of ceramics reinforced by CNTs as a function of the nanocomposites microstructures. Single-wall and multi-wall CNTs are either covalently or non-covalently functionalized, and colloidally mixed with alumina nanopowders. The intimately mixed powders are densified using spark plasma sintering. The microstructures including distribution and integrity of the CNTs within the resulting alumina/CNTs, are characterized using a battery of analytical methods. Mechanical properties are measured, and related to the microstructures of the ceramic/CNTs nanocmposites. In particular, in situ observations of propagation of cracks in the CNTs/alumina nanocomposites have been performed in 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 CNTs on the possible toughening mechanisms.

11:30 AM

(ICACC-S1-020-2015) Quantifying Amorphous Content of Seeded and Unseeded Polymer-Derived SiC-Based Ceramic

T. Key*[1]; I. Wolford[2]; M. O'Malley[2]; K. Keller[1]; C. Carney[2]; M. Cinibulk[2]; 1. UES & AFRL/RXCCM, USA; 2. AFRL/RXCCM, USA

Temperatures in excess of 1400°C are typically required to fully convert and crystallize allyhydridopolycarbosilane (AHPCS) pre-ceramic polymers to SiC. Limited by the current commercially available fibers, pyrolysis temperatures and times of PIP-based SiC/SiC ceramic matrix composites (CMCs) often result in a significant amount of non-crystalline material remaining in the matrix. In support of PIP-based matrix processing, the change in yield, density and crystallinity of STARFIRE SMP-10 (a commercial AHPCS) was studied as a function of processing temperature and time. Additionally, the weight fraction of non-crystalline material and the degree of templated grain growth in SiC loaded SMP-10 was quantified. Methods of analysis include X-ray diffraction and detailed microstructural characterization performed using scanning and transmission electron microscopy.

11:50 AM

(ICACC-S1-021-2015) Fractal Analysis of a Biocompatible Ceramic –Polymer Laminate

P. A. Robinson*[1]; J. Mecholsky[1]; C. A. Wilson[2]; 1. University of Florida, USA; 2. Michelin Americas Research and Development Corporation, USA

There are laminated composites that occur naturally (e.g. conch shells and crab chelae) and demonstrate techniques for improving mechanical properties such as toughness. We observed that the strength and toughness of a designed hydoxyapatite-polysulfone (HA-PSu) laminated composite was greatly influenced by the thickness and behavior of the PSu laminae. Toughness in the laminates was measured using an apparent toughness, KAPP, derived from the work of fracture, by comparing KAPP to the toughness values calculated using the fractal dimensional increment, D*, as a function of strain rate. In addition, D* was measured to assess the contribution of toughness from PSu laminae in the laminated composites. Laminate theory supports the hypothesis that PSu thickness is a key variable in the strengthening of HA/PSu composites. Mechanisms of toughness and strength in ceramic-polymer laminate composites were analyzed using a modified laminate theory.

S3: 12th International Symposium on Solid Oxide Fuel Cells (SOFC): Materials, Science and Technology

Materials for SOFC, Reversible (SOFC/SOE) and SOE Operation / Electrode Materials

Room: Crystal
Session Chairs: Toshio Suzuki, National Institute of Advanced Industrial Science and Technology; Jeff Stevenson, PNNL

8:00 AM

(ICACC-S3-008-2015) Reversible Solid Oxide Fuel Cells using Mixed Ionic-Electronic Conducting Electrolytes: Performance and Stability (Invited)

A. V. Virkar*[1]; G. Tao[2]; 1. University of Utah, USA; 2. Materials and Systems Research, Inc., USA

It has been long assumed that electrolyte in a solid oxide fuel cell or electrolyzer cell should exhibit the highest possible ionic transference number. Thus much of the materials work over the past three decades has been directed towards the development of purely ionic conducting electrolytes. In this talk theoretical analysis and experimental results on the performance and stability of reversible solid oxide fuel cells made with mixed ionic-electronically conducting (MIEC) electrolytes are presented. It is shown that performance in both fuel cell mode and electrolyzer mode of cells made using MIEC electrolytes (such as zirconia doped with yttria and ceria) is comparable to the performance achieved using purely ionic conducting electrolytes (such as zirconia doped with yttria). Cells made using MIEC electrolytes exhibit very stable performance, with little degradation even after 1500 h of testing. Stable performance is attributed to decreased spatial variability of oxygen chemical potential within the electrolyte. However, electrolyzer cells made using purely ionic conducting electrolytes exhibited greater degradation under similar operating conditions. Experimental results on cells and stacks made using MIEC electrolytes and purely ionic conducting electrolytes will be presented. Approach to designing cells with stable performance will be presented.

8:30 AM

(ICACC-S3-009-2015) Development of solid oxide cells and stack materials for intermediate temperature SOFC and SOEC applications (Invited)

D. Montinaro*[1]; A. Dellai[1]; G. Tiberio[1]; M. Rolland[1]; F. De Genua[1]; 1. SOFCpower 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. SOFCpower SpA is an Italian company which provides efficient energy solutions based on its proprietary planar SOFC technology. Company focuses are products that use natural gas either for heat and power generation (CHP) or for distributed power generation at high total and electrical efficiencies, respectively. Furthermore, the company is evaluating strategic technology options to integrate its planar SOFC stack technology to Intermediate Temperature Steam Electrolysis (ITSE) applications. In the present work we present the most recent results, achieved in SOFCpower, related to stack materials and ceramic processing development for conventional SOFC and SOE-mode as well as for reversible SOFC/SOE operation. The durability of the stack, related to the degradation of the most critical materials, under the different operating conditions is presented and discussed.

9:00 AM

(ICACC-S3-010-2015) Proton-Conducting Solid Oxide Electrolysis Cells (SOECs) with Chemically Stable Electrolytes (Invited)

E. Traversa*[1]; L. Bi[1]; 1. King Abdullah University of Science and Technology, Saudi Arabia

Promising emission-free renewable energy sources, such as solar power and wind power, are site-specific and intermittent. To get continuous power supply, energy storage is needed. Steam electrolysis by solid oxide electrolysis cells (SOECs) provides a highly-efficient and eco-friendly way of energy storage in the form of H2., Proton-conducting electrolyte based SOECs offer several advantages compared to conventional oxygen-ion electrolytes, such as no dilution of produced H2, no oxidation of Ni-based fuel electrode and more flexibility in choosing heat sources. Previous studies concerning proton-conducting SOECs were focused on the use of $BaCeO_3$ electrolytes due to the high conductivity and easy processability. However, barium cerate has been proved to be chemically unstable and unsuitable for practical applications, especially at high steam concentrations as in SOECs. In contrast, doped Y-BaZrO3 (BZY) can be an ideal electrolyte for SOECs due to its excellent chemical stability and high bulk conductivity. However, its use in SOECs is not deployed yet because of its large grain-boundary resistance and difficulty in processing. Here we report the successful application of BZY as electrolyte for proton-conducting SOECs, which showed an encouraging cell performance and a superior long-term stability.

9:30 AM

(ICACC-S3-011-2015) Dopant effects on $La_{0.4}Ce_{0.6}O_2$ sintering temperature for anode supported Solid Oxide Fuel Cells using $LaGaO_3$ electrolyte (Invited)

K. Hosoi[2]; J. Hong[2]; S. Ida[2]; T. Ishihara*[1]; 1. Kyushu University, Japan; 2. Kyushu University, Japan

Among transition metals (Co, Mn, and Fe), addition of Co as sintering aid improved densification and electrical conductivity of La-doped CeO_2 (LDC) as buffer layer for Sr- and Mg-doped $LaGaO_3$ (LSGM) electrolyte films. It was expected that using Co-LDC as buffer layer could decrease the co-sintering temperature of the electrolyte films So, in this study, influence of decreasing the sintering temperature (1473~1623 K) was investigated on electrochemical performance of anode supported solid oxide fuel cells applying LSGM electrolyte and Co-LDC buffer layers prepared by screen printing method. It was found that the sintering temperature could decrease to 1523 K, showing the maximum power density, ca. 1W/cm_2 at 973 K, and an open circuit voltage close to the theoretical value (ca.1.1V). This implies that Co-LDC shows no detrimental effect after sintering and thus is a promising buffer layer for LSGM electrolyte film prepared by sintering at lower temperatures. In this study, reversible operation of the cell is also studied and it was found that the prepared cell shows high efficiency for generation of hydrogen by steam electrolysis.

10:20 AM

(ICACC-S3-012-2015) Surface Segregation in LSCF: Effect of Atmosphere and Strontium Content

S. Basu*[1]; Y. Yu[1]; D. Cetin[1]; H. Luo[2]; K. Ludwig[3]; X. Lin[2]; U. Pal[1]; S. Gopalan[1]; 1. Boston University, USA; 2. Boston University, USA; 3. Boston University, USA

Surface segregation behavior and phase formation in LaxSr1-xCo0.2Fe0.8O3-δ (LSCF) has been studied as a function of the CO2 partial pressure in the atmosphere and the strontium content in the LSCF. Hetero-epitaxial LSCF thin films with x= 0.6, 0.7 and 0.8 were deposited on (110)-oriented NdGaO3 (NGO) substrates by pulsed laser deposition (PLD). The films were exposed to different CO2 partial pressures as a fixed oxygen partial pressure and compositional changes on the surface were measured using total reflection

x-ray fluorescence (TXRF) technique in real time at 800°C. Ex-situ electronic structure measurements were carried on the post-annealed samples using hard x-ray photoelectron spectroscopy (HAXPES). The post-annealed thin-films were also characterized by scanning electron microscopy, transmission electron microscopy and atomic force microscopy. The segregation and phase formation phenomena as a function of atmospheric CO2 partial pressure and Sr content will be discussed.

10:40 AM

(ICACC-S3-013-2015) Durability of Lanthanum Strontium Cobalt Ferrite (LSCF) Cathodes in CO2 and H2O Containing Air

B. Hu*[1]; M. K. Mahapatra[2]; V. Sharma[2]; S. Misture[3]; R. Ramprasad[2]; N. Minh[4]; P. Singh[2]; 1. University of Connecticut, USA; 2. University of Connecticut, USA; 3. Alfred University, USA; 4. University of California, San Diego, USA

The durability of the lanthanum strontium cobalt ferrite ((La0.60Sr0.40)0.95(Co0.20Fe0.80)O3-x, LSCF) cathodes has been studied in air using LSCF/GDC/LSCF symmetric cells under a wide range of humidification (0-20%) and CO2 levels (0-10%) at 750°C and 0-0.5 V cathodic biases . Post-test studies using scanning electron microscopy, X-ray photoelectron spectroscopy, Fourier transform infrared spectroscopy, and X-ray diffraction techniques revealed the formation and segregation of SrO particles in humidified air and SrCO3 in CO2-air on the LSCF surfaces. In 100-h tests, our observations indicate that the lower levels of CO2 (<0.5% CO2) may not affect the current density; higher levels of CO2 (~10% CO2) decrease the current density due to the formation of SrCO3 on the LSCF surface. Thermogravimetric analyses and Gibbs free energy calculations show the formation conditions of SrO and SrCO3 on LSCF surface. Reaction mechanisms during exposure to H2O and CO2 are proposed.

11:00 AM

(ICACC-S3-014-2015) A New Curvature Relaxation Technique to Perform Simultaneous, In Situ Oxygen Surface Exchange Coefficient and Stress Measurements on Dense or Porous Films

J. D. Nicholas*[1]; Q. Yang[1]; 1. Michigan State University, USA

With their unique combination of high power density, high efficiency, and fuel flexibility, Solid Oxide Fuel Cells (SOFCs) have the unique ability to reduce the environmental impact of today's hydrocarbon based economy while simultaneously providing a path to a CO_2-neutral economy utilizing biofuels, solar fuels or hydrogen. Unfortunately, the low oxygen surface exchange coefficients (*k's*) of SOFC cathode materials often limits overall SOFC performance. Further, efforts to engineer improved *k's* have been complicated by the large *k* variation for nominally identical materials reported in the literature. For example, literature *k* measurements performed on the archetypal SOFC material lanthanum strontium ferrite (LSF) at 650°C in air vary by over 5 orders of magnitude! To help understand this discrepancy, a new bilayer curvature relaxation (KR) technique providing reliable, in-situ, electrode-free, simultaneous measurement of film stress and *k* as a function of oxygen partial pressure and temperature was developed. KR measurements on dense and porous films show that the large LSF *k* variation reported in the literature is not caused by electrode or sample geometry artifacts. Further, the KR results demonstrate a dependence of the LSF oxygen surface exchange behavior on the LSF grain size and sample processing history.

11:20 AM

(ICACC-S3-015-2015) Defect equilibria and reaction kinetics of Pr doped ceria thin film by simultaneous *in situ* optical absorption and impedance measurements

J. Kim[1]; S. R. Bishop[1]; D. Chen[1]; N. H. Perry*[1]; H. L. Tuller[1]; 1. Massachusetts Institute of Technology, USA

An improved understanding of defect chemistry and surface exchange kinetics in oxide materials is essential for enhanced performance of solid oxide fuel cells and solid oxide electrolysis cells. In this work we were able to access the behavior of oxide thin films, in these regards by use of several experimental methods in tandem. With novel experimental apparatus, *in situ* optical absorption and electrode impedance measurement are simultaneously utilized, to investigate a Pr doped ceria thin film (PCO) at elevated temperature and controlled pO_2. This technique allows direct investigation of nonstoichiometry via chemical capacitance and absorption change and surface exchange kinetics via reaction resistance and absorption relaxation. The optical absorption coefficient exhibited a linear dependence on Pr^{4+} concentration, derived independently from the chemical capacitance. The surface exchange coefficient (k_{chem}), extracted from optical relaxation, is smaller than estimated values derived from electrode impedance. The non-contact optical absorption technique provides an additional, quantitative insight into the defect equilibria of thin films. The discrepancy in derived k_{chem} values suggests differences in surface chemistry at the unelectroded vs the electroded surface and/or an additional catalytic effects coming from the Pt metal contact.

S4: Armor Ceramics: Challenges and New Developments

Synthesis and Processing I

Room: Coquina Salon E

Session Chair: Victoria Blair, ORISE; Steven Kilczewski, ARL

8:30 AM

(ICACC-S4-012-2015) A Decontamination Process for the Fabrication of Transparent Nano-grain Magnesium Aluminate Spinel

A. Kundu*[1]; M. P. Harmer[1]; R. P. Vinci[1]; 1. Lehigh University, USA

The ceramics manufacturing industry had long standing challenges associated with poor reproducibility and unreliability in fabricated parts, which can be traced back in large part to the unknown and uncontrollable influence of impurities specifically the anionic impurities such as sulfur, chlorine which are often neglected. The so called "ultra-high purity" commercial powders can contain significant amount of such anionic impurities. A decontamination process has been developed for the reduction of these impurities from magnesium aluminate spinel. The process involves treating as-received powders in ultra-high vacuum with or without concurrent heating for extended period of time. The key advantage of the method is that it does not modify the physical characteristics of the powders such as particle size distribution. The decontaminated powders can be sintered to near theoretical density by hot pressing only without requiring any hot isostatic pressing step and without any addition of sintering additives. Minimal grain growth has been observed in the sintered material. The presentation will focus on the efficacy of the decontamination process in reducing impurities from spinel powders. The effect of the decontamination process on the optical and mechanical properties of fabricated parts will be discussed as well.

8:50 AM

(ICACC-S4-013-2015) Benign processing of complex-shaped transparent ceramics

Y. Wu*[1]; 1. New York State College of Ceramics at Alfred University, USA

Transparent ceramics could be made by dry and wet forming techniques. Gel-casting is a near-net shaping process for simple and complex shapes of ceramic fabrication. The conventional process has some disadvantages associated with toxicity, rigid conditions for reaction and high amount of organic addition. In this work, a new spontaneous gelling system was developed to process near-net shaping optical ceramics. The gelling process is very convenient, nontoxic, and low-cost, which can be conducted in air at room temperature with small amount of this organic. The mechanism of this process for the development of transparent ceramics was studied to understand in terms of the solid loadings of the slurries, gelling agent additions and sintering conditions.

9:10 AM

(ICACC-S4-014-2015) Grain Boundary Segregation Behavior of Rare-Earth Dopants in Magnesium Aluminate Spinel

A. Kundu*[1]; O. Kosasang[1]; Z. Yu[1]; M. P. Harmer[1]; R. P. Vinci[1]; 1. Lehigh University, USA

The presentation will focus on the relationship between grain boundary segregation and abnormal grain growth in rare earth doped magnesium aluminate spinel. Polycrystalline spinel samples with controlled doping of europium (Eu) and ytterbium (Yb) have been prepared and annealed for various time-temperature combinations. The dopants tend to segregate at the grain boundaries. The effect of the segregation on the microstructure evolution during sintering has been investigated. The nature of the segregation has been examined at an atomic scale with the aid of aberration corrected electron microscopy. Certain synthetic grain boundaries have also been fabricated utilizing spinel single crystals with well-defined crystallographic orientations for electron microscopy studies. In Eu-doped spinel a distinct microstructural transition has been observed at ~1500°C. At this temperature the grain size distribution transitions to a bimodal distribution (abnormal grain growth) from a uni-modal distribution indicating a discontinuous change in grain boundary mobility, a grain boundary complexion transition in certain fraction of the grains. No such transition has been observed in Yb-doped spinel. The onset of abnormal grain growth has been explored systematically as a function of time and temperature and the grain boundary segregation behavior associated with this transition has been investigated.

9:30 AM

(ICACC-S4-015-2015) Grain Boundary Complexions – Implications to Ceramic Armor Development (Invited)

M. Harmer*[1]; 1. Lehigh University, USA

Grain boundaries play a decisive role in determining the processing, microstructure and properties of engineering materials, including ceramic armor. One important aspect of grain boundaries, that has not been fully appreciated until recently, is that they can undergo rapid and discontinuous changes in structure and chemistry (and hence properties) at certain values of thermodynamic and interfacial parameters. These phase-like changes in the state of grain boundaries are referred to as grain boundary complexion transitions, to differentiate them from bulk phase changes. More precisely defined a grain boundary complexion is interfacial material or strata that is in thermodynamic equilibrium with the abutting phase(s). This talk will first introduce the general concept of grain boundary complexions and complexion transitions. We will then go on to examine how it may be utilized to optimize the processing and performance of ceramic armor materials.

10:20 AM

(ICACC-S4-016-2015) Understanding Intergranular Films and Grain Boundary "Phase" Transitions (Invited)

J. Luo*[1]; 1. UCSD, USA

Impurity-based, nanometer-thick, intergranular films (IGFs) have been widely observed in structural and functional ceramics, where they can often control the microstructural evolution and materials properties [Crit. Rev. Solid State Mater. Sci. 32, 67-109 (2007)]. These equilibrium-thickness IGFs can be considered as a class of grain boundary (GB) "phases," which is also called "complexions" [see an Overview: Acta Mater. 62, 1-48 (2014) and references therein]. In a broader context, GBs can exhibit phase-like transitions that drastically differ from their bulk counterparts. Recent discoveries of similar interfacial phenomena at free surfaces and in simpler metallic alloys, as well as thinner and discrete complexions such as bilayers and trilayers, further established a big picture. A long-range scientific goal is proposed to develop grain boundary "phase" diagrams as a useful materials science tool.

10:50 AM

(ICACC-S4-017-2015) van der Waals Interactions and Hamaker Coefficients: At Atomically Abrupt Grain Boundaries in $SrTiO_3$ And In Intergranular Films in Re-M-O-N:Si_3N_4 (Invited)

R. H. French*[1]; 1. Case Western Reserve University, USA

The optical properties and electronic structure of materials are critical are the origin of the quantum electrodynamic van der Waals – London dispersion (vdW-Ld) interactions, the universal long range interaction, which plays a critical role in wetting, interfacial energies, and mesoscale assembly. At the nanoscale, beyond the formation of individual chemical bonds during chemical synthesis, long-range interactions (LRIs), such as the vdW-Ld, electrostatic and polar interactions, dominate the nanoscale manipulation and assembly of materials for functional nanodevices. The London dispersion interaction is represented by the retarded Hamaker coefficient (A(L)), and can be calculated using Lifshitz theory from optical property-based electronic structure spectra as acquired in Vacuum Ultraviolet (VUV) Spectroscopy, Transmission Electron Energy Loss Spectroscopy (TEELS or from spectra of ab initio band structure calculations. Spatially resolved TEELS spectra show strong physical property gradients for Σ5 and near Σ13 grain boundaries in Fe doped SrTiO3. TEM studies in Re-M-O-N:Si3N4 have shown compositional variations between the triple points and the intergranular films, and compositional gradients across individual intergranular films. Changes in the London dispersion interaction energies for these two cases are considered using EMA layer and quadroid gradient approach.

11:20 AM

(ICACC-S4-018-2015) Low Temperature Synthesis of Boron Carbide Powders

D. Tucker[1]; S. Su[1]; I. T. Chang*[1]; P. Brown[2]; 1. University of Birmingham, United Kingdom; 2. DSTL, United Kingdom

Boron carbide (B4C) has unique physical properties that make it an ideal candidate material for lightweight body armour applications. Currently, it is formed in an electric arc furnace as a large billet of materials, which is then ground down into fine powders for subsequent densification into ceramic body armour. Such conventional production method of B4C powders requires high energy consumption and extensive grinding that led to a high cost of B4C powders. Recently, a low temperature synthesis (LTS) method for the production of B4C powder has been developed at University of Birmingham. It involves the formulation of an aqueous solution that contains the essential ingredients of Carbon and Boron sources. This is then followed by direct conversion of the aqueous solution into solid precursor powders for subsequent heat treatment operation at temperatures below 1500C. The as-synthesised B4C powders have unique characteristics, including low residual carbon content, equiaxed morphology and average particle sizes ranging from 250nm to 4microns, depending on the processing conditions. The LTS method offers a reduction of processing temperature and the elimination of extensive grinding step for the generation of ultrafine boron carbide powders. This paper presents a study on the effect of processing conditions on the characteristics of B4C powder produced by LTS method developed at Birmingham.

11:40 AM

(ICACC-S4-019-2015) Synthesis, Processing, and Fundamental Reaction Mechanism Study for Nanocrystalline Boron Carbide Powders

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

Well dispersed nanocrystalline boron carbide (B4C) powders were synthesized by the carbothermal reduction (CTR) reaction of molecular-scale mixed boron oxide (B2O3) and carbon precursors. Different low cost starting materials such as water soluble boric acid and sucrose as well as solvent soluble trimethyl borate (TMB) and phenolic resin (PR) were solution processed followed by pyrolysis and CTR. The reaction intermediates as well as the final products were characterized by different techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM), thermogravimetric analysis (TGA), and Raman microspectroscopy. The impacts of parameters such as the nature of starting materials used and their molar ratio, pyrolysis and CTR temperature and time, carrier gas flow rate or vacuum level, heating/cooling rate on product phase composition (e.g., B4C versus excess carbon and/or B2O3) and stoichiometry, crystallite size, powder morphology and surface area, etc. were studied. Using the results obtained by the aforementioned experiments coupling reaction kinetics and microstructure evolution studies, fundamental mechanism about the formation of high purity, well dispersed nanocrystalline B4C through the CTR reaction will be discussed.

S6: Advanced Materials and Technologies for Energy Generation, Conversion, and Rechargeable Energy Storage

Beyond Li-ion Battery: Sodium-ion Battery, Li-S and Li-air battery

Room: Tomoka A

Session Chairs: Claude Delmas, ICMCB -CNRS; Shirley Meng, University of California

8:30 AM

(ICACC-S6-009-2015) The Nax(Co,Mn)O2 and Nax(Fe,Mn)O2 layered oxides used in Na Batteries : structural transformations and redox processes (Invited)

D. Carlier*[1]; B. Mortemard de Boisse[1]; M. Guignard[1]; A. Wattiaux[1]; J. Cheng[2]; B. Hwang[2]; D. Filimonov[3]; C. Delmas[1]; 1. ICMCB-CNRS, France; 2. NTUST, Taiwan; 3. Lomonosov Moscow State University, Russian Federation

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, rechargeable sodium-ion batteries are investigated. We recently studied some NaxMO2 phases used as positive electrode in Na cells with a special focus on the structural transformations and redox processes occurring during cycling : P2-NaxCo2/3Mn1/3O2, P'3, P2 and O3-Nax(Fe,Mn)O2. The structures of all starting materials were determined by Rietveld refinement of their X-Ray diffraction patterns. The electrochemical study was carried out in sodium batteries with a solution of NaPF6 in PC as electrolyte. For all materials, a very good reversibility of the electrochemical process was observed. The structural modifications undergo by the materials during cycling were studied by ex-situ and in-situ XRD. Depending on the material, we observe either reversible Na/vacancy orderings in the interspace space or reversible MO2 sheet glidings. The redox processes were studied by ex-situ and in-situ XANES and Mössbauer spectroscopy.

9:00 AM

(ICACC-S6-010-2015) $Na_2FeP_2O_7$ as a positive electrode material for rechargeable sodium-ion batteries in nonaqueous and aqueous electrolytes

Y. Jung[1]; C. Lim[1]; J. Kim[1]; D. Kim*[1]; 1. KAIST, Korea (the Republic of)

Research on rechargeable sodium-ion batteries (SIBs) has been promoted to utilize large energy storage systems as one of alternatives to current lithium-ion batteries (LIBs) due to low cost and abundance in the world. In particular, iron-based compounds have an advantage in terms of price, which is a considerable factor for the application of SIBs. Recently, various pyrophosphate compounds have attracted much attention as sodium electrode materials due to their stable structure, good capacity retention, and high thermal stability. In this work, two types of $Na_2FeP_2O_7$ composites - amorphous carbon and reduced graphene oxide (rGO) - have been synthesized using a simple method that combines sol-gel and solid-state reaction, and their electrochemical properties have been investigated in both aqueous and nonaqueous electrolytes. The $Na_2FeP_2O_7$/C composite presents a reversible sodium intercalation and deintercalation without dissolution of electrode materials or side reactions in aqueous electrolytes. Although $Na_2FeP_2O_7$/C composite in organic solvents shows lower rate capability as compared to that in aqueous solution, $Na_2FeP_2O_7$/rGO composite exhibits much lower polarization, better rate capability and good cyclability in nonaqueous electrolytes.

9:20 AM

(ICACC-S6-011-2015) Electrochemically formed α'-NaV2O5: A promising zero strain electrode material for rechargeable sodium-based batteries

D. Muller-Bouvet[1]; R. Baddour-Hadjean[1]; M. Tanabe[1]; N. Huynh[1]; J. Pereira-Ramos*[1]; 1. CNRS, UMR7182, France

Orthorhombic V2O5 was identified as a promising cathode material for secondary lithium batteries since the 1970 and vanadium oxides with layered structures look quite promising. However, only a few works addressed the Na electrochemical insertion into such structures and to our knowledge, there is no study dedicated to room temperature (RT) sodium insertion into V2O5. We introduce in this work a layered material electrochemically formed at room temperature from the parent α-V2O5 compound, which is able to reversibly accommodate 0.8 Na+ ions/mole at 1.3 V vs. Na+/Na. This material, isostructural to the high temperature α'-NaV2O5 orthorhombic bronze, exhibits an attractive specific capacity of 120 mAh/g at C/10 rate at room temperature. XRD and Raman analyses provide evidence for very weak structural changes throughout the sodium intercalation process in this bronze, both at the long range order and atomic scale, involving only a negligible increase (< 1%) in the interlayer c parameter. This remarkable zero strain behaviour ensures a potentially long cycle life here demonstrated over 20 cycles. The large interlayer spacing of the electrochemically formed α'-NaV2O5 material (4.8 Å against 4.37 Å for V2O5) combined with the higher polarizability of Na ions compared to Li ions could explain such a reversible sodium insertion mechanism.

9:40 AM

(ICACC-S6-012-2015) Glass-ceramic joining materials for sodium-based battery

F. Smeacetto*[1]; M. Salvo[1]; M. Radaelli[2]; M. Broglia[2]; F. Cernuschi[2]; M. Ferraris[1]; 1. Politecnico di Torino, Italy; 2. RSE SpA, Italy

Sodium-beta-alumina batteries are considered attractive devices for utility-scale energy-storage applications. The main structure of these batteries is composed of molten sodium/sulfur or sodium/metal chloride as electrodes and beta-Al2O3 ceramic as the electrolyte. These batteries operate at a temperature around 300 °C, exhibit high power and energy densities, temperature stability, and low cost. A reliable sealant between the beta-alumina and alpha-alumina is needed for both safety and performance reasons. The requirements of an effective sealant include thermo-mechanical compatibility, chemical stability with Na at 300°C, excellent gas tightness, and reliable joining behaviour. This study focuses on the design, development, characterization and testing of a new glass-based sealants. The thermal and thermo-mechanical properties as well as the sintering behaviour of glass-ceramic sealants have been characterized by differential thermal analyses, heating stage microscopy and XRD studies. The compatibility at the interface between the glass-ceramic sealants and beta- and alpha-alumina is reviewed and discussed, before and after test with molten Na. Tests of a silica-based glass-ceramic sealant with Na at 300°C for several hours in real battery operating conditions showed no reaction or corrosion evidence, as demonstrated by SEM and EDS post mortem examinations.

10:20 AM

(ICACC-S6-013-2015) Electrical conductivity of Na_2O-Nb_2O_5-P_2O_5 glass with low melting temperature and fabrication of glass-ceramics composites with NASICON ($Na_3Zr_2Si_2PO_{12}$) for sodium ion batteries

T. Honma*[1]; M. Okamoto[1]; T. Togashi[1]; K. Shinozaki[1]; T. Komatsu[1]; 1. Nagaoka Univeristy of Technology, Japan

Thermal properties and electric conductivity of Na_2O-Nb_2O_5-P_2O_5 glass was investigated. In $60Na_2O$-$10Nb_2O_5$-$30P_2O_5$ glass exhibits moderate electrical conductivity as 10^{-7} Scm^{-1} at room temperature. We also examined the fabrication of glass-ceramics composite, which is consisted from NASICON($Na_3Zr_2Si_2PO_{12}$) and $55Na_2O$-$15Nb_2O_5$-$30P_2O_5$ glass. It was found that the composite of 90wt%NASICON-10wt% glass, which obtained by calcined at 900°C 10min, gives 4.5×10^{-4} Scm^{-1} electrical conductivity at room temperature. Na_2O-Nb_2O_5-P_2O_5 glass is suitable for filler material sodium ion batteries that requires low temperature heating.

10:40 AM

(ICACC-S6-014-2015) Preparation of Li-stabilized sodium β-alumina films by laser CVD

C. Chi*[1]; H. Katsui[1]; T. Goto[1]; 1. Engineering, Japan

Na-β/β″-alumina was well-known as a solid electrolyte for sodium sulfur battery, thermoelectric converter and gas sensor. This study aimed to preparing Na-β/β″-alumina and Li-stabilized Na-β/β″-alumina films by laser CVD. A continuous wave diode laser was employed. AlN was used as the substrate. The deposition temperature (T_{dep}) was measured by a thermocouple beneath the substrate. $Al(acac)_3$ (acac: acetylacetonate), Na(dpm) (dpm: dipivaloymethanate) and Li(dpm) were used as precursors. The molar ratio of Li/Al ($R_{Li/Al}$) and Na/Al ($R_{Na/Al}$) were adjusted by changing the vaporization temperature of Li(dpm) and Na(dpm). The total chamber pressure (P_{tot}) was changed from 200 to 1000 Pa. The crystalline phase of Li-Na-Al-O films was examined by XRD. The microstructure was observed by SEM and TEM. Na-β/β″-alumina films were prepared at T_{dep} = 1310–1390 K, $R_{Na/Al}$ = 20–80 and P_{tot} = 600–1000 Pa. The Na-β/β″-alumina films showed flake-like grains at P_{tot} = 600 Pa and polygonally dense facets at P_{tot} = 1000Pa. The deposition rates were 30–44 μm/h. By adding Li precursors at $R_{Li/Al}$ = 0.1–1, Li-stabilized Na-β/β″-alumina films were deposited at T_{dep} = 1100–1200 K, $R_{Na/Al}$ = 1.5 and P_{tot} = 800 Pa. The Li-stabilized Na-β/β″-alumina films had triangular and rectangular facets. The deposition rates of Li-stabilized Na-β/β″-alumina films reached 60 μm/h at T_{dep} = 1167 K.

11:00 AM

(ICACC-S6-015-2015) Na+-conducting glass ceramics for high temperature batteries

D. Wagner*[1]; A. Rost[1]; M. Fritsch[1]; J. C. Schilm[1]; M. Kusnezoff[1]; 1. Fraunhofer Gesellschaft IKTS, Germany

Sodium sulfur batteries with ion conducting ceramic separators operate at temperatures of 300°C in order to reach good cell efficiencies. Increased costs for temperature stable components and the operation of the battery systems are the consequences. By this view research on new sodium sulfur battery systems for decreased operating temperatures below 100°C has been started. Thin but dense separators with a high sodium ion conductivity at low temperatures in combination with a high chemical stability in combination with the liquid electrolyte are needed. Glass ceramics in the Na2O-Y2O3-SiO2-system are promising sodium ion conducting materials. They can be synthesized via melting of glasses, powder preparation, shaping and subsequent sintering and crystallization. A challenge is given by the controlled crystallization of the conductive phases from the glass and building of percolated crystalline microstructures. The glass powders are transferred into slurries followed by tape casting to form green substrates. Sintering of green substrates is a critical step during the entire process. Cracking, bulging and bloating has to be eliminated to get a plane and dense separator with a thickness <200μm. The sintered materials were characterized by density measurement, SEM, XRD, and impedance spectroscopy. Sodium conducting glass ceramics with densities > 95% and conductivities of 0.5 mS/cm (25°C) has been manufactured.

11:20 AM

(ICACC-S6-016-2015) Factors influencing Li-S battery cycle life – a combined in-situ analytical work (Invited)

R. Dominko*[1]; M. Patel[1]; A. Vizintin[1]; I. Arcon[2]; L. Stievano[3]; G. Aquilanti[4]; 1. National Institute of Chemistry, Slovenia; 2. Universtiy of Nova Gorica, Slovenia; 3. ICGM-UMR5253, Université Montpellier II, France; 4. Elettra-Sincrotrone Trieste S.C.p.A., Italy

Lithium–sulfur batteries (LSB) are one of the most promising candidates for green transportation owing to their various desirable characteristics including competitive cost, attractive energy density and low environmental impact. In spite of attractive properties, Li-S cells were not commercialized on the large scale. Issues related to the solubility and diffusion of the intermediate discharge/charge products (polysulfides) in organic electrolytes, insulating nature of sulfur and problems with metallic lithium are still subject of the research. The lack of understanding how small changes influence Li-S battery mechanism, particularly polysulfide shuttle mechanism, is one of the major reasons for holding that technology in the research laboratories. Among the factors that negatively affect the development of Li-S batteries is also a lack of in-situ techniques. Here we show application of three different in operando mode analytical techniques developed for Li-S batteries that are capable to detect changes related to polysulphides diffusion (migration). A selected systems (different electrolytes, ion selective separator, …) will discussed in terms of polysulphide migration.

11:50 AM

(ICACC-S6-017-2015) Microwave processing for improved ionic conductivity in LiO_2-Al_2O_3-TiO_2-P_2O_5 glass ceramics

C. G. Davis*[1]; A. Pertuit[1]; J. C. Nino[1]; 1. University of Florida, USA

LiO_2-Al_2O_3-TiO_2-P_2O_5 (LATP) glass-ceramics with a NASICON crystal structure are of great interest as solid state electrolytes for lithium air batteries because of their chemical stability and high room temperature ionic conductivity. It has been shown that the crystallization kinetics can greatly affect the ionic conductivity of glass ceramic electrolytes. LATP electrolytes were prepared by melt quenching methods, and crystallization was induced by both microwave and conventional heating for comparison. Here we will present the effects of microwave heating on the crystallization microstructure and ionic conductivity of glass ceramics, and demonstrate a 500% increase in the conductivity for microwaved samples. The effects of aluminum substitution on microwave LATP will also be discussed.

S7: 9th International Symposium on Nanostructured Materials: Innovative Synthesis and Processing of Nanostructured, Nanocomposite and Hybrid Functional Materials for Energy, Health and Sustainability

Nanotoxicity, Drug-delivery and Health Aspects of Engineered Nanostructures

Room: Coquina Salon B

Session Chairs: Sanjay Mathur, University of Cologne; Ausrine Bartasyte, FEMTO-ST Institute

8:30 AM

(ICACC-S7-001-2015) Electrical Characterization of Individual Inorganic Nanoparticles (Invited)

U. Simon*[1]; 1. RWTH Aachen University, Germany

Inorganic nanoparticles (NP) including metals, metal oxides, and chalcogenides exhibit size dependent electrical properties. This makes such NP promising for applications e.g. in energy conversion, information storage, or sensing devices. However, most of these applications rely on the integration of a multitude of NP instead of single ones. Thus, several applications utilize the integral properties of ensemble of NP, rather than the distinct properties of the individual nanoscale building blocks. In order to take full advantage of the nanoscale size for ultimate miniaturization, experimental techniques are required that allow analyzing the properties of individual particles in an environment that approaches the conditions to be applied for the desired application. Therefore we developed and evaluated methods which allow us to study the electrical properties of individual metal, metal oxide and chalcogenide NP either in a nanoelectrode (NE) configuration or by means of a flexible nanomanipulator (NM) set-up. In this report we will introduce our recent results on the charge transport properties of individual sub-20 metal NP in a lithographically fabricated NE and of sub-micron sized metal oxide and chalcogenide NP contacted in a NM set-up, which exhibit resistive switching properties and which therefore are considered promising for resistive memory devices.

9:00 AM

(ICACC-S7-002-2015) Star Shape Au/Ag with Nano Diamond for the Application in Hyperthemia (Invited)

R. Liu*[1]; S. Hu[2]; 1. University of Taipei, Taiwan; 2. National Taiwan Normal University, Taiwan

In this investigation, we demonstrate a simple synthesis route to fabricate muti-functional nanodiamond-star shape Au/Ag. Fluorescent nanodiamond was established by surface paasivation and urchin-liked Au nanoparticles can be obtained through one-pot synthesis, and combined via further thiolation of nanodiamond. The morphology of nanodiamond-star shape Au/Ag nanoparticles was identified by high-resolution transmission electron microscopic, and recognized through the diffraction patterns. Fourier transform infrared spectroscopy clearly monitored the evolution of the nanoparticles surface functionalization. High photo stability fluorescence of the materials was examined by high power laser irradiation and long-time storage at room temperature. Furthermore, to develop the bio-recognition of nanodiamond-star shape Au/Ag, the pre-modified transfferin was utilized to conjugate with the materials, and the validation of specificity and activity was confirmed in vitro using J5 cancer cell. Ultimately, this muti-functional material exist huge potential for application in simple synthesis, non-cytotoxic, long-term tracing and high photothermal therapy for effective treatment of cancer.

9:30 AM

(ICACC-S7-003-2015) Upconverting Lanthanide-Nanophosphors: New Players in Bioimaging and Energy Conversion Technologies?

E. Hemmer*[1]; M. Quintanilla Morales[1]; S. Rohani[1]; J. Marques[2]; B. S. Richards[3]; F. Légaré[1]; F. Vetrone[1]; 1. INRS, Canada; 2. Heriot-Watt University, United Kingdom; 3. Karlsruhe Institute of Technology, Germany

In the upconversion (UC) process, near-infrared (NIR) light is absorbed and converted into higher energy light, which is based on the stepwise excitation among energy levels with long lifetimes. UC emission is well-known for lanthanide (Ln) ions, such as Er^{3+}, Ho^{3+} or Tm^{3+}, doped in a suitable host material, e.g. $NaGdF_4$, absorbing in the NIR range and emitting in the ultraviolet, visible and NIR range. An enhancement of the emission intensity can be achieved by co-doping with Yb^{3+} ions. Tuning the emission properties of the Ln-nanophosphors provides emission over a wide wavelength range, which opens up the possibility for a wide range of applications from bioimaging to energy applications based on photovoltaics. Research on Ln-nanophosphors for biomedical applications has garnered significant interest in recent years and the number of *in-vivo* studies is constantly increasing. Yet, the efficiency of the UC process is known to be limited which is a major drawback to the point where it also restricts applications such as those for the energy sector. Thus, besides recently obtained results in UC-based bioimaging, the potential of upconverting Ln-nanophosphors as new players in energy conversion technologies will be discussed evaluating the photoluminescence quantum yield of $NaGdF_4$:Er^{3+},Yb^{3+} nanostructures as a function of their size, morphology and crystalline phase.

9:50 AM

(ICACC-S7-004-2015) Novel Solution Fabrication of Advanced Metal Oxide Nanomaterials for Environmental and Biomedical Applications (Invited)

K. Byrappa*[1]; K. Namratha[1]; 1. University of Mysore, India

Advanced metal oxides nanomaterials like ZnO, TiO2, NiFe2O4, CuFe2O4, and Fe3O4 possess a variety of technological applications in both environmental and biomedical fields. Processing of these advanced metal oxides through novel solution routes provide tailor made properties with a control over their size, shape, and surface chemistry as the process involved is highly useful for in situ surface modification and selective doping with controlled process parameters. In the present work a several surface modifiers have been used in the novel solution processing covering both mild hydrothermal and solvothermal conditions along with a wide range of active dopants both as single and codoped. The products obtained have been characterized using powder XRD, FTIR, UV-Vis, SEM, TEM, DLS, BET surface area. The environmental applications of these metal oxides have been explored through photocatalytic properties involving the degradation of several organic dyes under sunlight. The photocatalytic efficiency has been calculated for each compound separately. Similarly, the biological studies have been carried out in detail for these metal oxides using several biochemical assays on both gram positive and gram negative bacteria and also on chic embryos.

Integration of Functional Metal Oxide Nanostructures in Devices

Room: Coquina Salon B
Session Chairs: Sanjay Mathur, University of Cologne; Ulrich Simon, RWTH Aachen University

10:30 AM

(ICACC-S7-005-2015) Can $LiNbO_3$ be an alternative for PZT in vibrational energy harvesters? (Invited)

A. Bartasyte*[1]; M. Rakotondrabe[1]; T. Baron[1]; S. Ballandras[2]; 1. CNRS (UMR 6174) –UFC- ENSMM-UTBM, France; 2. Freq'n'Sys, France

Obtaining high power output from piezoelectric vibrational energy harvesters (PiVEHs) in many applications requires a high electromechanical coupling, hence PZT is preferred and commonly used. However, in short future, PZT has to be replaced by lead-free materials. $LiNbO_3$ (LN) presents figure of merit similar to that of PZT and is potential material for PVEHs. However, the studies of PiVEHs based on LN were limited so far by the difficulty to obtain LN films. Recently, the LN thin films of single crystalline quality on Si were achieved by wafer on wafer technology. Moreover, it was shown that pulsed-injection MOCVD is suitable method for deposition of high quality LN thin films, offering a possibility to obtain the films on larger and non-conformal surfaces and to develop more complex heterostructures. Hybrid harvesters have had increasing interest in the literature but the bulk of the work has simply involved adding multiple individual transducers placed into one package. Our research concerns the possibility of using an individual transducer element to scavenge multiple types of energy, i.e thermal and vibration. It was reported that combining piezoelectric and thermal effects could amplify the displacement in piezoelectric actuators, which therefore demonstrates that generated charges can be increased with a structure dedicated for hybrid harvesting.

11:00 AM

(ICACC-S7-006-2015) Atomic Layer Deposited VOx Thin Films for Resistive Switching Application

S. Wang*[1]; T. Singh[2]; N. Aslam[2]; H. Zhang[2]; S. Hoffmann-Eifert[2]; S. Mathur[1]; 1. Inorganic Chemistry, 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 single-layered and bilayered VOx thin films grown 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. Single-layered VOx films are 12- nm-as grown amorphous films and can be transformed into polycrystalline layers upon annealing. Bilayer-VOx films were produced by a coverage of one 6-nm-RTA-polycrystalline layer by one 6-nm-as grown layer. Capacitor structures fabricated from VOx films showed I-V characteristics interesting for the resistive switching applications. Depending on the electroforming conditions, bipolar-type memory switching with a resistance ratio ROFF/RON > 103 was obtained, and also a combination of memory and threshold switching. The latter 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.

11:20 AM

(ICACC-S7-007-2015) Constructing Electrochromic Nanocrystal-in-glass Composite Materials from Colloidal Building Units (Invited)

A. Llordés*[1]; T. W. Lee[1]; G. Garcia[1]; D. J. Milliron[2]; 1. Lawrence Berkeley National Laboratory, USA; 2. The University of Texas at Austin, USA

The integration of building units into heterogeneous architectures yields materials wherein the components and their interfaces are both essential in defining structure and functionality. Our approach to construct such composites is to chemically link inorganic clusters to colloidal nanocrystals, in aqueous solution. Upon film processing, the clusters condense forming an amorphous matrix that, surrounds and remains covalently bonded to the embedded nanocrystals. Unlike conventional solution methods, e.g. sol-gel or coprecipitation, this colloidal route allows excellent control of composition, structure and volume fraction, as well as enabling room temperature processing. This versatility offers the opportunity to, deliberately, combine functional materials. For instance, by linking plasmonic nanocrystals, e.g. Sn-doped In2O3, to amorphous Nb2O5, we demonstrate a unique dual-band electrochromic response, i.e independent modulation of visible and near-infrared light transmittance. Electrochromic window coatings with this functionality has the potential to revolutionize thermal control and lighting in buildings. Moreover, synergistic reorganization at the crystal-glass interface resulted in a 5-fold enhancement of optical contrast. These results highlight the tremendous opportunity to manipulate amorphous structure by covalently bonding it to nanocrystals, and thereby, realize new functionalities.

11:50 AM

(ICACC-S7-008-2015) Novel Group III-Nitride Optochemical Nanosensors (Invited)

J. Teubert*[1]; M. Eickhoff[1]; 1. Justus-Liebig-Universität Giessen, Germany

Group III-nitride (III-N) nanowires (NWs) and nanowire heterostructures (NWHs) are a topic of current research. Besides the possibility of fabricating novel, nanoscaled optoelectronic devices with improved stability and efficiency the excellent optoelectronic properties and the high chemical and electrochemical stability of III-N nanostructures allows the realization of novel optochemical transducers as a base for integrated sensor systems with optical read-out. We show that the photoluminescence properties of GaN/InGaN nanowire heterostructures sensitively responds to the exposure to different gases and allows the realization of novel optochemical transducers. We will demonstrate that the low operation temperatures of these transducers even allows the identification of specific molecular parameters characterizing the interaction with the nanowire surface. Concepts for integration of III-nitride NW transducers into optochemical sensor systems and the characterization of such sensor systems are also presented. For application in liquid solutions we address the bias-dependent luminescence response of III-N NWs to variations of the pH value in electrolyte solutions and we discuss this behavior in terms of photoactivated hole transfer to RedOx-levels in the electrolyte solution. A new approach for time-resolved imaging of (bio-)chemical processes is discussed.

S8: 9th International Symposium on Advanced Processing and Manufacturing Technologies for Structural and Multifunctional Materials and Systems (APMT9)

Novel Ceramic Processing II

Room: Coquina Salon A
Session Chairs: Zoltan Lences, Institute of Inorganoc Chemistry, Slovak Academy of Sciences; Hisayuki Suematsu, Nagaoka University of Technology

8:30 AM

(ICACC-S8-011-2015) Si-based Functional Ceramics from Preceramic Polymers (Invited)

G. Soraru*[1]; 1. University of Trento, Italy

Si-based Polymer Derived Ceramics, PDCs, are nanostructured multifunctional materials, which originates from organic networks through pyrolysis in controlled atmosphere. Contrary to conventional powder processing route the PDC approach allows fabricating difficult to shape components such as thin films, fibers and micro-mesoporous solids. This presentation focuses on the processing of novel high surface area and high porosity PDC aerogels of the Si-C-N-O systems for energy and sensors applications (Li-ion batteries, CO2 capture, NO2/H2 sensing) and on Si-B-O-C glass fibers with improved alkali resistance for cement reinforcement.

9:00 AM

(ICACC-S8-012-2015) Influence of Lanthanoid Dopant and N/O Substitution on the Electronic Structure and Luminescent Properties of Silicon Oxynitride Phosphors (Invited)

Z. Lences*[1]; M. Hrabalova[1]; I. Ibrahim[1]; L. Benco[1]; P. Sajgalik[1]; 1. Institute of Inorganoc Chemistry, Slovak Academy of Sciences, Slovakia

In this study europium and cerium-doped MgSiN2 and LaSi3N5 have been synthesized from Si/Mg2Si/Si3N4 or LaSi/Si/Si3N4 mixtures doped with Eu2O3, Sm2O3 or CeO2 by direct nitridation. The emission band of LaSi3N5:Eu phosphor was in the green light region, while MgSiN2:Eu emitted red light. The influence of Ce and Sm addition on the luminescent properties of LaSi3N5 and MgSiN2 phosphors will be also discussed. First-principles density-functional theory (DFT) calculations were performed to enhance the understanding of the electronic structure of the stoichiometric LaSi3N5 and La/Eu (La/Sm or La/Ce) and N/O substituted ternary nitrides. The electronic structure and band gaps were calculated also using the hybrid functional (HSE06) which gives results in reasonable agreement with experimental data. Silicon oxynitride-based phosphors were prepared also from polymer derived Si-O-C-(N) precursors and Al-alkoxide. Depending on the host lattice, i.e. O-sialon or beta-sialon, on the substitution level Si/Al and N/O, and on the doping RE (RE = Eu, Sm, Ce) content blue, green, orange and red light emitting phosphors were prepared.

9:20 AM

(ICACC-S8-013-2015) Effect of Starting Particle Size on Flexural Strength of Crack-Free, Dense SiOC Ceramics

J. Eom*[1]; Y. Kim[1]; 1. University of Seoul, Korea (the Republic of)

The effect of starting particle size on the flexural strength of bulk SiOC ceramics were investigated in polysiloxane-derived SiOC ceramics prepared by a conventional ceramic processing route. Crack-free, dense SiOC discs with 6-7 mm thickness and a 30 mm diameter were successfully fabricated from commercially-available polysiloxane without additives or with the 1 mol% Ba additive. Agglomerates formed after pyrolysis of polysiloxane led to the formation of domain-like structures surrounded by pores after sintering. The flexural strength of bulk SiOC is strongly dependent on the domain size formed and Ba addition. Both minimization of the agglomerate size in the starting powders by milling after pyrolysis and judicious selection of additives which reinforce the SiOC structure are efficient ways to improve the flexural strength of bulk SiOC ceramics. The incorporation of 1 mol% Ba into the SiOC glass improved the flexural strength of bulk SiOC ceramics significantly by the formation of both Si-O-Ba bonds and a compact silicon suboxide structure in the bulk Ba-modified SiOC. Typical flexural strength of bulk Ba-doped SiOC ceramics fabricated from submicron-sized SiOC powders was 220 MPa at room temperature.

9:40 AM

(ICACC-S8-014-2015) Glass-ceramic Proppants from Sinter-Crystallization of Waste-derived Glasses

E. Bernardo*[1]; M. Marangoni[1]; P. Colombo[1]; 1. University of Padova, Italy

Glass-ceramic proppants are currently produced by thermal treatment of glass beads, in turn obtained by a flame spheroidization apparatus. A sintering approach, if already applied to ceramic (e.g. bauxite) proppants, has not been used for glass-ceramics yet. The present investigation aims at evidencing the feasibility of glass-ceramic spheres by sinter-crystallization, i.e. viscous flow sintering with concurrent crystallization, of fine glass powders (<100 μm), in turn obtained by the melting of inorganic waste, such as red mud from Bayer process or municipal solid waste incinerator fly ash, or low-cost minerals. Whereas dense and highly crystallized monoliths are achievable by sintering at the glass crystallization temperature (TC), applying fast heating (i.e. direct insertion of samples in the furnace) and short holding times (not exceeding 30 min) on pressed powders, dense glass-ceramic beads are obtained by firing well above Tc (Tc+100°C), in order to enhance the viscous flow and promote the spheroidization of powder clusters, previously formed by casting fine powders on a rotating drum. The high degree of crystallinity and the uniform microstructure were found to contribute positively to the mechanical properties (compressive strength exceeding 120 MPa, for beads with a diameter of 1 mm, approximately).

10:20 AM

(ICACC-S8-015-2015) Catalytic Combustion Type Carbon Monoxide Gas Sensor With Novel Oxidation Catalysts (Invited)

N. Imanaka*[1]; A. Hosoya[2]; S. Tamura[3]; 1. Osaka University, Japan; 2. Osaka University, Japan; 3. Osaka University, Japan

Unfortunately, a significant problem associated with conventional catalytic combustion-type CO gas sensors is that the catalysts (for example, Pt/Al2O3 or Pd/Al2O3) require operating temperatures over 400 degree C for the complete CO oxidation. Since other gases such as methane and volatile organic compounds (VOCs) can also combust at such elevated temperatures, this type of sensors always lacks of selectivity for the target CO gas. Recently, we have developed a low-temperature catalytic combustion-type CO gas sensor, by employing the novel 10 wt% Pt/Ce0.68Zr0.17Sn0.15O2.0 catalyst at 70 degree C, which temperature is more than 300 degree C below the conventional ones. Furthermore, the high thermoelectric material of aluminum nitride (AlN) was incorporated as an intermediate heat transfer layer with the oxide catalyst to from double layer during the process of the sensor fabrication. Here, novel type of catalytic combustion type carbon monoxide gas sensor was realized, exhibiting excellent sensing performance that shows an enhanced sensivity and also drastically accelerated the response to CO at the moderate temperature of 70 degree C.

10:50 AM

(ICACC-S8-016-2015) Continuous Spray Synthesis of Doped-Pyrochlore Oxide Catalysts for Hydrocarbon Reforming

J. Yancey*[1]; M. Smith[2]; D. Berry[2]; D. Haynes[2]; D. Shekhawat[2]; E. M. Sabolsky[1]; 1. West Virginia University, USA; 2. National Energy Technology Laboratory, USA

Improved performance of nano-catalysts with complex stoichiometry and morphologies will increase the demand for continuous, high-yield synthesis methods. Doped oxide catalysts with pyrochlore and perovskite structures are of particular interest in catalysis due to their ability to be modified by many metal dopants, which permit direct modification of the electrocatalytic properties. The purpose of this study is the synthesis of complex pyrochlore nano-catalysts using a continuous spray synthesis process. This spray synthesis method permits control of catalyst properties with continuous production. An aqueous solution containing various metal salts and organic additives was utilized to control the final nano-catalyst morphology and phase purity. The key variables identified include precursor composition, residence time, in-situ sintering temperature, and concentration. The surface area, crystallite size, and morphology of the catalyst were measured using BET, XRD, and SEM, and the performance of the catalyst was tested in a hydrocarbon reforming reactor. The results were confirmed by a series of experiments predicting and verifying catalyst reforming characteristics.

11:10 AM

(ICACC-S8-017-2015) Refractory Oxide/Silicide based Sensors for High Temperature Harsh Environmental Applications

E. M. Sabolsky[1]; K. Sabolsky[1]; R. C. Pillai*[1]; G. A. Yakaboylu[1]; S. Chockalingam[1]; B. Armour[1]; A. Teter[1]; M. Palmisiano[2]; 1. West Virginia University, USA; 2. ANH Refractories Company Technology Center, USA

Currently, expensive precious metals such as Pt, Pd and Rh are used for high temperature sensor applications in harsh environments. This work demonstrates the use of low cost refractory oxide/silicide composite conductive to form temperature and stress/strain sensors. The oxide and silicide inks were prepared by mixing the powder with polymer vehicles and screen printed on tape casted alumina substrates and subsequently sintered without delamination and cracking. The structural, thermal and morphological studies were performed by using x-ray diffraction (XRD), dilatometer and scanning electron microscopy (SEM). The electrical performance of the temperature sensors and thermocouples were measured between 100-1500 °C. In addition, the performance of the temperature sensors were evaluated by longevity test for 150 h in reduced conditions. The thermoelectric response of the temperature sensors indicates excellent stability, durability and reproducibility during thermal cycling in H2/N2 environment at 1000 °C. The stress/strain sensors were tested under flexural mode using a ring on ring configuration. The embedded strain sensors showed linear relation between force and the resistance.

11:30 AM

(ICACC-S8-018-2015) A Hydrophilic Treatment of Polypropylene Film for Particle Induced X-ray Analysis of Human Blood

H. Suematsu*[1]; S. Takahashi[1]; M. Fujita[2]; T. Kikuchi[3]; T. Sasaki[4]; Y. Oguri[5]; T. Suzuki[1]; T. Nakayama[1]; K. Niihara[1]; 1. Nagaoka University of Technology, Japan; 2. National Hospital Organization, Japan; 3. Nagaoka University of Technology, Japan; 4. Nagaoka University of Technology, Japan; 5. Tokyo Institute of Technology, Japan

It has been known that human beings need 36 elements to maintain the health conditions. With the progress of researches in this field, the number and the effect of the essential elements are increasing, however, the concentrations of the new essential elements in the human body to be detected are decreasing. That is the reason why comprehensive trace element analyses in human blood are important. Among many elemental analyses methods, particle induced X-ray emission (PIXE) analysis is one of the X-ray spectroscopy analysis methods. Comparing to ordinal electron induced analysis methods, incident accelerated ions can decrease the background white X-ray intensity to increase the signal to noise ratio. Furthermore, different from other solution methods, it is easy to detect all heavy trace elements in organic matter after a single experiment. One of the difficulties in this method is to prepare homogeneous and thin sample films on organic matter sample holders. We have attempted hydrophilic treatment of polypropylene films utilizing an atmospheric plasma jet. After the application of the plasma jet formed by a He gas nozzle and a power source operated at 15 kV, 14 mA and 45 kHz, the contact angle of distilled water was decreased from 80 to 43 degree. By utilizing this treatment, we concluded that a new method to prepare human blood samples for PIXE analyses was developed.

11:50 AM

(ICACC-S8-019-2015) Electrical properties of textured CaCu3Ti4O12 thin films with non-linear resistivity deposited by RF Sputtering

C. R. Foschini*[1]; A. Z. Simoes[2]; R. Tararam[3]; C. O. Paiva-Santos[3]; E. Longo[3]; 1. UNESP, Brazil; 2. UNESP, Brazil; 3. UNESP, Brazil

The discovery of the colossal dielectric constant (CDC) in the CaCu3Ti4O12 (CCTO) generates a great scientific interest in this perovskite type of material. The CCTO, with no dopants, displays also strong current-tension nonlinear behavior with possibility to be used as varistor. The CCTO electrical behavior has been intensively discussed in the literature and has been attributed to intrinsic and extrinsic defects. However, there is no agreement in the literature about the mechanisms which allow explaining the origin of these properties. The main objective of this work was to deposit compact thin films on Si/SiO2/Ti/Pt substrates by RF sputtering technique using CCTO targets prepared by mixed oxide method. Post annealing in nitrogen and oxygen atmosphere of nano-sized CCTO films were evaluated by X-ray Photoelectron Spectroscopy (XPS) and X-ray Diffraction (XRD). Films morphology was characterized by Field Emission Scanning Microscopy (FE-SEM) and show homogeneous microstructure. The dependence of annealing atmosphere on the AC and DC transport measurements was analyzed. Results and electrical properties of the films suggest the existence of polaronic defects due changes in the chemical composition.

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

Structural-property Relationships of Existing Systems II

Room: Ponce DeLeon
Session Chair: Eric Wuchina, Office of Naval Research

8:30 AM

(ICACC-S12-011-2015) Thermal Properties of Zirconium Diboride Ceramics (Invited)

W. G. Fahrenholtz*[1]; G. Hilmas[1]; 1. Missouri University of S & T, USA

The thermal properties of nominally phase pure zirconium diboride ceramics have been investigated. Previous reports of the room temperature thermal conductivity of zirconium diboride ceramics range from values as low as ~30 W/m-K to as high as ~120 W/m-K. Typically, these ceramics have been produced by hot pressing of commercial powders. Recent research at Missouri S&T has focused on systematically identifying the factors that are responsible for the range of thermal conductivity values that have been reported. The effect of carbon, a common additive used to promote densification, was systematically studied. Small carbon additions improved relative density, which increased thermal conductivity to values as high as ~95 W/m-K at room temperature. However, after second phase carbon inclusions formed, thermal conductivity decreased. The effects of transition metal additions were also studied, but it was found that all additions decreased thermal conductivity. Further increases in thermal conductivity were achieved through reactive hot pressing of ZrH2 and B, which produced ZrB2 ceramics with room temperature thermal conductivities of more than 120 W/m-K. The presentation will discuss the fundamental aspects of composition and microstructure that affect total thermal conductivity as well as the phonon and electron contributions to thermal conductivity.

9:00 AM

(ICACC-S12-012-2015) Electron and Phonon Contributions to the Thermal Conductivity of ZrB_2

G. J. Harrington[1]; G. Hilmas*[1]; W. G. Fahrenholtz[1]; 1. Missouri University of Science and Technology, USA

Zirconium diboride (ZrB_2) is a candidate ultra-high temperature ceramic (UHTC) for use as a leading/trailing edge material in hypersonic vehicles. In this application, one of the potential advantages to a UHTC, like ZrB_2, is its high thermal conductivity which would enhance the conduction of heat away from the control surfaces. In order to understand what controls the total conductivity of ZrB_2 ceramics, an analysis of the electron and phonon contributions is necessary. These contributions are not readily obtained through direct measurements and are most often obtained by the calculation of the electron contribution to conductivity using Wiedemann-Franz law and electrical resistivity measurements. The biggest uncertainty in this analysis is use of the proportionality constant between thermal conductivity and electrical resistivity (the Lorenz number). The analysis of "pure" and "impure" ZrB_2 are presented with respect to determination of the electron and phonon contributions to total thermal conductivity from elevated temperature measurements of thermal conductivity and electrical resistivity. For the most pure materials, the Lorenz number deviated negatively from the theoretical value, while close agreement was obtained for ZrB_2 with higher transition metal contamination. Electrical resistivity measurements approaching 2000°C will also be discussed as deviations in linearity with temperature were observed.

9:20 AM

(ICACC-S12-013-2015) Phase Stability in Tantalum Carbides and its Relationship to Microstructure and Mechanical Behavior

G. B. Thompson*[1]; X. Yu[1]; C. R. Weinberger[2]; 1. University of Alabama, USA; 2. Drexel University, USA

Using a variable-composition ab initio evolutionary algorithm, the stability of various tantalum carbide compounds at ambient pressure and at 0K was investigated. The results revealed that TaC, Ta6C5 and Ta2C are the lowest energy configurations with Ta4C3 and Ta3C2 having slightly higher energies. The vacancy ordered Ta6C5phase had three energetically degenerate structures. A competition between vacancy ordered and stacking fault variation of the phases was seen, with the latter becoming more favorable with lower carbon content. The close formation enthalpy of each stable and metastable phase appears to 'frustrate' the carbide in the co-precipitation of multiple phases for substoichiometric compositions. Density functional theory calculations also provided the elastic constants for each of the stable and metastable phases. As the carbon content increased, the elastic constants values increased. This has been associated with the change in metallic to more covalent bonding of the carbide from the density of states and will be used to help elucidate the anomalous rise in hardness seen in some, but not all, metal carbides. The collective results of this computational work provide insight into why specific tantalum carbide phases form and the consequences they have on microstructure and properties.

9:40 AM

(ICACC-S12-014-2015) Thermal Properties of ZrB_2-HfB_2 Solid Solutions

J. Lonergan*[1]; D. McClane[1]; W. G. Fahrenholtz[1]; G. Hilmas[1]; 1. Missouri University of Science and Technology, USA

The effect of HfB_2 additions on the thermal properties of high purity ZrB_2 was studied. Reactive hot pressing of ZrH_2, B, and HfB_2 powders was used as a synthesis method. Samples were hot pressed at 2100°C and 50 MPa with Hf additions ranging from 0.01 to 1.5 wt%. Microstructures and compositions were characterized using scanning electron microscopy and x-ray diffraction analysis. Thermal conductivity was calculated from heat capacity, thermal diffusivity, and density for temperatures ranging from 25°C to 200°C. The electron contribution to the total thermal conductivity was estimated from measured electrical resistivity using the Wiedemann-Franz law. The phonon contribution was estimated by subtracting the electron contribution from the total thermal conductivity. At room temperature, diffusivity decreased from 0.47 cm^2/s for a Hf content of 0.01 wt% to 0.36 cm^2/s for a Hf content of 1.5 wt%. Electrical resistivity was also affected by varying Hf content and increased from 6.54 μΩ-cm for 0.01wt.% Hf to 7.37 μΩ-cm for 1.50 wt% Hf. Thermal conductivities varied from 100 W/m•K to 135 W/m•K, depending on Hf content. The reasons for decreased thermal conductivity with increasing Hf additions will be discussed.

Structural Stability under Extreme Environments

Room: Ponce DeLeon

Session Chair: Greg Hilmas, Missouri University of Science and Technology

10:20 AM

(ICACC-S12-015-2015) High-Temperature Materials for Hypersonic Applications (Invited)

E. Wuchina*[1]; 1. Office of Naval Research, USA

In the last decade, the interest and research on ultra-high-temperature materials for hypersonic vehicle and weapon applications has increased dramatically in the US and worldwide. Research funded by the US Office of Naval Research is focused the development of Materials and Processes, mechanical behavior/life prediction methodologies, and affordable fabrication capabilities for DoD propulsion systems and aerostructures. This is accomplished through basic and applied programs leading to advances in the understanding and development of high temperature materials for extreme thermal loading in oxidizing environments. This includes combustion/propulsion flowpaths and aerosurfaces, including leading edges and nosetips for a variety of high speed vehicles. An objective of sponsored basic research is to provide a fundamental understanding of the chemistry and physics of materials in extreme environments, particularly at temperatures above 2000°C. In addition to the new ICME-related activities that will be described, current investments that provide more near-term offrams to platforms will be described, including Investments in polymer and organometallic precursors, and programs in characterization and testing of materials for thermostructural and thermochemical response in relevant environments.

10:50 AM

(ICACC-S12-016-2015) High temperature mechanical properties of UHTCs: Present and future perspectives

E. Zapata-Solvas*[1]; D. Gómez-García[2]; D. D. Jayaseelan[3]; A. Domínguez-Rodríguez[2]; W. E. Lee[3]; 1. CSIC-US, Spain; 2. University of Seville, Spain; 3. Imperial College London, United Kingdom

Ultra-high temperature ceramics (UHTCs) are promising candidates for hypersonic applications as a consequence of their high melting point, in excess of 3000 °C for ZrB2 and HfB2 UHTCs. The UHTCs community has traditionally focused on the development of more oxidation resistant UHTCs composites as a consequence of poor oxidation resistance of monolithic UHTCs. Oxidation resistance has been the focus of UHTCs development in the last decade, whereas other properties, such as high temperature mechanical properties remain somewhat neglected. Moreover, UHTC components have to withstand high stresses during hypersonic re-entries (≈500 MPa at 2000 °C), which calls into question the reliability of UHTCs components. More recently, mechanical properties of UHTCs at high temperatures are being increasingly studied within the UHTCs community. Flexural strength is the chosen property to study the reliability of UHTCs under hypersonic conditions. However, little is known about whether any deformation mechanism is active at high temperature or not. In this work, the deformation mechanisms of HfB2-based UHTCs to 2000 °C and the role of different second phases (SiC and La2O3-SiC) on the deformation mechanism are analyzed. Cavitation or reaction damage and its effect on ductility of traditional UHTCs composites points towards the need for a new approach for UHTC alloys under hypersonic conditions.

11:10 AM

(ICACC-S12-017-2015) General trends in electronic structure, stability, chemical bonding and mechanical properties of ultrahigh temperature ceramics TMB2 (TM=transition metal)

Y. Zhou*[1]; H. Xiang[1]; Z. Feng[1]; Z. Li[1]; 1. Aerospace Research Institute of Materials & Processing Technology, China

The electronic structure, stability, chemical bonding and mechanical properties of 3d, 4d and 5d transition metal diboride TMB2 were investigated using first-principles calculations based on density functional theory. All the primary chemical bonds, i.e., metallic, ionic and covalent have contributions to the bonding of TMB2. The number of valence electrons of transition metals or the valence electron concentration (VEC) of TMB2 has strong effects on the lattice parameters, stability and mechanical properties of TMB2. Both lattice constants a and c decrease with VEC, with c decreases faster than a, which is attributed to the enhanced TM d-B p (sp2) bonding. Bulk modulus B of TMB2 increases continuously with VEC due to the enhanced TM d-B p (sp2) and TM dd bonding. Shear modulus G increases with VEC, reaching a maximum at VEC=3.33, and then decreases with further increase of VEC. YB2 and MnB2 have low Young's modulus and are predicted to have good thermal shock resistance. According to Pugh's criterion (G/B<0.571), MnB2, MoB2 and WB2 are predicted as ductile or damage tolerant UHTCs. All the TMB2 based UHTCs have high hardness and they can only be machined by electrical discharge method.

11:30 AM

(ICACC-S12-018-2015) Protections against oxidation by UHTC deposition and/or infiltration on Carbon/ Carbon composites

A. Allemand*[1]; C. VERDON[2]; O. SZWEDEK[2]; Y. LE PETITCORPS[2]; T. PIQUERO[1]; 1. CEA, France; 2. LCTS, France

The hafnium carbide compound is an ultra high refractory ceramic (UHTC); as a result it could be of interest for the protection of carbon/carbon composites against oxidation at high temperatures. However HfC and most of these metallic carbides present a non stoechiometric composition with carbon vacancies. As a consequence, the oxidation resistance is poor at low temperatures (500-1000°C). In order to overcome this main drawback the HfC can be associated with a carbide (SiC) presenting a better oxidation resistance at lower temperatures. Three coating routes have been studied; the first one is the Chemical Vapour Deposition and/or Infiltration (CVD/CVI) which enables to obtain very thin coatings, the second one is the Spark Plasma Sintering (SPS) technique which permits to get thicker coatings of interest for understanding the oxidation mechanism involves at temperatures as high as 2000°C. And the third one is the Reactive Melting Infiltration (RMI) which enables to infiltrate this alternate SiC/HfC coating inside a dense carbon/carbon composite. This study describes the CVD/CVI, SPS and RMI conditions for the deposition and infiltration of the alternate SiC/HfC coating. Oxidation tests have been performed under air until 2000°C and show that a ten alternate layer can be efficient during 300s. The oxidation mechanism will be discussed.

11:50 AM

(ICACC-S12-019-2015) A Diffusion-Based Oxidation Model for Cracking In UHT Ceramics

K. Nikbin*[1]; 1. ICL, United Kingdom

In the high temperature regime (>1600oC) ceramics can exhibit failure owing to oxidation and creep in some ways similar to metals at lower temperatures. A combined creep continuum damage, multiaxial ductility, environmentally assisted time dependent material oxidation and crack growth model based on a gas/solid interface diffusional properties 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 and material oxidation distributed from the surface interface depending on the mechanism of damage proposed. The model can be used to predict surface damage owing to oxidation provided that the kinetics of the process are known. In the case of parabolic oxidation kinetics the distribution of damage in the oxidized layer is assumed to follow Fick's second law of diffusion. Owing to the complexity of the oxidized layer an equivalent diffusivity is used, which can be estimated numerically if the parabolic rate constant is known. Experiments on a representative three point bend geometry are being performed to derive basic material properties to input into the model and validate its capability in predicting damage and cracking in ultra-high temperature ceramics.

S13: International Symposium on Advanced Ceramics and Composites for Sustainable Nuclear Energy and Fusion Energy

Ceramics for Advanced Fission Concepts

Room: Tomoka B
Session Chair: Lance Snead

8:30 AM

(ICACC-S13-011-2015) Mechanical Behaviour of SiC/SiC composites after immersion in a Sodium environment at 550°C and up to 2000h (Invited)

C. Sauder*[1]; J. Braun[1]; F. Balbaud[2]; F. Rouillard[3]; C. Gueneau[4]; 1. DEN/SRMA/LTMEX, France; 2. DEN/DADN, France; 3. DEN/DPC/SCCME/LECNA, France; 4. DEN/DPC/SCCME/LM2T, France

Owning to recent progress in the fabrication of stoichiometric fibers with a good stability under neutron irradiation, SiC/SiC composites are candidates for nuclear applications such as channel tube guide for SFR reactors (SFR). Indeed, a recent patent demonstrates that the use of SiC/SiC composites, for this application, could significantly improve the safety of SFR. In this work, the interaction between SiC/SiC composites and sodium has been studied at 550°C (nominal temperature of the coolant in SFR) up to long times (2000h). Tensile mechanical behaviour of composites, before and after immersion in sodium environment, will be presented. At last, features of the stress-strain behaviour will be discussed with respect to microstructural analysis.

9:00 AM

(ICACC-S13-012-2015) SiC-SiC Composite Technology Needs and Developments for the Energy Multiplier Module Reactor, EM2 (Invited)

C. A. Back*[1]; C. P. Deck[1]; H. E. Khalifa[1]; G. M. Jacobsen[1]; J. Opperman[1]; O. Izhvanov[1]; J. Sheeder[1]; J. Zhang[1]; H. B. Chen[1]; 1. General Atomics, USA

Silicon carbide is an attractive material for advanced nuclear reactors because of its high temperature behavior and resistance to neutron irradiation damage. It may be employed in advanced accident-tolerant Light Water Reactor (LWR) fuel cladding, or more generally for gas-cooled reactors, which can achieve a higher efficiency using a Brayton cycle and operate at higher temperatures than conventional thermal reactors. In the advanced gas-cooled Energy Multiplier Module EM2, SiC and SiC-SiC composite materials are employed for the fuel cladding, as well as for a broader range of reactor core components, to meet the demanding 30-yr lifetime goal. This presentation will cover the range of SiC-SiC technology needs and development needed for the EM2 reactor.

9:30 AM

(ICACC-S13-013-2015) Corrosion of Materials in Molten LiF-BeF2 (FLiBe) Salt for Fluoride Salt-Cooled High Temperature Reactor (Invited)

K. Sridharan*[1]; G. Cao[1]; G. Zheng[1]; M. Anderson[1]; 1. University of Wisconsin, USA

The Fluoride Salt-Cooled High Temperature Reactor (FHR) is among the advanced nuclear reactor concepts being considered by the U.S and other nations. The FHR offers many advantages including higher temperature and atmospheric pressure operation and high degree of passive safety. The primary coolant in the FHR will be molten LiF-BeF2 (FLiBe) and the secondary coolant is also likely to be a fluoride salt. Materials corrosion in molten fluoride salts is an important challenge because the protective oxide layer is readily fluxed away in this environment. Furthermore, even trace amount of impurities (e.g., moisture, oxygen, and metals) can dramatically accelerate corrosion. FHR will use metallic, ceramic, and composite components for its construction. AISI 316 stainless steel and Hastelloy-N are being considered for the reactor vessel, and SiC-SiC and C-C composites are being considered for control rod/housing and core barrel applications, respectively. Nuclear graphite will be used as reflector and moderator in the reactor core and the TRISO fuel particles consist of CVD SiC and pyrolytic carbon coatings. The results of corrosion tests performed on these materials in 7Li enriched FLiBe at 700oC as evaluated by weight change measurements, electron microscopy, and x-ray diffraction will be presented along with salt purification and redox control approaches.

Joining Technology for Nuclear Ceramics I

Room: Tomoka B
Session Chair: Christina Back

10:20 AM

(ICACC-S13-014-2015) Recent Progress in Development and Testing of Low Activation, Radiation Tolerant Joints for Ceramic Accident Tolerant Fuel Cladding

H. E. Khalifa*[1]; G. M. Jacobsen[1]; C. A. Back[1]; 1. General Atomics, USA

Silicon carbide and silicon carbide fiber reinforced, silicon carbide matrix (SiC SiC) composites are candidate materials for nuclear fuel cladding due to their retention of strength at elevated temperature, neutron flux, and in the presence of steam. A reliable means to join silicon carbide components is imperative to the successful implementation of SiC based structural nuclear materials. This work focuses on a joint material selected for low activation and is expected to behave well under reactor operating conditions. Bench tests show it delivers a high purity Beta SiC joint material that has the strength and permeability performance capable of withstanding internal pressures associated with LWR operation. Out of pile and in pile tests will be summarized in terms of the pre and post irradiation mechanical testing and microstructural evolution. No degradation in joint strength was observed following irradiation.

10:40 AM

(ICACC-S13-015-2015) Properties of Al2O3 – CaO glass joints of silicon carbide tubes

M. Gentile*[1]; T. Abram[1]; 1. The University of Manchester, United Kingdom

This research work studies the microstructure and the properties of glass Al2O3-CaO material after laser irradiation. The Al2O3-CaO glass was used as joining material during laser brazing of SiC/SiC tubes for nuclear applications. The physical properties and corrosion resistance of the braze material were investigated using secondary electron microscopy, thermal analysis and autoclave tests, while the mechanical properties of the braze were analysed carrying out four points bending tests. Electron optical observations reveal that at the end of the laser treatment Al2O3-CaO joints had a compact and homogeneous microstructure with good adhesion to the silicon carbide substrate. The joined silicon carbide specimens survived autoclave tests and they were resistant at very high temperatures, the measured shear strength for the joints was of about 50 MPa. The experimental results show that glass Al2O3-CaO material is resistant in extreme environmental condition and therefore is suitable to be used as joining material for laser brazing of silicon carbide.

11:00 AM

(ICACC-S13-016-2015) Brazing of SiCf/SiCm composite plates

E. Jacques[1]; L. Maillé*[1]; Y. Lepetitcorps[1]; C. Lorrette[2]; 1. Laboratoire des Composites Thermostructuraux, France; 2. CEA Saclay, France

The present work is part of the Fourth Generation reactors program where is described the methodology and the results for joining SiC substrates by metallic silicides with SiC powder reinforcements. The more severe temperature in service are in the range of 1000°C but short time incursions at 1600 or 2000°C have to be anticipated. One of the key issues is the joining of the SiCf/SiCm composites to seal the combustible cladding. We describe the results for joining SiC and SiCf/SiCm plates at liquid state using disilicides. Joint integrity and joint strength can be improved by adding small SiC particles to the silicides powders. The assemblies have been performed in an inductive furnace. Wettability tests and thermo-mechanical properties analysis have been carried out on the joints and will be introduced. Cross sections of the assembly were prepared to study the joint/substrate chemical bonding, the cracking and the crack deflection in the vicinity of the interface. Post thermal treatments in the solid state performed under a controlled atmosphere have been carried out in order to study the thermal stability of the assembly. Finally, results on 4-bending point mechanical tests will be presented to validate the compositions.

11:20 AM

(ICACC-S13-017-2015) Evaluating Ceramic Joints in Annular Geometries: Preliminary Test Design and Analysis

Y. Katoh*[1]; T. Koyanagi[1]; J. Kiggans[1]; 1. Oak Ridge National Laboratory, USA

The application of silicon carbide ceramic composites to nuclear systems will require robust and hermetic joining in annular geometries. Examples of such integration requirements include end-plugging of fuel rods for light water reactors and advanced fast reactors and manifold sections in meander tube-based helium-cooled fusion blankets. The three-dimensionally shaped bonding surfaces in these applications impose additional challenges, in terms of processing, radiation effects, and testing, as compared to flat bonding surfaces in two-dimensional joints. This paper will discuss preliminary development of test article geometries and test methods for ceramic joints in annular geometries, which are reasonably representative of joining practices in assumed nuclear applications, adequate for determination of properties of interest, and applicable for evaluation of environmental effects including influences of neutron irradiation.

11:40 AM

(ICACC-S13-018-2015) He Irradiation on Glass Ceramics for Nuclear Applications

V. Casalegno*[1]; L. Gozzelino[1]; T. Moskalewicz[2]; R. Gerbaldo[1]; G. Ghigo[1]; S. Rizzo[1]; F. Laviano[1]; M. Ferraris[1]; 1. Politecnico di Torino, Italy; 2. AGH University of Science and Technology, Poland

SiC/SiC composites are very promising materials for use in fusion reactors; a critical issue for a wider use of these materials is the development of suitable joining methods to assemble large SiC/SiC components; on the other hand, the use of joining materials having radiation hardness comparable to SiC is needed. Glass ceramics such as CaO–Al2O3 (CA), SiO2–Al2O3–Y2O3 (SAY) and SiO2–Al2O3–MgO (SAMg) showed big potentialities as joining materials and their preliminary radiation tests under neutron beam are encouraging. This study focuses on the radiation hardness of CA, SAY and SAMg by means of 5.5 MeV He-ions up to fluences able to induce

in localized regions of the samples tenths of displacements per atom (dpa), i.e. a damage comparable with that expected for locations in nuclear fusion apparatus. The samples were subsequently examined by TEM to correlate the micro/nanostructural changes with the dpa and the He concentration distribution and to detect changes in crystalline and amorphous phases. Analysis of irradiated samples showed that in correspondence to the He implantation zone, the microstructure is slightly changed; dislocation loops, high density of small bubbles, accompanied by voids were detected in some irradiated areas. Cracks formation was observed to initiate close to bubble clusters. No grain amorphization was detected all along the irradiated area.

FS1: Geopolymers, Chemically Bonded Ceramics, Eco-friendly and Sustainable Materials

Synthesis, Processing and Microstructure, Porosity, Composites I

Room: Oceanview

Session Chairs: Waltraud Kriven, University of Illinois at Urbana-Champaign; Claus Rüscher, LUH

8:30 AM

(ICACC-FS1-001-2015) Effect of the reactivity of the alkaline solution on geopolymer formation (Invited)

S. Rossignol[1]; A. Gharzouni*[1]; E. Joussein[1]; 1. SPCTS, France

Geopolymer materials have gained tremendous interest as promising new class of binders, environmentally friendly and with good working properties. Taking into account that the used precursors affect strongly the properties of the final materials, this study focuses on the effect of the alkaline solution reactivity and the metakaolin properties on the geopolymer formation. For this purpose, several geopolymer samples were synthesized from two alkaline solutions and four metakaolins. The structural evolution of formed geopolymers was investigated using FTIR spectroscopy and pH value during the formation. The mechanical properties were measured by compression tests. The results allow to evidence that the type and the amount of siliceous species and non bridging oxygen atoms control the alkaline solution reactivity. The effect of metakaolin reactivity is more significant when activated with a poorly reactive alkaline solution. However, the alkaline solution governs the reaction when it is highly reactive. Therefore, the extent of depolymerization of the alkaline solution and the reactivity of the metakaolin are crucial parameters that control the rate of polycondensation and the mechanical properties of the geopolymer materials.

9:00 AM

(ICACC-FS1-002-2015) Plant ashes as activator for alkali activation (Invited)

H. Rahier*[1]; A. Peys[2]; B. Blanpain[2]; Y. Pontikes[2]; 1. Vrije Universiteit Brussel, Belgium; 2. KU Leuven, Belgium

Alkali activation is a way to minimize the environmental impact of constructions on our environment. The alkaline activators however need substantial energy for their production and they can be rather expensive, especially for people in developing countries. Ashes from biomass incineration often contain a large proportion of possible activators such as Ca or K oxides or carbonates. These ashes are mostly regarded as waste. Some ashes were screened and tested on their ability to act as an activator for (meta)kaolinite. Oak/beech, cotton and maize ashes were compared in this study. The chemical composition does not only change largely with the type of plant but also with the part of the plants. To produce inorganic polymers two main options were tried out. The ash was mixed with the dry clay and water was added, or only the soluble content of the ash was used for alkali activation. The reactivity and the mechanical properties of the obtained inorganic polymers are investigated and a preliminary study into the structure of the material is made. A compressive strength of about 20 MPa was obtained for compositions were the pure ash was added to metakaolinite. The samples also proved to be stable in water.

9:30 AM

(ICACC-FS1-003-2015) Use of Diatomite as Fumed Silica Alternative in a Geopolymer Formulation

C. Bagci*[1]; W. M. Kriven[2]; 1. Hitit University, Turkey; 2. University of Illinois at Urbana-Champaign, USA

Diatomite of Turkish origin was used as an alternative silica source to replace fumed silica in a geopolymer formulation. As-received diatomite was calcined at 400 °C for 5 h in an open air furnace and then dissolved with potassium hydroxide (KOH) and deionized water for overnight magnetic stirring to make water glass. In addition, a KOH solution with fumed silica was prepared by the same route. Both KOH alkaline solutions were mixed with metakaolin (Al2O3•2SiO2) separately. The viscous and homogenous slurries were poured into a mold to obtain bar geopolymer samples at ambient temperature and cured in a constant 50 °C temperature/humidity oven for 24 h. XRD and SEM analyses were used to compare the morphology of both types of geopolymers as well as the as-received diatomite. Room temperature 4 point flexure and compressive strength of both geopolymer samples were also investigated. The results were briefly discussed with respect to the possibility of using the diatomite as an alternative cheap silica source to make geopolymer.

10:10 AM

(ICACC-FS1-004-2015) Effect of triglyceride source on the physical properties of geopolymer foams obtained by the saponification / peroxide / gelcasting combined route (Invited)

M. S. Cilla*[1]; M. R. Morelli[2]; P. Colombo[3]; M. D. Innocentini[4]; 1. Federal University of São Carlos, Brazil; 2. Federal University of São Carlos, Brazil; 3. University of Padova, Italy; 4. University of Ribeirão Preto, Brazil

The adoption of the saponification/peroxide/gelcasting combined route has already proved effective to the production of geopolymer foams with a total porosity of ~85 vol%, open porosity as high as ~70 vol%, average cell size (D_{50}) of 318 μm, and possessing a specific surface area of 50 m^2/g. The saponification reaction consists of the hydrolysis of the triglycerides found in oils or fats, plus glyceride, a water soluble molecule (glycerol) which can be extracted by water after the curing process. The combined use of the two techniques (saponification and gelcasting) leads to interconnected porosity: the in situ formation of the soap molecules is exploited to generate macro-porosity and also peroxide was added to contribute to the macro-pore formation. Moreover, since different oils and fats have different physicochemical characteristics, this work aimed to evaluate such difference on physical properties, mainly porosity, permeability and specific surface area (important for filtration or adsorption applications) of the produced geopolymer foams.

10:40 AM

(ICACC-FS1-005-2015) Effect of fiber length on dynamic and static mechanical properties of milled, carbon fiber-reinforced, potassium geopolymer composite (Invited)

S. Cho*[1]; R. D. Schmidt[2]; E. D. Case[2]; W. M. Kriven[3]; 1. University of Illinois at Urbana-Champaign, USA; 2. Michigan State University, USA; 3. University of Illinois at Urbana-Champaign, USA

Randomly oriented 60 and 100 μm short carbon fibers were added to reinforce potassium geopolymer with different contents (5, 10, 15 and 20 wt%). Single-Edge Notched Beam (SENB) testing determined the effect of fiber length on fracture toughness. Uniaxial and biaxial compressive strengths were measured by compression and ring on ring (ROR) tests, respectively. Moreover, Young's modulus, shear modulus and Poisson's ratio were determined by dynamic measurements such as impulse excitation (IE) and resonant ultrasound spectroscopy (RUS) methods. In addition, various theoretical models and Weibull statistics were considered for further analyses of the measured values.

11:10 AM

(ICACC-FS1-006-2015) Alkaline solubility evaluation of raw materials as geopolymerization preliminary step (Invited)

R. Cioffi*[1]; B. Liguori[1]; 1. University Parthenope, Italy

The formation of geopolymers from natural minerals, calcined clays, industrial by-products or a combination of them has been widely explored. Solubility tests in alkaline solution let to directly determine the amount of reactive silicate and aluminate species. Several parameters can affect the solubilisation of silicon and aluminum in alkaline media, such as the molarity of the solution, the solid-to liquid ratio, the time of contact and the mixing conditions. In order to set up a method to test the ability of a material to react in alkaline media, different aluminosilicate source have been selected: one mineral (zeolitized tuff), two industrial by products (coal fly ash and silt), one reservoir clay sediment and one commercial metakaolin. Accordingly two different tests have been selected to determine the release of Si and Al in alkaline solution: (1) by mixing 0.5 g of solid with 20 ml of alkaline solution (NaOH) for fixed times under continuous stirring. The variables studied are: the concentration of the alkaline solution (3 and 7 M) and the time of dissolution (5, 10, 24 and 72h). (2) by putting into contact 0.5 g of solid with 500 ml of alkaline solution (NaOH) in static condition at 60°C. The variables studied are: the concentration of the alkaline solution (3 and 7 M) and the time of dissolution (1, 3, 7 and 14 days). Mass solution/solid ratio: 1000.

FS4: Additive Manufacturing and 3D Printing Technologies

Additive Manufacturing and 3D Printing Technologies II

Room: Coquina Salon G

Session Chairs: Soshu Kirihara, Osaka University; Jens Günster, BAM

8:30 AM

(ICACC-FS4-008-2015) Dense powder beds for powder-based additive manufacturing of ceramics (Invited)

J. Günster*[1]; C. M. Gomes[1]; T. Mühler[2]; A. Zocca[3]; J. G. Heinrich[2]; 1. BAM, Germany; 2. TU Clausthal, Germany; 3. Università di Padova, Italy

Many of the most successful and precise additive manufacturing (AM) technologies are based on the deposition layer-by-layer of a flowable powder. Since the first pioneering patents for powder based AM many developments have been introduced, greatly extending the use of different materials, improving the physical properties of the components built and enhancing the accuracy of the process. Still very important issues remain nowadays, hampering a completely autonomous production of parts and even restricting the freedom of design by means of these technologies. One of the major issues is the low density and stability of the parts during the building process, which implies the need of support structures in most of the AM technologies: The powder bed surrounding the part has an essential role, since it should support the structure during building, until it's ready for removal. Nonetheless, the deposition of new layers generates lateral forces often resulting in a displacement of the part built. Therefore, support structures are normally built along with the part to prevent this shifting, even though they would not be strictly necessary. Three approaches for the stabilization and densification of powder beds will be presented: The Layerwise Slurry Deposition process LSD, the application of a gas flow though the powder bed and the Selective Volume Sintering of ceramic powder compacts.

9:00 AM

(ICACC-FS4-009-2015) Fabrication of three-dimensional ceramic microstructure using a plastic mold prepared by streolithograhy

J. Tatami*[1]; S. Maruo[1]; 1. Yokohama National University, Japan

Wet molding using a slurry is one of the typical powder processes to make bulk body. In this study, we prepared a very small plastic mold by streolithography, followed by wet molding using a dense slurry to make a ceramic green body. When the plastic was eliminated by firing in air, we determined the firing profile based on the master decomposition theory in order to inhibit formation of cracks in green body. After organics were eliminated, several kinds of three-dimensional ceramic microstructure were fabricated by firing at higher temperatures. A plastic mold was also prepared by two-photon stereolithography in order to fabricate a ceramic having much smaller structure. As a result, we successfully obtained a three-dimensional ceramic sintered body of several micrometer level.

9:20 AM

(ICACC-FS4-010-2015) Fabrication of Micro Ceramics Components by Nanoparticles Paste Stereolithography

S. Kirihara*[1]; 1. Osaka University, Japan

Through computer aided design, manufacturing and evaluation, ceramics dendrite structures with spatially ordered micro cavities were successfully fabricated by using stereolithography of an additive manufacturing process. Micrometer order ceramic lattices were propagated spatially in computer graphic space. Photo sensitive liquid resins with ceramics nanoparticles were spread on a grass substrate by using a mechanical knife edge, and ultra violet micro patterns were exposed by digital micro mirror devices to create cross sectional solid layer. After these layers stacking, obtained composite precursors were dewaxed and sintered in an air atmosphere. Alumina micro photonic crystals with a diamond lattice structure were fabricated to control electromagnetic waves in terahertz frequency ranges. Subsequently, artificial bones of calcium phosphate with dendritic scaffold structures were modeled to realize excellent biological compatibilities. Moreover, Solid electrolyte dendrites of yttria stabilized zirconia with spatially ordered porous structures were fabricated for fuel cell miniaturizations.

9:40 AM

(ICACC-FS4-011-2015) New Materials for Additive Manufacturing of High-Performance Ceramics (Invited)

M. Schwentenwein*[1]; J. Homa[1]; 1. Lithoz GmbH, Austria

The Lithography-based Ceramic Manufacturing (LCM) process is an additive manufacturing (AM) technique especially designed for the fabrication of precise and strong ceramic objects. The layer-by-layer building principle enables the direct production of the 3D objects from the respective CAD data. This paper focuses on the development of new materials for this technology. Photocurable suspensions on the basis of zirconia, tricalcium phosphate (TCP) and silica were prepared and processed by the LCM process. Especially the development of an AM approach for the fabrication of dense zirconia parts with a theoretical density of up to 99.4 % and a 4 point bending strength above 650 MPa significantly broadens the applicability of AM for the production of functional ceramic parts. The fabrication of defined scaffolds and cellular structures made from bioresorbable TCP provides opportunities towards application in the biomedical field eg. as bone replacement material while silica-based compounds structured by means of LCM can be used as cores for the casting of a broad variety of metals and especially for superalloys. Thus, the addition of zirconia, TCP and silica as standard materials for the LCM process significantly improves its versatility and the impact of AM of high-performance ceramics in general, especially in the direction of tough ceramics, biomedical applications and investment casting.

10:30 AM

(ICACC-FS4-012-2015) Fabrication of alumina bulk by powder layer stacking process

M. Hotta*[1]; N. Kondo[1]; T. Ohji[1]; 1. National Institute of Advanced Industrial Science and Technology (AIST), Japan

Alumina green body was fabricated by powder layer stacking process, and the green body was heated to obtain alumina bulk. Density and microstructure of the specimens were investigated.

10:50 AM

(ICACC-FS4-013-2015) Ceramics 3D Printing by Selective Inhibition Sintering

J. Zhang*[1]; B. Khoshnevis[1]; 1. University of Southern California, USA

Selective Inhibition Sintering (SIS) has been proven effective in producing polymeric and metallic parts. Due to the low cost and high quality of SIS printing, the impact of SIS printing in the 3D printing industry could be disruptive. The potential of SIS is further extended to the field of ceramics, another important but hard to print material, by the same mechanism of creating an easy to break sacrificial mold. Due to the high sintering temperature of ceramics, a dry powder inhibitor is applied for inhibition and a specific powder delivery system is implemented. Experiments have shown the feasibility and ease of printing out ceramic parts. Additional experiments are underway to increase the part accuracy and to optimize sintering process.

11:10 AM

(ICACC-FS4-014-2015) Additive Manufacturing of drainage segments for cooling system of crucible melting furnaces

M. Fateri*[1]; A. Gebhardt[1]; G. Renftle[1]; 1. FH Aachen, Germany

The cooling process in induction based crucible melting furnaces for Industrial applications is one of the important and challenging factors in production and safety engineering. Accordingly, proper implementation of the cooling system of the furnace using optimum cooling guides and fail-safe features are critical in order to improve the safety of the process. Regarding this, manufacturing of porous material with high electrical isolation for the drainage segments of the cooling channels is examined in this study. Consequently, various geometries with different porosities using glass and ceramic powder are fabricated using Selective Laser Sintering (SLS) process. The manufactured parts are examined in a prototype furnace testing and the feasibility of the SLS manufacturing of parts for this application is discussed.

FS5: Single Crystalline Materials for Electrical, Optical and Medical Applications

Semiconductor I

Room: Tomoka C

Session Chairs: Leo Schowalter, Crystal IS; Matthias Bickermann, Leibniz Institute for Crystal Growth (IKZ) Berlin

8:30 AM

(ICACC-FS5-009-2015) SiC crystal growth of elecrical and optical devices (Invited)

K. Kakimoto*[1]; 1. Kyushu University, Japan

This paper focuses on crystal growth of understanding and control of SiC for electrical and optical requirements. SiC is a promising material for devices operating at high temperatures, high power and high frequency. The physical vapor transport (PVT) method has been most successful and common method for growth of bulk SiC crystals. SiC is known to exist under a wide variety of polytypic forms more than 200 which have different characteristics and the requested polytype is different depending on a device. However, reliable explanation of the polytypic control has not been reported so far. Several growth parameters such as the growth temperature, pressure in a furnace, supersaturation, vapor-phase stoichiometry, impurities and polarity of seed surface have been discussed to influence the polytype stability. Thus, the control of polytype is a complex problem. In this study, we focused attention on the nucleation stage of crystal growth and dependence of process parameters, such as temperature of a seed, pressure in a furnace and surface polarity of a substrate, on formation of specific polytypes of SiC in a process of PVT.

9:00 AM

(ICACC-FS5-010-2015) Recent progress in SiC single crystal wafers for power electronic device applications (Invited)

T. Fujimoto*[1]; 1. Nippon Steel & Sumitomo Metal Corp., Japan

Remarkable progress has been made in the research field of silicon carbide (SiC) power devices. SiC single crystals are a key material, and physical vapour transport (PVT) method is now a widely adopted growth process for fabricating SiC crystals. Up to now, the PVT method has been developed markedly, giving rise to the realization of 100mm diameter SiC crystals with much lower levels of the dislocation density. Research attempts for larger diameter SiC crystals in our laboratory, partly supported by New Energy and Industrial Technology Development Organization (NEDO), have also led to success in realisation of 150mm-diameter SiC crystals. In view of high-power device applications, a special attention has paid to a particular type of the dislocations dependently of the device structures to be fabricated, for example, basal plane dislocations (BPDs) and threading screw dislocations (TSD). In our talk, a possible mechanism for the SiC single crystal growth in PVT based upon the Si-C binary system is firstly introduced. This contributes surely to the marked improvement of the crystallinity in larger diameter crystals. A brief review of the dislocation reduction in our laboratory is then reported, specifically with regard to the BPD density which can be reduced by optimizing growth conditions in viewpoint of the residual shear stress component during the growth.

9:30 AM

(ICACC-FS5-011-2015) Germanium: From the first application of Czochralski crystal growth to the foundation of high-efficiency multi-junction solar cells (Invited)

B. Depuydt[1]; K. Dessein*[1]; 1. Umicore, Belgium

Being the pioneer material in the history of electronics, germanium has regained a lot of interest as a semiconductor material for opto-electronic and electronic applications. We present how developments in the growth of germanium single crystals and the processing of crystals into wafers have enabled the optimal exploitation of the properties of germanium for applications in infrared optics, gamma-radiation detection, photovoltaics and LEDs. For each application, we will explain the relevant material properties and required crystal specifications, and their implications on the crystal growth technology. Surface properties of Germanium wafers will be discussed with regard to their use as substrate for high-efficiency multi-junction solar cells for space application and CPV (Concentrated Photovoltaics).

10:20 AM

(ICACC-FS5-012-2015) Homoepitaxial growth on single-crystal β-Ga_2O_3 substrates by molecular beam epitaxy (Invited)

K. Sasaki*[1]; M. Higashiwaki[2]; A. Kuramata[1]; S. Yamakoshi[1]; 1. Tamura corporation, Japan; 2. National Institute of Information and Communications Technology, Japan

Gallium oxide (β-Ga_2O_3) has recently received a lot of attention as a potential material for power devices. Ga_2O_3 has an extremely large bandgap of 4.6-4.9 eV. The breakdown electric field strength is expected to be 8 MV/cm from the bandgap, and the carrier

concentration can be controlled over a wide range from 10^{16}-10^{19} cm^{-3} by doping. Baliga's figure of merit, a basic parameter showing how suitable a material is for power devices, is several times larger than that of 4H-SiC or GaN. Another important feature of Ga_2O_3 is that a large single-crystal substrate can be fabricated by using the melt growth method at atmospheric pressure. This ability would directly lead to easy low-cost mass production and is a big advantage over SiC and GaN substrates. In this study, we developed a technique enabling homoepitaxial growth of Ga_2O_3 for power device applications. We studied the relation between the orientation of the Ga_2O_3 substrate and the epitaxial growth rate and found an orientation that can grow at over 3 μm/h. Moreover, we found that the carrier concentration could be controlled and a smooth surface could be obtained through optimization of the growth temperature. Ga_2O_3 MOSFETs fabricated using this technique showed excellent characteristics, including a high breakdown voltage of over 350 V and complete channel pinch-off.

10:50 AM

(ICACC-FS5-013-2015) Halide Vapor Phase Epitaxy of β-Ga2O3 (Invited)

Y. Oshima*[1]; E. G. Villora[1]; K. Shimamura[1]; 1. National Institute for Materials Science, Japan

β-Ga2O3 possesses the widest bandgap (4.8 eV) among the transparent conductive oxides. This large value, only surpassed by diamond, confers to this compound an extraordinary potential for high-power devices in comparison with its counterparts SiC and GaN. Nowadays, β-Ga2O3 single crystals are grown from melt by the EFG technique, while homoepitaxial thin films are deposited by the MBE technique. From the technological point of view, another growth technique is demanded to realize high-speed growth and cost-competitive device fabrication. In this work, we demonstrate the growth of β-Ga2O3 by the HVPE technique. β-Ga2O3 thin films were deposited on c-plane off-angled sapphire substrates. GaCl and O2 were used as source materials, and the reaction took place on the substrate at 1050 degrees C. X-ray ω-2θ scans confirmed the growth of (-201)-oriented layers. X-ray pole figure measurements indicated the presence of six in-plane orientations, in accordance with the substrate symmetry. With the off-angle increase, however, one of the in-plane orientations was strongly favored, thus achieving almost heteroepitaxial layers. The deposition rate increased linearly with the feeding rate of the source materials, reaching high-speed growth rates over 100 μm/h. Therefore, these results indicate the high-potential of the HVPE technique for the growth of thick and thin β-Ga2O3 layers for the cost-effective production of β-Ga2O3 power devices.

11:20 AM

(ICACC-FS5-014-2015) Recent progress of GaN substrates manufactured by VAS method (Invited)

T. Yoshida*[1]; T. Suzuki[1]; T. Kitamura[1]; Y. Abe[1]; H. Fujikura[1]; M. Shibata[1]; T. Saito[1]; 1. Hitachi Metals, Ltd., Japan

High-quality GaN bulk substrates with a diameter of more than 100 mm are required for high-brightness optical devices and power devices. Further, to suppress losses in high-power devices, ultra-low resistivity substrates are required. Commercial GaN substrates are 50 mm in diameter and are n-type doped with Si and/or O. They are manufactured by separating a thick GaN layer hetero-epitaxially grown by hydride vapor phase epitaxy. Owing to hetero-growth, the substrates exhibit some amount of bowing. The bowing increases with the crystal diameter. Further, heavy doping needed to reduce resistivity increases the number of dislocations. Hence, it is difficult to manufacture high-quality, large, and ultra-low resistivity substrates. In this paper, we report the fabrication of such substrates by void assisted separation (VAS), which enables low and uniform dislocation density in GaN growth on a c-sapphire substrate via a porous sacrificial layer and spontaneous separation. The substrate bowing was found to increase with crystal diameter, and substrates with a diameter of more than 100 mm and radius of curvature of about 10 m were fabricated. Using Ge as a dopant instead of Si provided ultra-low resistivity of 0.14 Ωm without deterioration of crystallinity in spite of the heavy doping. These results will greatly contribute to the realization of high-performance, low-cost nitride devices.

FS6: Field Assisted Sintering and Related Phenomena at High Temperatures

Field Assisted Sintering Phenomena

Room: Coquina Salon H

Session Chair: Thomas Tsakalakos, Rutgers University

8:30 AM

(ICACC-FS6-011-2015) Effect of electric field on kinetics of chemical reaction

S. K. Jha*[1]; R. Raj[1]; 1. University of Colorado, Boulder, USA

TiO2 and Al2O3 are known to react with each other beyond 1150 C to form Al2TiO3, which is being considered for high temperature application because of its low thermal expansion coefficient. Chemical reaction is a diffusion driven phenomena, so as we go higher in temperature the kinetic of reaction also improves. In other studies, the sintering temperature of many ceramic oxides such as 3YSZ, TiO2, BaTiO3 and many others have been brought down by few hundreds of degree centigrade with the help of electric field; this method of sintering has been termed as flash sintering. Application electric field has shown to improve the diffusion rate by 2-3 orders (depending on material) of magnitude higher than that for conventional sintering at equivalent temperature, as observed in terms of sintering rate. In consecutive studies, flash sintering has shown an improvement on constrained sintering; thus establishing a different mechanism of sintering all together. This work tries to investigate this effect of electric field on the chemical reactions. X ray diffraction confirms the expedited kinetics of reaction under flash and effect of dopant with field has also been studied. Kinetics of reaction has been quantified in terms of extent of chemical reaction with time under electric field and its relation with the current density passing through has been established.

8:50 AM

(ICACC-FS6-012-2015) Carbon nanotube (CNT)-copper composites: Powder, Spark Plasma Sintering, microstructure and mechanical properties (Invited)

C. Estournes*[1]; C. ARNAUD[1]; C. GUIDERDONI[1]; G. CHEVALLIER[3]; D. MONCEAU[4]; J. HUEZ[4]; D. MESGUICH[1]; A. WEIBEL[1]; A. PEIGNEY[1]; F. LECOUTURIER[2]; C. LAURENT[1]; 1. CIRIMAT, France; 2. LNCMI, France; 3. PNF2/CNRS, France; 4. CIRIMAT, France

Copper is one of the most widely used metals for its interesting electrical and thermal properties. However its poor mechanical strength limits its use for structural applications. CNTs exhibit a high electrical conductivity and excellent mechanical properties and are a promising reinforcement. CNT-Cu composites have interesting tribological properties. CNT-Cu nanocomposite powders were prepared by mixing a CNT suspension in water with a commercial copper powder (0.5-1.5 μm) using short-time sonication. The CNT-Cu suspension was immersed in liquid N2 and freeze-dried at -40°C for 48 h in a primary vacuum (P < 20 Pa). The powders were consolidated by SPS. The microstructure of the powders and bulk composites is studied mainly by electron microscopy. The influence of CNTs on densification will be discussed. The results of microhardness and tensile mechanical tests will be presented and compared with those obtained on pure copper. Friction tests were performed using a ball-on-flat geometry in reciprocating mode. Wear tests were performed in the same conditions as the friction tests, but in rotative mode. The microhardness of the composites is higher than that for

Cu whereas the friction coefficient, wear and wear rate are lower by a factor of about 3-4. The influence of the number of walls and carbon content on the microstructure and properties is discussed.

9:20 AM

(ICACC-FS6-013-2015) Sintering by intense thermal radiation (SITR): a combinational study of temperature distribution by simulation and experiments

D. Li*[1]; Z. Shen[1]; 1. Stockholm University, Sweden

Conduction, convection and radiation are three ways of heat transfer encountered during sintering. Thermal radiation taking place between two distant bodies even without medium relies on the difference between the fourth power of their absolute temperatures according to the well-known Stefan-Boltzmann's law. The importance of radiation transfer is significantly enhanced at high temperatures compared with conduction and convection. In this study, we modified the pressure-less spark plasma sintering set-up to generate intense thermal radiation, aiming at rapid consolidation of hard-to-sinter ceramic foams (e.g. Si3N4 and SiC families). Often, it is required to apply elevated temperatures (>1800 degC) and prolonged dwell time (a few hours) by conventional sintering methods to sinter this category of ceramics with low thermal conductivity. Effects of different geometries and materials of the radiation system on the temperature distribution were simulated by COMSOL Multiphysics software. Further verification experiments were implemented to validate the simulation results. Rigid SiC, Si3N4 and SiC-Si3N4 foams were fabricated with consuming only ~30 min for the entire processes. This radiant sintering technique proved to be effective and can also be extended to rapidly consolidate other ceramic materials.

9:40 AM

(ICACC-FS6-014-2015) Field Assisted Sintering of alumina-silica based materials

M. Biesuz*[1]; V. Sglavo[1]; 1. University of Trento, Italy

Several works has been done in the last years about Field Assisted Sintering of ceramics. Many crystalline materials were studied such as zirconia, ceria, alumina and ceramic conductors. Other works were focused on the so called Flash Softening of glasses and showed that the glass transition temperature could be influenced by the application of an electrical field. In this work we analyze the effect of the application of an E-field on the sintering behavior of a composite materials that is a mixture of a crystalline and a vitreous phase. In fact, a large part of the traditional and technical ceramics contains both these phases. The crystalline phase used is α-alumina while the glass is vitreous silica obtained by hydrolyzing a TEOS solution in ethanol. Also magnesium nitrate is added in order to reduce the glass transition temperature of silica. The glass final composition results in 80 wt% of SiO2 and 20 wt% of MgO. Two different amounts of glasses are mixed with alumina: 5 wt% of glass-95 wt% of Al2O3 and 10% of glass -90 wt% of Al2O3. The FAS behavior of these materials are studied by dilatometric tests up to 1450°C. Also the glass behavior is analyzed.

10:20 AM

(ICACC-FS6-015-2015) Multi and Single-Mode Microwave Sintering for Field-Enhanced Texturing of Alumina

R. E. Brennan*[1]; R. Pavlacka[1]; C. Weiss Brennan[1]; C. G. Fountzoulas[1]; 1. US Army Research Laboratory, USA

Energy coupled to matter (ECM) research, in which external physics-based fields (electric, magnetic, acoustic, etc.) are applied to produce materials with enhanced structural and multifunctional properties otherwise unattainable by conventional processing methods, is being explored for its ability to go beyond traditional processing factors and lead to materials innovations. Microwave sintering is an ECM technique that results in highly efficient heating, allowing for high density materials to be processed at lower temperatures and shorter times, and leading to smaller grain-size microstructures and improved mechanical properties. Both multi-mode and single-mode (electric/magnetic field-separated) microwave sintering were used to study the effects of field application on texturing, grain growth, and phase development of rare earth-doped alumina (Al2O3). The microwave processing conditions were found to have a profound influence on both the crystal structure and relative amounts of the secondary phases that formed in the doped alumina. X-ray diffraction and scanning electron microscopy were used to study the surface and inner regions of the microwave sintered pellets with respect to the crystal structure, phase content, and grain size/morphology. Our results showed that the nature of the microwave field (single mode E-field versus multi-mode) affected the phase development of rare-earth doped Al2O3.

10:40 AM

(ICACC-FS6-016-2015) High Performance Tooling Materials for High Pressure and High Temperature Direct Current/Spark Plasma Sintering of Bulk Nano-Crystalline Materials

L. S. Walker*[1]; 1. GT Advanced Technology, USA

To enable the fabrication of large bulk nano-crystalline materials tooling materials must be developed that can perform at higher pressures than conventional graphite. In this study we investigate the potential materials for die tooling based on conductive ceramic materials and composite systems to achieve high pressures at high operating temperatures. The goal is to produce tooling capable of densifying relatively large samples (2+cm diameter) of bulk nano-materials using pressures > 200 MPa and temperatures >1000°C. This study includes material selection, densification optimization of the tooling materials, near net shape densification of tooling components, and testing of the final tooling assembly to densify nanocystalline materials at conditions beyond the limitations of standard graphite tooling materials.

11:00 AM

(ICACC-FS6-017-2015) In situ time resolved EDXRD study on field assisted densification of Boron Carbide

H. Bicer*[1]; E. K. Akdogan[1]; B. Visser[2]; I. Savkliyildiz[1]; T. E. Ozdemir[1]; W. A. Paxton[1]; Z. Zhong[3]; T. Tsakalakos[1]; 1. Rutgers, The State University of New Jersey, USA; 2. University of Groningen, Netherlands; 3. Brookhaven National Laboratory, USA

Boron carbide (B4C) is a high temperature covalent bonded material with unique properties that make it an important candidate for wide range of high performance applications. In situ characterization of densification of B4C under superimposed electric and thermal field have been investigated by means of EDXRD with a polychromatic 200keV synchrotron probe. Implementation of EDXRD in this study is the first of its kind in monitoring the evolution of nanoparticulate matter at the unit cell scale enabling one to analyze transient behavior. Electric field assisted densification of B4C powder is performed under a range of electric fields. At temperatures as low as 700oC, maximum current draw reached to 10A (limited by power supply), corresponding to an instantaneous power absorption. The maximum current draw is accompanied by an anomalous volume expansion of the unit cell which relaxes as the electric field is reduced. The observed anelastic volume expansion and contraction is accompanied with an increase in density up to 95%. No appreciable grain growth or phase transformation was observed in SEM analyses. The ultralow process temperatures and time clearly indicate that mass transport in this nanoparticulate system under the action of both thermal and electrical fields are of an electrochemical origin in which particle-particle contacts and associated tunneling phenomena should play a role.

11:20 AM

(ICACC-FS6-018-2015) Combining wet chemistry synthesis routes and Spark Plasma Sintering to perform ferroelectric nanostructured ceramics

C. Elissalde*[1]; G. PHILIPPOT[1]; M. ALBINO[1]; R. EPHERE[2]; R. BERTHELOT[1]; U. CHUNG[1]; G. CHEVALLIER[2]; A. WEIBEL[2]; A. PEIGNEY[2]; J. MAJIMEL[1]; B. BASLY[1]; S. MORNET[1]; C. AYMONIER[1]; M. MAGLIONE[1]; C. ESTOURNES[2]; 1. Université Bordeaux- ICMCB-CNRS, France; 2. Université Paul Sabatier- CIRIMAT-LCMIE, France

Integration of ferroelectric materials in electronic devices requires improved strategies and reliable approaches to design innovative ceramics with adjustable functionalities. Grain size, strain and interfaces can be exploited in ferroelectric materials to tailor their properties. We will emphasize the great potentiality of combining wet chemistry synthesis routes and Spark Plasma Sintering (SPS) to perform nanoscale-designed ferroelectric ceramics and composites. The supercritical fluids technology enables to obtain in a single step well crystallized Ba1-xSrxTiO3 (BST with 0< x <1) and BaTi1-xZrxO3 (BTZ with 0< x <1) nanoparticles (average grain size below 20 nm). SPS allows to perform dense nanostructured ceramics while keeping the initial grain size. Sol gel and thermolysis routes are well suited to design coated ferroelectric particles. Starting from core@shell particles, low losses composite made of uniform distribution of sub-micrometric sized BT and MgO particles was obtained in situ during the SPS process. The impact of the nanostructure, grain size and strain effects on the dielectric properties will be discussed.

11:40 AM

(ICACC-FS6-019-2015) Hybrid SPS-Hot Press Sintering of WC-based Hardmetals

P. A. Olubambi*[1]; T. G. Langa[1]; G. T. Motsi[1]; 1. Tshwane University of Technology, South Africa

The utilization of spark plasma sintering (SPS), also known as field assisted sintering (FAST) and pulsed electric current sintering (PECS) has been observed as effective technique for rapid consolidation of fully dense materials. Nevertheless, the effectiveness of this technique for sintering some classes of materials, especially non-conductive materials and larger samples with controlled and homogenized stoichiometry, microstructure and phases can sometimes be compromised. Technological efforts have therefore been focused on varying means for improving the effectiveness of SPS consolidation methods. In this study, the effectiveness of the sintering techniques of hybrid SPS and Hot Press sintering technique for the consolidation of tungsten carbide containing varying amounts of cobalt contents and chromium is investigated and compared with conventional SPS techniques. Conventional WC-Co and WC-Co-Cr powders were sintered using conventional SPS machine and in both SPS and hybrid heating modes in a hybrid SPS-hot press machine. The effectiveness of the sintering techniques are assessed with respect to microstructural and phase interactions studied using SEM and XRD techniques as well as their mechanical properties.

2nd European Union - USA Engineering Ceramics Summit

Advanced Ceramic Technologies: Current Status and Future Prospects II

Room: Coquina Salon F

Session Chairs: Girish Kale, University of Leeds; Alexander Michaelis, Fraunhofer IKTS

8:30 AM

(ICACC-PRECS-008-2015) Future potential of advanced ceramics and contribution of Fraunhofer for technology transfer to industry (Invited)

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

In a joint effort the German Ceramic Society (DKG), the German Society for Materials Research (DGM) and the German Alliance of the Ceramic Industry (VKI) has recently published an experts report on the «future potential of advanced ceramics» for industry. Due to their broad spectra of favourable properties advanced ceramic materials offer enormous potential for innovations in the buisness segments of energy- and environmental technology, mechanical engineering and engine construction, mobility, electronic appilcation and life science. Results of this study and contributions of Fraunhofer to address the identified challenges especially in the field of technology transfer from the laboratory to fabrication are presented. The joint application of structural and functional ceramic technology allows for unique combination of electronic, ionic (electrochemical) and mechanical properties enabling for development of new, highly integrated systems. This is illustrated with specific examples for Fuel Cell, Li-Ion and high temperature Na-metal batteries as well as ceramic membrane systems development.

9:00 AM

(ICACC-PRECS-009-2015) Tiny Bubbles: Porous Wall Hollow Glass Microspheres (PWHGMs) in Energy, Environmental Remediation, Defense and Medicine (Invited)

G. Wicks*[1]; 1. Wicks Consulting Services, LLC, USA

A new class of materials, called Porous Wall Hollow Glass Microspheres (PWHGMs), was developed at the Savannah River National Laboratory. These tiny glass micro-balloons are about one-half the diameter of a human hair and can range in size from 2 to 100 microns. The thin outer shells are about one micron thick and what makes these microspheres one-of-a-kind is that the team has been able to induce and control an interconnected, through-wall porosity, on a scale of 100 to 1,000 Angstroms. This porosity is then used to fill the microspheres with a variety of materials, including solids, liquids and gases, which result in unique composites having a variety of unique properties. This microsphere technology has been involved in more than a dozen different programs and applications in areas of energy, environmental remediation, defense and in medicine. PWHGMs have been patented, licensed, and are now being advanced for commercialization in various areas and disciplines, at the Applied Research Center of SC.

9:30 AM

(ICACC-PRECS-010-2015) Metal Oxide Semiconductors for Energy Harvesting Applications (Invited)

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

Metal oxide nanostructures with hetero-contacts and phase boundaries offer unique platform for designing materials architectures for sensing applications. Besides the size and surface effects, the modulation of electronic behaviour due to junction properties leads to modified surface states that promote selective detection of analytes. The growing possibilities of engineering nanostructures in various compositions (pure, doped, composites, heterostructures) and forms (particles, tubes, wires, films) has intensified the research on the integration of different functional material units in a single architecture to obtain new sensing materials. In addition, new concepts of enhancing charge transduction by surface functionalization and use of pre-concentrator systems are promising strategies to promote specific chemical interactions, however the challenge related to reproducible synthesis and device integration of nanomaterials persist. This talk will present how chemically grown and designed nanoparticles, nanowires and nanocomposites of different metals and metal oxides open up new vistas of material properties, which can be transformed into advanced material technologies.

10:20 AM

(ICACC-PRECS-011-2015) Phase transformation and ac-electrical conductivity of $Ho_2(Zr_xTi_{1-x})_2O_7$ solid solution series (Invited)

G. Kale*[1]; M. Shafique[2]; S. Mudenda[1]; D. O'Carroll[1]; Y. Iqbal[2]; R. Ubic[3];
1. University of Leeds, United Kingdom; 2. University of Peshawar, Pakistan; 3. Boise State University, USA

Binary oxide compounds of the type $A_2B_2O_7$ where A is a divalent cation and B could be tetravalent or pentavalent cation crystallise in pyrochlore structure. Pyrochlore is a superstructure of MO_2 type of oxide compounds crystallising in cubic fluorite structure. The value of cation radius ratio of r_A/r_B determines the stability of fluorite or pyrochlore structure in $A_2B_2O_7$ type of compounds. High temperature solid state ceramic route has been used to synthesise the fine powders of eleven different compositions in the solid solution series of $Ho_2(Zr_xTi_{1-x})_2O_7$ for $0 \le x \le 1$ at an interval of x=0.1. X-ray diffraction of powder samples have shown that as x increases from 0 to 1 the binary oxide compounds transforms from pyrochlore structure to fluorite around x = 0.6 - 0.7. Rietveld structure refinement of X-ray diffraction data has been done to determine the lattice constants of all the eleven compositions of the entire solid solution series. The variation of lattice constant was found to be linear as a function of increasing values of x. Ac-impedance spectroscopy between 0.1 Hz to 10^6 Hz was used to determine the conductivity of all the eleven compositions of the solid solution series in $Ho_2(Zr_xTi_{1-x})_2O_7$ over a range of temperatures between 573 - 1173 K. Results of this investigation have been correlated with the value of x and temperature in this paper.

10:50 AM

(ICACC-PRECS-012-2015) Ceramics in Electrochemical Energy Conversion, Energy Storage and Fuel Synthesis (Invited)

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

Ceramics are currently being used in many electrochemical energy conversion and storage systems. These include solid oxide fuel cells (SOFC), solid oxide electrolyzers (SOEC), oxygen separation membranes, hydrogen separation membranes, synthesis of gaseous and liquid fuels, alkali metal batteries and alkali metal thermoelectric generators, to name a few. The devices operate over a wide range of temperatures, from room temperature to 1000oC, and under harsh environmental conditions. Fundamental physical, chemical, and mechanical properties, which can depend upon materials composition and microstructure, dictate the durability of these materials in the applications environment. A unique attribute is that small changes in electrochemical properties can substantially influence their mechanical durability. Failure of these materials in applications often involves fracture or delamination, similar to many applications of structural ceramics in engineering applications. Yet, the mode of failure is almost always quite different from that typically encountered in structural ceramics. For example, in electrochemical systems, failure involves slow crack growth under electrochemical conditions. The role of physical, chemical, and electrical properties on durability of such ceramics in electrochemical systems will be discussed and contrasted with applications in which the load is purely mechanical.

11:20 AM

(ICACC-PRECS-013-2015) Metal-Supported Polymer-Derived Ceramics for Hydrogen Generation (Invited)

S. Bernard*[1]; C. Salameh[1]; U. B. Demirci[1]; P. Miele[1]; 1. European Membrane Institute, France

Proton exchange membrane fuel cell-based systems are attractive alternatives to current energy conversion technologies due to their potential to directly convert hydrogen into electrical energy. They consist of three subsystems - fuel cell stack, hydrogen generator, and hybrid power management system. Despite recent advances, there are still several issues which limit the widespread use of the fuel cell technologies. One of the most critical issues is the hydrogen source to meet the overall energy requirements for civil vehicle applications. 95% of hydrogen is produced from natural gas which means evolution of CO2. Liquid-phase hydrogen carriers such as alkaline solutions of sodium borohydride NaBH4 are attractive alternatives because of zero emission (excepted water) and high efficiency. However, the hydrolysis of NaBH4 is exothermic, very alkaline and requires catalysts. For that purpose, we develop porous ceramic supports for the growth of metallic nanoparticles and the use of the resulting nanocatalysts for the catalytic hydrolysis of NaBH4. Our main results concerning structural, textural and thermal properties of polymer-derived ceramics are reported. Their performance for the generation of hydrogen from sodium borohydride is discussed. Results show that the metal-supported ceramics are interesting nanocatalysts in pursuit of practical implantation of NaBH4 as a hydrogen source for fuel cell.

11:50 AM

(ICACC-PRECS-014-2015) Wettability and reactivity of refractory oxides in contact with liquid Ni alloys

R. Purgert*[1]; J. Sobczak[2]; N. Sobczak[3]; R. Asthana[4]; R. Nowak[2]; M. Homa[2]; G. Bruzda[2]; B. Korpala[2]; 1. Energy Industries of Ohio, USA; 2. Foundry Research Institute, Poland; 3. Motor Transport Institute, Poland;
4. University of Wisconsin-Stout, USA

Information on high temperature bahaviour of refractory oxides in contact with Ni-based alloys is of great practical importance, particularly in order to select a proper material for making foundry appliances (crucibles, moulds, filters, etc.) needed for melting and casting of Ni-based superalloys. A sessile drop method has been applied for investigation of wettability kinetics and reactivity of a large family of metal oxide substrates with liquid Ni-based alloys at a temperature of 1500°C. Both contact and non-contact heating procedures followed by drop pushing or drop sucking for in situ opening the interfaces were used. Real time melting, wetting, spreading and solidification behaviour of the alloy on a ceramic substrate was recorded by high-speed CCD camera. The chemistry and structure 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 alloying additions, contact time and type of ceramic material have been investigated. The results obtained are dissused from point of view of thermodynamic and kinetic factors affecting reactivity in selected oxide/Ni systems.

4th Global Young Investigator Forum

Theoretical Modeling and Applications

Room: Coquina Salon C
Session Chairs: Rumi Kitazawa, Japan Aerospace Exploration Agency; Mahmood Shirooyeh, University of Southern California

8:30 AM

(ICACC-GYIF-012-2015) Computational Materials Science: Where Theory meets Experiment (Invited)

D. E. Vanpoucke*[1]; 1. Ghent University, Belgium

In contemporary materials research, we are able to create and manipulate materials at ever smaller scales: the growth of wires with nanoscale dimensions and the deposition of layers with a thickness of only a few atoms are just two examples that have become common practice. At this small scale, quantum mechanical effects become important, and this is where computational materials research comes into play. Using clever approximations, it is possible to simulate systems with a scale relevant for experiments. The resulting theoretical models provide fundamental insights in the underlying physics and chemistry, essential for advancing modern materials research. As a result, the use of computational experiments is rapidly becoming an important tool in materials research both for predictive modeling of new materials and for gaining fundamental insights in the behavior of existing materials. Computer and lab experiments have complementary limitations and strengths; only by combining them can the deepest fundamental secrets of a material be revealed. In this presentation, we focus on the application of computational materials science for ceramic materials, nanowires on semiconductor surfaces, and flexible metal-organic frameworks.

8:50 AM

(ICACC-GYIF-013-2015) Dynamical and Dielectric Properties of MP2O7 (M = Ti, Zr, and Hf): A First-Principles Investigation

H. Xiang*[1]; Y. Zhou[1]; Z. Feng[1]; 1. Aerospace Research Insitute of Materials and Processing Technology, China

A first-principles investigation on the structural and vibrational properties of MP2O7 (M=Ti, Zr and Hf) has been performed with density functional theory (DFT). Using density functional perturbation theory, the Born effective charge tensors, the IR-active phonon frequencies at the center of the Brillouin zone, and the dielectric constants of MP2O7 were obtained. The anomalously large values of Z* implied the covalent bonding nature of MP2O7. The frequencies of zone center IR-active modes were closely associated with the local structural and chemical environments of atoms. The electronic and static dielectric permittivity were analyzed in detail. Our theoretical results highlight the vital role of MO6 octahedron in the determination of the properties of MP2O7.

9:10 AM

(ICACC-GYIF-014-2015) Synthesis of hollow silica spheres via sol-gel process in water-in-oil microemulsion medium and encapsulation of organic/inorganic materials with one-pot synthesis

M. Pyeon*[1]; T. Hwang[2]; S. Mathur[1]; 1. University of Cologne, Germany; 2. Korea Institute of Industrial Technology, Korea (the Republic of)

Hollow silica spheres are of great interest in many application areas due to its structural advantage, chemical stability, etc. Especially in pharmaceutical, medical We present facile route to synthesize hollow silica spheres (HSS) and encapsulate organic (Ascorbic acid) and inorganic (TiO2 nanoparticles) materials in HSS. Moreover, polyaniline is also tested as an encapsulated material. By doing this, we could confirm that in-situ synthesized polyaniline could be encapsulated in HSS while silica shell is formed from the border of micelle. Transmission electron microscopy combined with line-scanned EDS (Energy-dispersive X-ray spectroscopy) analysis has conducted to confirm the feature of synthesized particles and to see whether organic/inorganic materials are encapsulated or not. Based on the results, we simply describe possible mechanism to form secondary materials encapsulated hollow silica spheres schematically.

9:30 AM

(ICACC-GYIF-015-2015) Feasibility of Sintering Carbide Ceramic by SPS technique under Pressureless Sintering Conditions

S. Kannan*[1]; S. J.K.[1]; M. T.S.R.Ch[1]; S. C[1]; H. R.C.[1]; 1. BHABHA ATOMIC RESEARCH CENTRE, India

Sinterability of monolithic B4C was investigated under pressure-less sintering condition using spark plasma sintering facility (SPS). In the present study, carbide (B4C) material was processed with modified die setup instead of traditional/conventional plunger and die set assembly. This kind of assemblage recreates the pressure-less sintering conditions in spark plasma sintering unit. The main objective of this modified setup is to synergize the uniqueness of processing “complex shaped products” by pressure-less sintering and processing of “fine grain microstructural products” by rapid heating action offered by spark plasma sintering. Densification experiments of B4C were conducted at temperatures in the range of 1900°C to 2300°C for the holding period of 0-15min under no load condition. The Pros and Cons of this method for the fabrication of high dense ceramic structures and the resulted microstructures of the sintered material are discussed in this presentation.

9:50 AM

(ICACC-GYIF-016-2015) Size dependent strain relaxation in GaN nanorods fabricated using Ni nanomasking and reactive ion etching: A top-down approach

A. Kumar*[1]; M. Latzel[2]; M. Heimann[2]; G. Sarau[2]; S. Christiansen[2]; V. Kumar[1]; R. Singh[1]; 1. Indian Institute of Technology Delhi, India; 2. Max Plank Institute for Science of Light, Germany

GaN layers grown on sapphire suffer from compressive stress due to large lattice and thermal mismatch between GaN layer and sapphire. This stress can be reduced by creating GaN nanostructures leading to reduction in quantum confined Stark effect. [1] In present study, a top-down approach had been employed for fabricating vertically standing GaN nanorod using Ni nanomasking and reactive ion etching. It was found that diameter and density of GaN nanorods can be tuned by tuning Ni thickness. Diameter and density of the nanorods was found to increasing and decreasing, respectively with increase in Ni thickness. By changing thickness of Ni film between 5 and 15 nm, diameter can be tuned between 100 and 300 nm while density can be changed from 4 ×10^9 to 8 × 10^8 cm^-2 approximately. Raman measurements were also performed on GaN nanorods and it was compared with epitaxial film. Strain relaxation is observed only when thickness of the Ni film was more or equal to 10 nm. A Schottky diode is also fabricated on single GaN nanorod and current-voltage characteristics at room temperature were also performed. This approach can also be used for fabricating nanorods for nano-photovoltaic and nano-electronic applications.

Additive Manufacturing

Room: Coquina Salon C
Session Chairs: Danny Vanpoucke, Ghent University; Valerie Wiesner, NASA Glenn Research Center

10:30 AM

(ICACC-GYIF-017-2015) Engineering application of Menger sponge

R. Kitazawa*[1]; 1. Japan Aerospace Exploration Agency, Japan

Menger sponge is a kind of fractals. Mass of ideal Menger sponge is zero, however, Menger-sponge-like material (Menger material) is able to be fabricated. Takeda et al. reported that photonic crystal which has Menger-sponge-like structure trapped electromagnetic wave. Carpinteri et al. reported numerial simulation of fractal stress/strain behavior in the center of ideal Menger sponge. In this study, attempts were as follows, (i) Three dimensional stress/strain simulation, and (ii) compressive tests of well characterized Menger materials and composites fabricated by 3D printing. Three dimensional stress/strain distribution of Menger material under compressive strain was simulated. Menger material showed high strain energy distributed around the center. Low strain energy distributed around the surface of the material. The same tendency was showed in Menger-sponge-like composite (Menger composite), High modulus Menger material of which holes were filled with low modulus material. Menger materials, Menger composites and cube materials for reference were fabricated by 3d printing and characterized in detail. Stress/strain curves during compressive tests were obtained, and damages were observed for each specimens. Numerical and experimental results were compared. Engineering application of Menger sponge as shock absorption material was suggested. Including optical character, further application will be presented.

10:50 AM

(ICACC-GYIF-018-2015) Characteristics of a Zirconia Ceramic Processed by the Additive Manufacturing Method of Contour Crafting (CC)

M. Vali*[1]; M. Shirooyeh[1]; A. Mansourighasri[1]; P. W. Rehrig[2]; O. Kwon[2]; B. Khoshnevis[1]; 1. University of Southern California, USA; 2. Saint-Gobain, USA

Contour crafting is an Additive Manufacturing method that can be used for fabrication of ceramic parts with high surface quality and geometric accuracy at high processing speed. This method employs a computer-generated design containing sliced cross-sectional profiles of a CAD model to reconstruct the 3D part using ceramic paste as a raw material. In the current research a well-dispersed suspension of high-purity yttria-stabilized ZrO_2 was used as the feed material. The stability and rheology of the aqueous suspension were studied. After the printing step, the produced ceramic parts with desired shapes were sintered in a furnace. A series of studies was conducted on structural formability, as well as the effect of the processing parameters on surface quality and microstructural properties. This research suggests that high quality zirconia ceramic components with desired characteristics can be fabricated with the Contour Crafting technology.

11:10 AM

(ICACC-GYIF-019-2015) 3D Printing of Ceramic Suspension Gels (CeraSGels) to Produce Ceramic Components with Near-Net Shape Geometries

L. Rueschhoff*[1]; A. Diaz-Cano[1]; M. Michie[1]; V. L. Wiesner[2]; J. P. Youngblood[1]; R. W. Trice[1]; 1. Purdue University, USA; 2. NASA Glenn Research Center, USA

A syringe-type 3D printer was modified to produce complex-shaped ceramic components by printing aqueous ceramic suspension gels (CeraSGels). CeraSGels consist of ceramic powder (>46 vol%), dispersant, water-soluble polymer and water. Suspensions have been shown to exhibit yield-pseudoplastic behavior through parallel-plate rheometry. By utilizing the unique flow properties of CeraSGels, near-net shaped ceramic parts were 3D printed without heating or cooling of the suspensions and without the use of any curing agents or further chemical processes. Initial 3D printing efforts have focused on ceramic systems of alumina and zirconium diboride. 3D printed parts prior to binder burnout and sintering were easily handled after forming at ambient temperatures. Preliminary microstructural and mechanical results will be presented to prove this a viable process for forming near-net ceramic parts with complex geometries.

S1: Mechanical Behavior and Performance of Ceramics & Composites

Processing - Microstructure - Mechanical Properties Correlation II

Room: Coquina Salon D

Session Chair: Yanchun Zhou, Institute of Metal Research

1:30 PM

(ICACC-S1-022-2015) Theoretical Prediction and Experimental Investigation on the Thermal and Mechanical Properties of Bulk Yb_2SiO_5 and β-$Yb_2Si_2O_7$ (Invited)

Y. Zhou*[1]; H. Xiang[1]; 1. Institute of Metal Research, China

Silicon-based ceramics such as SiC, Si3N4 and SiC-matrix composites exhibit low density, high strength and reliability at elevated temperatures and show potential applications in gas turbine engines to improve their performance. However, the principle obstacle to the applications of these materials as hot structural components in gas turbine engines is the lack of environmental durability in combustion environments. To solve this problem, an environmental barrier coating (EBC) is needed to protect the silicon-based ceramics. Recent works demonstrate that rare-earth silicates, especially Yb2SiO5 and Yb2Si2O7, are promising candidates for EBCs due to their superior high-temperature stability, outstanding durability in water vapor, and desirable chemical and mechanical compatibility with silicon-based matrix. However, the mechanical and thermal properties of Yb2SiO5 and Yb2Si2O7 have been barely investigated. In this presentation, structural, mechanical, and thermal properties of Yb2SiO5 and β-Yb2Si2O7 investigated using a combination of first-principles calculations and experimental investigations will be presented. Theoretically, anisotropic chemical bonding and elastic properties, damage tolerance and low thermal conductivity are predicted.

2:00 PM

(ICACC-S1-023-2015) Comparative study on MAX-phase coatings produced by different thermal spray methods

D. Manitsas*[1]; N. Markocsan[1]; C. Lyphout[1]; S. Björklund[1]; N. Curry[1]; 1. University West, Sweden

In this work, we demonstrate a comparative study on Ti2AlC coatings produced by different thermal spray methods, as Ti2AlC is one of the most studied materials from the MAX phase family. Microstructural analysis for High Velocity Air Fuel (HVAF), Cold Spray and High Velocity Oxygen Fuel (HVOF) sprayed Ti2AlC (sprayed with Maxthal 211 powder) coatings were investigated using a scanning electron microscopy equipped with energy dispersive x-ray spectrometer (EDS). The volume fraction of the porosity was determined using the ASTM standard E562, a systematic manual point counting procedure for statically estimating the volume fraction by means of a point grid. The phase characterization of the as-received powder and the as-sprayed coatings was conducted using an X-ray diffractometer with Cr Kα radiation. Impact of spray parameters on the porosity and the mechanical properties of the coatings are also discussed.

2:20 PM

(ICACC-S1-024-2015) Phase Transformation Study on β-eucryptite

Y. Chen*[1]; I. E. Reimanis[1]; 1. Colorado School of Mines, USA

β-eucryptite (LiAlSiO4) is of interest because of its reversible pressure-induced phase transformation. In the present work, several experiments are performed with the goal of correlating the structure with mechanical compressibility and examining methods to alter properties via rare earth element doping. In situ diamond anvil cell testing with x-rays was performed at the Cornell High Energy Synchrotron Source to study the pressure-induced phase

transformation. Formation of the high pressure ε-eucryptite phase has been found after 2.75GPa. Lattice parameters were calculated to discuss the crystal structure of the new phase. Mg doped samples were also tested under high pressure in order to better understand the structure and property relationship.

2:40 PM

(ICACC-S1-025-2015) FIB milled micro-cantilever beams: A fracture toughness study of VACNT/ amorphous silicon nitride composites

S. Vasudevan*[1]; A. Kothari[1]; X. Liang[1]; P. Loya[2]; Y. Yang[2]; J. Lou[2]; B. W. Sheldon[1]; 1. Brown University, USA; 2. Rice University, USA

Vertically aligned carbon nanotube (VACNT) arrays grown on a tri-layer Fe/Al/Mo catalyst were infiltrated with amorphous silicon nitride using low pressure chemical vapor deposition. Focussed Ion Beam (FIB) was then employed to mill notched cantilever beams of micron sized dimensions on these composite coatings. A nanoindentor was used with a berkovich tip to load the cantilevers on the free end and the displacement response was recorded. The load displacement curves were analyzed and modelled using a finite element method (FEM) software ABAQUS® to estimate the fracture toughness properties of these composite films. An R-curve behavior is seen and is attributed to the bridging effect of the carbon nanotubes in the crack wake. The present study also explores the key contribution of nanopores formed during the fabrication stage in altering the fracture toughness of the composite.

3:20 PM

(ICACC-S1-026-2015) Graphene Oxide/Carbon Nanotube Hybrid Reinforced Alumina Nanocomposites with Improved Properties

B. Yazdani*[1]; F. Xu[2]; Y. Xia[1]; Y. Zhu[1]; 1. University of Exeter, United Kingdom; 2. The University of Nottingham, United Kingdom

Carbon nanotubes (CNTs) and graphene nanoplateles (GNPs) have offered new possibilities to improve functional and mechanical properties of advanced ceramics. However, the homogenous dispersion of CNTs and GNPs in ceramic matrix has proved to be a tough challenge owing to different surface chemistry and insoluble characteristics of ceramics. Recent studies have showed that it is possible to form highly dispersed GO (graphene oxide)-CNT aqueous suspensions without any surfactant. By changing the GO/CNT concentration, a new class of carbon material, named Graphene-CNT aerogels became accessible which may find applications in energy storage devices. In this report, we apply such surfactant free, highly dispersed and interconnected GO/CNT hybrid into Al2O3 matrix to create multifunctional nanocomposites with improved properties. Wet-dispersion technique was used to achieve uniform GO-CNT dispersion within Al2O3 powder and hot-press process was used to prepare densified nanocomposites. At optimal GO/CNT combination, fracture toughness and bending strength of the nanocomposites increased against monolithic Al2O3. SEM studies revealed GO/CNT dispersion and Al2O3 grain size in the matrix. Interface studies based on TEM analysis is used to study toughening mechanisms. On top of the mechanical properties, thermal and electrical properties of the hybrid nanocomposites will also be discussed.

3:40 PM

(ICACC-S1-027-2015) Growth of SiC nanowires in porous substrates by low pressure CVI

Y. Liu*[1]; J. Men[2]; L. Cheng[2]; Z. Shen[1]; L. Zhang[2]; 1. Stockholm University, Sweden; 2. Northwestern Polytechnical University, China

SiC nanowires (SiCNW) are nano-sized single crystal of excellent mechanical properties, chemical stability and high-temperature oxidation resistance.In this presentation, we reported the growth of SiCNW in porous substrates of graphite, silicon carbide and silicon nitride by low pressure chemical vapor infiltration (CVI). It was found that the growth position, deposition conditions and addition of catalysts all have important influence on the growth rate and morphologies of the formed SiCNW. Without the addition of any catalyst, the growth of SiCNW follows the model that the gas phase nucleates first and grows continuously along both the axial and radial directions, subsequently. With the addition of catalysts, the growth of SiCNW can be explained by the "VLS" mechanism. Low pressure chemical vapor infiltration is suitable for in situ growth of SiCNW in porous substrates due to the low growth temperature of SiCNW and high permeability of the reaction gases in porous substrate. In situ formed SiCNW with tailored size and morphologies demonstrate potentials for strengthening the C/SiC andSiC/SiC composites or for functionalizing the SiC or Si3N4 based porous ceramics for energy and environmental applications.

4:00 PM

(ICACC-S1-028-2015) Anisotropy of high thermal conductive AlN-graphen nanocomposites

D. Kata*[1]; P. Rutkowski[1]; L. Jerzy[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. In the form of monocrystal or polycrystals AlN is used in electronic devices thus squeeze out conventional materials like SiO2, Al2O3 or BeO. The AlN is applied for sensors and heat exchanger to improve their sensitivity and efficiency. Due to the thermal properties, it is also used in the arms industry as the parts of a high-power and high resolution radars. The new AlN-graphen nanohybryds were prepared by SHS to demonstrate anisotropic features and to find innovative applications for these polycrystals. The 30% of anisotropy in thermal conductivity, elastic properties and fracture toughness was obtained. The structures, morphologies, and microstructures of the hybrids were examined by X-ray diffraction, SEM and TEM methods. It is showed that graphen 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 graphen content and sintering conditions was showed.

4:20 PM

(ICACC-S1-029-2015) Mechanical and optical behavior of non-stoichiometric magnesium aluminate spinel due to varied annealing times during processing

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

Magnesium-aluminate spinel ($MgO \bullet Al_2O_3$) is a material of interest because of its optical transparency and mechanical properties. In an effort to enhance the mechanical properties, a second phase was added by precipitation from non-stoichiometric spinel. $MgO \bullet nAl_2O_3$ was prepared where n=0.95, 1.00, and 1.50 to study precipitation from magnesia-rich, stoichiometric, and alumina-rich spinels, respectively. Powders of these compositions were hot pressed, hot isostatic pressed, then annealed at 1300°C for 1, 3, and 5 hours to allow precipitation of either MgO (n=0.95) or Al_2O_3 (n=1.50). For the n=0.95 specimen, second phase MgO accounted for 1.0% of the final structure after HIPing. The amount of MgO present increased to 1.3% after annealing for 3 hours, while the maximum transmission dropped from 74% to 70%. For the n=1.00 specimen, no precipitation was observed during annealing, and maximum transmission remained at 83% even after annealing. For the n=2.00 specimen, the amount of Al_2O_3 present increased from 3.0% to 16.7% from HIPing to annealing, while the maximum transmission dropped from 40% to 16%. Mechanical properties are measured as a function of annealing time.

4:40 PM

(ICACC-S1-030-2015) Strategies for Laser Powered Heat Engines utilizing Refractories for Energy Conversion

J. Günster*[1]; J. Lüchtenborg[2]; T. Mühler[2]; J. Melcher[3]; 1. BAM, Germany; 2. TU Clausthal, Germany; 3. German Aerospace Center DLR, Germany

Currently Lasers are the only technology available, enabling the massless transfer of energy in a multi kW regime. The fact that laser systems can provide energy with minimum losses over long distances through a medium like air, in practice some miles, has stimulated the development of different strategies for the conversion of laser light into useable mechanical work. Here, efficiency is not always a major concern, but also taking advantage of the high energy density provided by lasers. The present study follows up a strategy in which a heat engine is utilized for energy conversion. In this approach a refractory material is used for absorbing laser light, dissipating the energy provided into heat and transferring this heat to the working fluid of a heat engine. Units driven by such an engine could operate autonomously in contaminated areas without carrying additional mass for batteries or fuel with the potential risk of its contamination during the mission. The presentation will introduce basic strategies for the conversion of laser light into useable mechanical work by a heat engine and will present first results obtained by employing refractories for energy conversion.

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

Advanced Thermal Barrier Coatings: Processing and Development

Room: Coquina Salon G

Session Chairs: Douglas Wolfe, Pennsylvania State University; Eric Jordan, Birla Carbon

1:30 PM

(ICACC-S2-001-2015) Development and Commercialization of Solution Precursor Plasma Spray Thermal Barrier Coatings (Invited)

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

Significant advances have been made in the development and commercialization of Solution Precursor Plasma Spray (SPPS) Thermal Barrier Coatings (TBCs). Three SPPS TBCs have been developed with improved properties: SPPS YSZ, Low K SPPS YSZ, and SPPS YAG. The improved properties derive from the unique microstructural features produced using the SPPS process. All three coatings benefit from a strain-tolerant microstructure provided by through-coating-thickness cracks and by ultra-fine splats (<2 microns). Low thermal conductivity (Low K) is generated by planar arrays of porosity, called IPBs: inter-pass boundaries, that give SPPS YSZ TBCs a thermal conductivity of 0.6 watt/moK, about 50% of APS YSZ. In the case of SPPS YAG (yttrium aluminum garnet), the SPPS strain-tolerant microstructure provides excellent thermal cycling durability, despite having greater thermal expansion mismatch strains compared to APS YSZ. SPPS YAG TBCs exhibit phase and thermal stability capability up to 1600oC, more than 200oC greater than APS YSZ. The fabrication of SPPS TBCs is now being conducted at commercial sources using production plasma guns. These fabrication trials will be described and a comparison made with the Suspension Plasma Spray (SPS) process.

2:00 PM

(ICACC-S2-002-2015) TBC Life Prediction in the Face of Non simple temperature time histories

E. H. Jordan*[1]; N. Patel[1]; 1. University of Connecticut, USA

It is more common than not that aviation gas turbines will be exposed to thermal cycle durations and maximum temperatures that are not repeated as is done in the vast majority of laboratory tests. In commercial aviation, aircrafts can fly different duration flights even during a single multi-destination flight plan and military aircrafts typically have an even greater variability in flight history. In this work, simple two level tests were run in which the temperature or cycle duration was changed approximately half way through the expected life. The remaining life following that change was then predicted by a linear damage rule and based on the decay of the measured TGO stress. The results indicate that the linear damage rule and predictions based on TGO stress were reasonably successful for midlife change in maximum temperature but considerably less successful if the cycle duration was changed.

2:20 PM

(ICACC-S2-003-2015) Change in Structure and Thermal Conductivity of (La1-xGdx)2Zr2O7 TBCs Fabricated by Suspension Plasma Spray after Heat Treatment

S. Kim*[1]; C. KWON[1]; Y. OH[1]; S. LEE[1]; H. KIM[1]; B. JANG[2]; 1. Korea Institute of Ceramic Engineering and Technology, Korea (the Republic of); 2. National Institute of Materials Science, Japan

Rare-earth zirconate oxides with pyrochlore and/or fluorite have been investigated as candidate materials for future TBCs. Pyrochlore and fluorite have analogous cubic structures 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, (La1xGdx)2Zr2O7 TBCs are fabricated by suspension plasma spray with a variety of suspension preparation conditions, such as conventional or high energy ball milling. Phase formation, microstructures, and thermal conductivities are examined with the deposited coatings of (La1-xGdx)2Zr2O7 compositions. The change in structures and thermal conductivities after heat treatment is investigated as well.

2:40 PM

(ICACC-S2-004-2015) Engineered Multilayered Multimaterial Thermal Barrier Coatings for Enhanced Durability and Functionality

V. Viswanathan*[1]; G. Dwivedi[1]; S. Sampath[1]; 1. Center for Thermal Spray Research, Stony Brook University, USA

The durability of novel plasma sprayed TBCs is of significant interest to determine possible implementation challenges as well as to realize functional benefits such as lower thermal conductivity and resistance to CMAS like attack. Gadolinium Zirconate (GZO) is one such candidate material which has demonstrated significant property benefits and hence presents an interesting TBC material to be investigated from a durability perspective. Results from this investigation suggest that while the improved thermo-chemical properties of GZO coatings could offer immense potential, the penalties associated with their lower fracture toughness present significant challenges in fabricating such coatings for higher durability. Engineered multilayered architectures of YSZ and GZO that enable optimization of location specific properties provide a means to address such implementation challenges. We experimentally demonstrate that the layer arrangement of such multilayered TBC systems comprising of low fracture toughness compositions plays a critical role in determining their cyclic life. Utilizing the benefits of processing science to engineer the microstructure of the constituent layers as well the overall multilayered TBC system, we outline the critical factors that require concurrent consideration to enable such multilayered multimaterial coatings to provide enhanced durability

3:20 PM

(ICACC-S2-005-2015) Enhancing Toughness of Thermal Barrier Coating (TBC) Materials via Lattice Modification and Secondary Phases

M. P. Schmitt*[1]; A. K. Rai[3]; R. Bhattacharya[3]; D. Zhu[4]; D. E. Wolfe[2]; 1. The Pennsylvania State University, USA; 2. The Pennsylvania State University, USA; 3. UES Inc., USA; 4. NASA Glenn Research Center, USA

Durability is a primary concern for estimating the lifetime of thermal barrier coating (TBC) and toughness is a key factor in coating durability when experiencing erosive and cyclic wear mechanisms. Generally, advanced coatings such as the rare earth zirconate pyrochlores ($RE_2Zr_2O_7$) possess higher temperature limits (>1200 °C) and lower thermal conductivities than 7YSZ yet exhibit lower toughness values. In this work, advanced TBC materials have been investigated with an aim to reduce thermal conductivity compared to 7YSZ while maintaining as good or better toughness values. This is attempted through several methods: expansion of the tetragonal field via 4^+ valent cation substitution, incorporation of secondary phases, and strain field modification. The advanced TBC materials are then compared with baseline 7YSZ and $Gd_2Zr_2O_7$ and materials system optimization is discusses.

3:40 PM

(ICACC-S2-006-2015) Enhancing the contribution of ferroelastic toughening via morphological synergy

J. A. Krogstad*[1]; 1. University of Illinois Urbana Champaign, USA

The contribution of ferroelastic switching to the toughness of thermal barrier coatings (TBCs) may not always seem significant relative to other toughening mechanisms. However, time and time again, the durability suffers in novel TBC systems lacking this mechanism. The contribution of ferroelastic switching to the toughness of ceramic coatings 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. However, thermal barrier coatings rarely conform to these assumptions—especially over the lifetime of the coating. This presentation will review the synergy between ferroelastic switching and other morphological features—e.g. dense vertical cracks, non-switching phases, microstructural texture, grain size—in conventional t'-8YSZ coatings and proposed next generation TBC systems. Micromechanical methods under development to strategically probe specific microstructural configurations will also be described.

4:00 PM

(ICACC-S2-007-2015) Isothermal Oxidation of βNiAl Bond Coat Deposited onto CMSX-4 Superalloy for Thermal Barrier Applications

A. D. Chandio*[1]; X. Zhao[2]; Y. Chen[1]; P. Xiao[1]; 1. The University of Manchester, United Kingdom; 2. Shanghai Jiao Tong University, China

Thermal barrier coatings (TBCs) are extensively used to protect turbine hardware exposed to high temperatures to enhance both the component life and engine working efficiency. TBC consists of topcoat (yttria-stablized-zirconia,YSZ), bond coat (BC) and a reaction layer grown on BC called thermally grown oxide (TGO). BC is designed to offer slow growing and intact TGO which provides good adhesion of YSZ to substrate. Pt-βNiAl BC is commonly employed in the TBC system. But oxidation performance of undoped βNiAl needs further study in order to understand the effect of Pt and/or other possible dopants on performance of βNiAl as matrix of bond coats. Therefore, the present study is focused on oxidation of the undoped βNiAl BC to work out the mechanisms behind its poor spallation resistance using pack cementation method. The results demonstrated that major degradation mode of βNiAl BC is interdifussion i.e. migration of substrate species into BC and thereafter at TGO/BC interface, resulting in the formation of complex oxides such as TiO2, Ni2AlO4 along with Al2O3. This is followed by accelerated TGO growth rates and stresses rendering spallation. In addition, the phase transition from βNiAl to γ'-Ni3Al was found that has complex detrimental effects on the TGO adhesion and its growth. Discussion on oxidation phenomena has been made.

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(ICACC-S2-008-2015) Atomic Scale Observations of Oxide in Thermal Barrier Coatings

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

Atomic scale observations of the thermal grown oxide (TGO) formed between platinum-modified bond coat and yttria-stabilized-zirconia (YSZ) ceramic top coat were performed by using a novel technique which is known as ASTAR. This technique offers the possibility to acquire reliable orientation/phase maps with a spatial resolution down to 2nm on a field emission gun transmission electron microscope (TEM). With the micro-texture information which includes mainly the crystal orientation of α-alumina columnar grains, the possible growth mechanism of the TGO layer has been discussed. This is aimed to reveal the stress evolution in the TGO layer during oxidation at elevated temperature and also to further understand the complex failure mechanisms of thermal barrier coating system (TBCs).

S3: 12th International Symposium on Solid Oxide Fuel Cells (SOFC): Materials, Science and Technology

Interconnects and Coatings

Room: Crystal

Session Chairs: Prabhakar Singh; Scott Barnett, Northwestern University

1:30 PM

(ICACC-S3-016-2015) Chemical and microstructural investigations for chromium transport in intermediate temperature solid oxide electrolysis cells (Invited)

U. F. Vogt*[1]; J. Kim[1]; A. Brevet[2]; C. Rado[2]; K. Couturier[2]; F. Lefebvre-Joud[2]; A. Zuettel[3]; 1. Empa, Switzerland; 2. CEA, France; 3. EPFL, Switzerland

As Ferritic stainless steels (FSS) are known to form volatile chromium species at elevated temperatures in oxidizing atmospheres, Cr transport from steel interconnects to solid oxide electrolysis electrodes is still a challenging issue. The transport of chromium from commercial Crofer 22APU and K41X steels through LSMC and LNF contact coatings into adjacent (La0:8Sr0:2)MnO3-δ (LSM) oxygen electrodes was investigated after aging treatments in oxygen atmosphere at 700°C, representing SOE anodic conditions, by scanning and transmission electron microscopy with quantification of the chromium distribution in contact layers, respectively by energy dispersive spectroscopy (EDS) and analysis of chromium transported into adjacent SOE anodes by inductively coupled plasma optical emission spectrometry (ICP-OES). While the contact layers significantly decreased the emission of Cr vapors from the alloys, up to 4 atom% of Cr were detected throughout the contact coatings by energy dispersive x-ray spectroscopy after 3000h. The introduction of a dense (Co,Mn)3O4 coating on the steel surface prevented the diffusion of Cr into the contact layers and is expected to lead to extended lifetimes of interconnects and SOE cells by reducing Cr transport to the electrode by up to 75%.

2:00 PM

(ICACC-S3-017-2015) Electrical and Microstructural Evolutions of La0.67Sr0.33MnO3 Coated Ferritic Stainless Steels after Long-term Aging at 800°C

C. Liu*[1]; P. Yang[1]; W. Shong[1]; R. Lee[1]; J. Wu[1]; 1. Institute of Nuclear Energy Research, Taiwan

Sr-doped LaMnO3 (LSM) coated ferritic stainless steels are commonly used as metallic interconnect for planar solid oxide fuel cells (pSOFCs). Four kinds of specimens of LSM coated ferritic stainless steels designated as C1, Z1, Z2, and I1 were employed in this study. The La0.67Sr0.33MnO3 protective films with a thickness of ~3.5 μm were successfully deposited on the surfaces of the four commercial ferritic stainless steels by pulsed DC magnetron sputtering. The evolutions of electrical and microstructural properties of the four LSM coated ferritic stainless steels aged in an air atmosphere at 800°C for 10,103 hours have been investigated. Area specific resistance (ASR) measurement showed that the initial values of the specimens of C1, Z1, Z2, and I1 aged at 800°C were 3.51, 1.15, 1.25, and 1.38 mΩcm2, respectively. The corresponding ASR values became 49.9, 16.4, 19.4, and 4.6 mΩcm2 respectively after aging at 800°C for 10,103 hours in an air atmosphere. In addition, a two-step coating process was conducted for depositing a LSM protective film on the substrate C1 using pulsed DC magnetron sputtering. The preliminary results of microstructural observation revealed that the crevices in the film resulted from LSM shrinkage at elevated temperatures could be mitigated effectively by applying the two-step coating process.

2:20 PM

(ICACC-S3-018-2015) Long-term Validation of Surface Treatment of AISI441 Interconnect for SOFC Applications in a Generic Stack Fixture Test

Y. Chou*[1]; J. Choi[1]; J. Stevenson[1]; E. Stephens[1]; 1. Pacific Northwest National Lab, USA

To bridge the gap between "button" cell testing and real sized SOFCs of industry teams, Pacific Northwest National Laboratory (PNNL) has developed a generic stack test fixture to validate and evaluate candidate SOFC materials, processing, and test conditions. For planar SOFCs, ferritic stainless steel AISI441 is considered as a leading candidate for interconnect material. A challenge has occurred for AISI441, due to Cr-oxide scale spallation. Approach to enhance the oxide scale adhesion by surface blasting was proposed and showed promising results on stand along small coupons. In this work, AISI441 was blasted with two grits (#40 and #80) followed by (Mn,Co)-spinel coating and tested in a generic stack fixture with 2"x2" LSM-based commercial cells. The cells were tested in constant current mode at 800oC with IV sweep and EIS taken periodically. Upon completion of ~6000h stability test, the cells were subjected to ~10 deep thermal cycles. Results of cell stability performance and thermal cycle behavior will be reported. In addition, post-mortem and microstructure analysis will also be conducted to have a comprehensive assessment of the surface treatment for AISI441 interconnect.

2:40 PM

(ICACC-S3-019-2015) Process Dependent Microstructure and Electrical/Protective Performances of Plasma Sprayed MCO Coatings in SOFCs

S. Han*[1]; R. Seshadri[1]; Y. Chen[1]; R. Gambino[1]; S. Sampath[1]; 1. Stony Brook University, USA

Manganese cobalt spinel ($Mn_{1.5}Co_{1.5}O_4$, MCO) coatings are prepared by air plasma spray (APS) process to protect from Cr-poisoning of cathode side in intermediate temperature-solid oxide fuel cells (IT-SOFCs). Spray parameters are manipulated in terms of hardware, gas contents, mass flow rate, and power to find relationship among process conditions, microstructure and functional properties. These various spray conditions are mapped on 2-dimensional thermal and kinetic energies space via diagnosing particle temperature and velocity in the plasma plume. Dense MCO coatings are generated by increasing thermal and kinetic energies, in contrast low temperature and velocity used coatings contain microcracks and pores that lower coating residual stress. As-sprayed coatings contain mixed phases of rock salt phases and $Mn_xCo_{3-x}O_4$ spinels due to rapid quenching and preferential vaporization of manganese and oxygen during the spray process. Post annealing process can recover oxygen in the coatings as well as allow phase transition from trapped rock salt to spinel which are demonstrated by thermogravimetric analysis (TGA)/differential scanning calorimetry (DSC), XRD, and antiferromagnetic signal from magnetic hysteresis study. In addition, coatings with high density show excellent conductivity about ~40 S/cm at 800 °C and protection characteristics.

3:20 PM

(ICACC-S3-020-2015) Development of Cost-Effective YSZ Coating Methods for SOFC Interconnects

C. Kim*[1]; R. K. Brow[2]; F. Dogan[2]; 1. MO-SCI Corporation, USA; 2. Missouri University of Science and Technology, USA

Solid oxide fuel cells (SOFCs) require robust seals that can prevent intermixing of air and fuel, remain inert in reducing and oxidizing environments while in contact with SOFC materials, and maintain their effectiveness through repeated thermal cycles. Recent research has focused on "compliant (or viscous)" glasses that remain vitreous over time in the SOFC stack operating environment, and are able to tolerate relative motion between the surfaces being sealed without the development of permanent leaks. Certain glasses (under investigation by MO-SCI and others) considered for this sealing application have broadly desirable thermo-mechanical properties and thermo-chemical characteristics, but have been found to chemically react with both bare and aluminized stainless steel SOFC interconnects, consequently forming phases that may adversely affect the integrity of the seal. On the other hand, these glasses do not react with the yttria-stabilized zirconia (YSZ) electrolyte used in most SOFC designs. Thus, YSZ could be an attractive barrier layer between the metallic SOFC interconnect and the sealing glass. Using a YSZ polymeric precursor solution method, well-adhered crack-free coatings of YSZ were formed on 441 stainless steel substrates. The YSZ-coating adhesion strengths were measured by a stud-pull method and were greater than 30 MPa. Coating parameters and micrographic studies will be discussed.

3:40 PM

(ICACC-S3-021-2015) NTN Composite Interconnect for SOFC

A. Malakhov*[1]; S. McPhail[2]; S. Somov[1]; 1. Solid Cell Inc, USA; 2. ENEA, Italy

Solid Cell has developed an SOFC interconnect material called the NTN. It is a two phase composite (cermet) consisting of Ni as the metal phase and TiO2-Nb2O5 solid solution as the oxide phase. Adjusting the relative mass percent of each phase enables precise control over the coefficient of thermal expansion of the NTN interconnect. Functionally, the oxide phase provides the NTN with mechanical strength and corrosion resistance, while the metal phase promotes electrical conductivity, thermal conductivity, and plasticity. The NTN does not contain any species of Cr, eliminating the need for a Cr barrier layer - a common problem with standard metallic interconnect materials. On a materials cost basis, it is also less expensive than the popular Plansee CFY interconnect. To date, the NTN has been tested continuously at Solid Cell for over 2 calendar years. The results have shown a stable area specific resistance (ASR), excluding a few yet unexplained resistivity spikes. The reported testing has been carried out in an isothermal environment with H2/N2 gas mix in the anode simulation chamber and ambient air in the cathode simulation chamber. Ni mesh has been used as the fuel side contact material; Pt mesh as the air side contact material. Additional experiments using various cathode contact materials have been conducted by third parties and these results will be presented.

4:00 PM

(ICACC-S3-022-2015) Sintering, Mechanical, Electrical and Oxidation Properties of Ceramic Intermetallic TiC-Ti_3Al Composites from Nano-TiC Particles

Z. Fu*[1]; K. Mondal[1]; R. Koc[1]; 1. Southern Illinois University Carbondale, USA

Our present work deals with the development of a new material system for Solid Oxide Fuel Cells (SOFC) interconnect application based on TiC-Ti_3Al. Nano-size TiC powders utilized in this research were synthesized using carbon coated TiO_2 precursors from a patented process. The pressureless sintering of TiC-Ti_3Al in vacuum was applied at temperatures between 1300-1500°C and content of Ti_3Al was varied in the range of 10-40 wt. %. XRD and SEM were used for phase evaluation and sintering behavior. Relative density increased markedly with increasing sintering temperature because of grain growth and formation of Ti_3AlC_2 secondary phase. A dense product (>95% TD) can be made from nanosized TiC powders with 10 and 20 wt. % Ti_3Al, but with about 10% porosity for 30 and 40 wt. % Ti_3Al. The mechanical properties were determined from Vickers hardness and fracture toughness calculations. Vickers hardness decreased and fracture toughness increased with increasing Ti_3Al content. The electrical conductivity and oxidation resistance of TiC-Ti_3Al cermets were investigated to evaluate the feasibility for SOFC interconnect application. The electrical conductivity measurements in air at 800 °C for 100 hours were made using Kelvin Method 4 wire 2 point method. The results will be reported in this paper.

4:20 PM

(ICACC-S3-023-2015) Advanced metallic alloy design for SOFC interconnect application

C. Hsu*[1]; A. Yeh[2]; 1. National Tsing Hua University, Taiwan; 2. National Tsing Hua University, Taiwan

The scope of this research focuses on developing new metal alloys for SOFC interconnect application. Alloy designs have been based on CALPHAD-base Jmatpro and Thermo-calc simulations. Experimental procedure include arc melting the samples, thermal analysis, heat treatment studies, evaluations of properties including oxidation, electrical conductivity and thermal expansion at 800°C, results are presented with comparisons to those of commercial alloy systems. In this work, newly designed alloys have shown great potential as interconnect materials with improved service life cycle for SOFC application.

S4: Armor Ceramics: Challenges and New Developments

Synthesis and Processing II

Room: Coquina Salon E

Session Chair: Kris Behler, ARL; Jerry LaSalvia, ARL

1:20 PM

(ICACC-S4-020-2015) Bulk Silicon doped Boron Carbide

C. Besnard*[1]; P. Brown[2]; F. Giuliani[3]; L. J. Vandeperre[1]; 1. Imperial College London, United Kingdom; 2. Defence Science and Technology Laboratory Porton Down, United Kingdom; 3. Imperial College London, United Kingdom

Light weight ballistic protection materials are attractive and essential for a number of applications. Boron carbide should be a good armour ceramic because of its excellent properties: it is one of the hardest materials in the world (25-35 GPa), it has a low density (2.52 g.cm-3), a high melting point (2450 °C), a high Young's modulus (440 GPa) and a high Hugoniot Elastic Limit (HEL 17-20 GPa). However, boron carbide shows a premature fragmentation at higher impact velocities, > 900 m.s-1. Its structure collapses and there is a loss of shear strength leading to a deterioration of the ballistic properties. This behaviour has been widely attributed to the amorphisation of the material under high pressure. It has been reported that Si doping should suppress the amorphisation, but making large quantities of Si doped boron carbide has to date remained difficult. In this paper a process will be described which allows to dope boron carbide with silicon via a bulk process. X-ray diffraction results show a clear indication of silicon incorporation in the structure. This will be supplemented with transmission electron microscopy and Raman investigations of indentations to clarify whether amorphisation is suppressed.

1:40 PM

(ICACC-S4-021-2015) Synthesis and Processing of Boron-Rich Boron Carbide

T. Munhollon*[1]; R. Haber[1]; W. Rafaniello[1]; 1. Rutgers University, USA

Boron-rich boron carbide has been produced using two varying synthesis routes. Amorphous boron was added to rapid carbothermally synthesized boron carbide during the sintering step to produce dense boron-rich boron carbide with varying stoichiometries (13 at. % C to 20 at. % C). Spark plasma sintering was used to densify all the samples to near theoretical densities. Microstructures showed little porosity and carbon pullouts. X-ray diffraction, scanning electron microscopy and Knoop hardness were used to determine stoichiometry, grain structure and hardness. In the second route, boron was added to boron carbide precursor and then reacted using rapid carbothermal reduction. Characterization using carbon/sulfur analyzer was used to determine total carbon content. X-ray diffraction was used to determine phases and free carbon content. The resulting powders were densified using spark plasma sintering and subsequent characterization was carried out.

2:00 PM

(ICACC-S4-022-2015) Densification and Microstructure of Boron Carbide with Al- and Si-Based Additives

K. D. Behler*[1]; D. A. Manoukian[1]; A. Z. Hutchinson[1]; J. LaSalvia[1]; 1. U.S. Army Research Laboratory, USA

The propensity to form grain boundary films in boron carbide using additives based on Al and Si compounds is investigated. Precursors for Al_2O_3 (Al alkoxide), SiO_2 (TEOS), and their mixtures were added in varying amounts and compositions to H.C. Starck HS Grade boron carbide powder through a wet-chemistry process in an effort to improve mixing and coat particle surfaces. Hot-pressing parameters such as temperature, dwell time and atmosphere were varied to determine their effect on densification and resulting microstructures. Densification was monitored in-situ using dilatometry and the resulting densities were measured using Archimedes' method. XRD and XRF were used to identify phases and determine Al and Si content in the pre- and post-densified powders, respectively. Resulting microstructures were characterized using optical and scanning electron microscopy. EDS and Raman spectroscopy were used to identify and map the distribution of Al- and Si-based additives within the microstructures. Experimental procedures and results are presented.

2:20 PM

(ICACC-S4-023-2015) Optimization of Water Based Boron Carbide Suspensions Gels for Room-Temperature Injection Molding to Produce Complex-shaped Armor Components

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

Room-temperature injection molding of rheologically designed ceramic suspension gel (CeraSGel) is proposed as an advanced processing technique to produce complex shaped boron carbide components for armor applications. Water-soluble polymer, dispersant, powder and water are the CeraSGel constituents, which in the right proportions tailor the suspension's rheology. Dispersant selection was performed via zeta potential measurements in order to evaluate electrostatic effects of common dispersants used in ceramics systems. Proposed formulations can be injected at room temperature and use less polymer than similar techniques with comparable solid loading. Additionally, the effect of dispersant molecular weight and volume percent was studied and optimized revealing behavior not reported in previous studies. Finally, the CeraSGel can be injected and demolded in less than an hour, obtaining a machinable green piece. The proposed method applied to boron carbide allows the fast and easy formation of complex shaped components with high hardness, low density and high melting point, making it a promising process for armor production.

2:40 PM

(ICACC-S4-024-2015) Synthesis and Crystallization Behavior of Amorphous Boron Nitride

M. Ornek*[1]; C. Hwang[1]; R. A. Haber[1]; 1. Rutgers University, USA

Amorphous Boron Nitride (a-BN) has been one of important starting materials for the synthesis of hexagonal or cubic BN. However, information on the synthesis methods and the characteristics of a-BN is not sufficient in literature. Main purpose of this presentation is to understand the conversion of chemicals to a-BN and the effects of starting material composition and heat treatment conditions on the formation of a-BN. H3BO3 and C3H6N6 were used as starting materials and the starting composition range was selected to be between 1:1 and 6:1 (H3BO3:C3H6N6, mole). As the preparation method, two-step solid state reaction method was applied: the 1st heat-treatment at 200 °C for 2 h in air and the 2nd heat-treatment at determined temperatures between 400 and 1,000 °C for 3 h in N2 gas atmosphere. Raman spectroscopy on 1:1 and 1.5:1 series showed that samples heat-treated at between 400 °C and 1000 °C are amorphous materials. And 3:1 series showed amorphous characteristics up to 800 °C heat treatment and crystalline peak after 900 °C heat treatment, which corresponds to the bonding peak of hexagonal BN phase. In the case of 6:1 series, crystallization peak was observed after 800 °C heat treatment. In summary, the crystallization temperature in H3BO3-C3H6N6 system seems to decrease with increasing H3BO3 content. Detailed results of various characterizations will be discussed in the presentation.

3:20 PM

(ICACC-S4-025-2015) c-BN seeding effect on the phase transition of *a*-BN(OC) compounds

C. Hwang*[1]; M. Ornek[1]; V. Domnich[1]; W. Mayo[2]; S. Miller[2]; R. Haber[1]; K. Reddy[3]; K. Hemker[3]; 1. Rutgers University, USA; 2. H&M Analytical Services, Inc., USA; 3. Johns Hopkins University, USA

Cubic boron nitride (*c*-BN) is one of the hardest materials, only second to diamond, and has been used in the fields of machining and grinding. Its low chemical reactivity with ferrous metals and high thermal stability in oxidizing conditions make it particularly suitable for engineering hardened steels and alloy steels. *c*-BN was first synthesized from hexagonal BN (*h*-BN) by Wentorf under high pressure and high temperature (over than 6.0 GPa and 1300 °C) in the presence of a suitable catalyst. Since then, reducing the pressure and temperature for *c*-BN synthesis has long been a challenge from the viewpoints of academic research and industrial applications. Here, we report the effect of *c*-BN seeding on the phase transition of amorphous BN (*a*-BN) or BNOC compounds. Various *a*-BN(OC) compounds, which were prepared through a solid-state reaction method and a plasma spraying method, were used as starting materials and *c*-BN with sizes of micrometer- and nanometer-scale was used as seed crystals. The phase transition tendency of *a*-BNs in the presence of *c*-BN seeds at a relatively low pressure range of 1-3 GPa was studied using XRD, Raman spectroscopy, TEM, electron energy loss spectroscopy, and FE-SEM. It was found that without *c*-BN seeds *a*-BN transformed only to *h*-BN and with *c*-BN seeds *a*-BN seems to be facilitated to transform to *c*-BN. The detailed characterization results will be discussed in the presentation.

3:40 PM

(ICACC-S4-026-2015) Influence of Powder Oxygen Content on Silicon Carbide Microstructure and Properties

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

Silicon carbide is an important material in industry and defense due to its favorable mechanical, chemical and thermal properties. In the presence of oxygen, silicon carbide powders will react to form a thin oxide layer (SiO_2) on their surfaces. This oxide layer can inhibit the densification of solid-state sintered silicon carbide and result in undesirable effects on the dense microstructure. In this study, commercially available silicon carbide powders with varying levels of oxygen content were densified via spark plasma sintering (SPS) with boron carbide and carbon additives. Several silicon carbide samples with varying microstructures were produced and the densified samples were characterized to determine the effect of the starting powder's oxygen content on their microstructure and mechanical properties.

4:00 PM

(ICACC-S4-027-2015) An investigation of Fe-B-C composites produced using spark plasma sintering

P. P. Rokebrand*[1]; I. Sigalas[1]; M. Herrmann[2]; 1. University of the Witwatersrand, South Africa; 2. Fraunhofer - Institute of Ceramic Technologies and Systems (IKTS), Germany

Fe-B-C composites were produced using iron and boron carbide powders. The powders were mixed to produce various compositions, ranging from 80 vol% Fe to 3 vol% Fe. Spark plasma sintering (SPS) was used to densify the composite powder green compacts. The sintering temperatures used ranged from 900°C for the composites with high iron content to 2000°C for those with a high boron carbide content. It was evident that during the sintering process the iron reacted with the boron carbide. XRD analysis showed the presence of FeB, Fe_2B, Fe_3C, $Fe_{23}(B,C)_6$ and residual carbon as reaction products. The phases present in each of the individual composites were dependent on the initial composition. Even at a concentration of 80 vol% iron and relatively short sintering soak time of 15 min at 900°C, the majority of the iron reacted to produce a hard Fe_2B ceramic phase. SEM analysis of the composites with a high B_4C content showed weak bonding between the FeB and the B_4C phases. Addition of Ti and its effects on the Fe-B-C system were also observed. The composites were found to have hardness values between 9.8 and 34.6 GPa with the higher hardness' being associated with the higher boron carbide content. The fracture toughness values determined were in the range of 2.8-5.3 $MPa.m^{0.5}$; with evidence of the titanium addition improving the fracture toughness of the materials with a higher boron carbide concentration.

4:20 PM

(ICACC-S4-028-2015) Densification of Boron Carbide by SPS and Comparison Properties with Hot Pressed Boron Carbide

M. F. Toksoy*[1]; R. A. Haber[1]; W. Rafaniello[1]; 1. Rutgers University, USA

High quality boron carbide powders were synthesized by Rapid Carbothermal Reduction. Synthesized and commercial boron carbide powders were densified by Spark Plasma Sintering and hot press. Densities, microstructures and hardness were compared and evaluated. Hardness results were improved with RCR synthesized materials. SPS sintered samples exhibited improved hardness compared to hot pressed samples.

4:40 PM

(ICACC-S4-029-2015) Synthesis and spark plasma sintering of tantalum carbide/boride powder

B. Mehdikhani*[1]; G. Borhani[1]; S. Bakhshi[1]; 1. Malek-e-ashtar University of Technology, Iran (the Islamic Republic of)

In this study, mechanochemcical process(MCP) is applied to synthesize ultrafine TaC powders. In this research, nano powder composite TaC-TaB2 was produced using mixtures of tantalum carbide and boron carbide as raw materials via mechanochemical process. The phase characterization during process and after sintering was utilized by X-ray diffractometry (XRD). The morphology of synthesized powder and SPS samples were studied by using scanning electron microscopy (SEM) and field emission scanning electron microscopy techniqes.TaC-TaB2 composite powder has been synthesised by a low temperature solid-state reaction between tantalum carbide and boron carbide. Studies show that by milling of powders TaC and B4C, TaB2 phase and the resulting composite TaC-TaB2 is composed. Prolonging the milling time up to 12 h resulted in a decrease of grain size to nano scale along with increasing strain and a slight increase in lattice parameter of TaC phase. Using fine tantalum carbide/boride composite (TaC-TaB2) powder, monolithic TaC-TaB2 ceramics with a relative density of 85% was obtained by spark plasma sintering(SPS)at 1900 degree centigrade . It is considered that the small particle size of TaC-TaB2 powder is important factor for preparing dense TaC-TaB2 ceramics with fine microstructure.

S6: Advanced Materials and Technologies for Energy Generation, Conversion, and Rechargeable Energy Storage

Energy Harvesting and Storage

Room: Tomoka A

Session Chairs: Hua-Tay Lin, Guangdong University of Technology; Ryoji Funahashi, National Institute of Advanced Industrial Science & Technology

1:30 PM

(ICACC-S6-018-2015) Development and application of oxide and silicide thermoelectric modules (Invited)

R. Funahashi*[1]; Y. Matsumura[1]; R. O. Suzuki[2]; S. Katsuyama[3]; T. Takeuchi[1]; E. Combe[1]; T. Barbier[1]; 1. National Institute of Advanced Industrial Science & Technology, Japan; 2. Hokkaido University, Japan; 3. Osaka University, Japan

Oxide thermoelectric materials are considered to be promising ones because of their durability against high temperature, no content of toxic elements etc. Many types of modules using p-type $Ca_3Co_4O_9$ and n-type $CaMnO_3$ have been produced. The maximum power density of the module reaches 4.3 kW/m^2 at 973 K of temperature for the heat source. In order to enhance power generation, cascade modules consisting of oxide and Bi_2Te_3 modules have been produced. The maximum power density of 7.8 kW/m^2 has been obtained at 1000 K. Thermoelectric materials showing high conversion efficiency in the middle temperature range (473-773K) and high oxidation resistance are indispensable. Recently, a silicide material with n-type property and oxidation resistance has been discovered. The composition and crystal structure of the silicide are found out $Mn_3Si_4Al_2$ and hexagonal $CrSi_2$ structure, respectively. Enhancement of Seebeck coefficient is observed by substitution of Mn by Cr. The maximum dimensionless thermoelectric figure of merit is about 0.3 at 573 K in air for $Mn_{2.7}Cr_{0.3}Si_4Al_2$. The silicide modules consisting of 14 pairs of the legs have been fabricated using p-type $MnSi_{1.75}$ and n-type $Mn_{2.7}Cr_{0.3}Si_4Al_2$ devices. Power generation and durabilty tests of the modules have been carried out. The maximum density of power against the area of the substrate is as high as 3.9 kW/m^2.

2:00 PM

(ICACC-S6-019-2015) Quest for Higher Performance Thermoelectric Materials via Defect Engineering (Invited)

J. He*[1]; T. M. Tritt[1]; 1. Clemson University, USA

Defects, often perceived as material performance limiters, turned to be a key performance enhancer of thermoelectric (TE) material. In this talk we will present case studies in filled CoSb3 skutterudite, Bi, n-type Bi2Te3, and Mg2Si involving point defects ("0-Dimensional defect"), grain boundaries ("2-Dimensional defect"), and nanoinclusions ("3-Dimensional defect"). By deliberately exceeding the filling fraction limit of Pr and in situ forming nanoinclusions, we observed a significant figure of merit improvement in Pr-filled CoSb3. In Bi, we optimized the pulse ON-OFF ratio in spark-plasma-sintering processing so as to selectively optimize the grain boundaries, as a result, all three individual TE properties were simultaneously enhanced. In n-type Bi2Te3, we adopted a chemical-exfoliation-spark-plasma-sintering procedure to introduce interfacial charged point defects that not only optimize the band filling but also lead to a favorable multi-tier preferential carrier scattering. In Mg2Si, its TE performance was significantly improved via synergistically implementation of three different types of point defects, namely, Sb dopants, Mg vacancies and Mg interstitials. These examples showcase the promise of defect engineering as a key approach to further optimizing the performance of TE material.

2:30 PM

(ICACC-S6-020-2015) Novel Materials for Thermoelectric Applications via Collaborative Theoretical and Experimental Studies (Invited)

L. M. Woods*[1]; G. Nolas[1]; 1. University of South Florida, USA

Thermoelectricity is an attractive way to convert heat to electrical energy. In order to operate efficiently, however, devices must be composed of materials with suitable transport properties, such high carrier conductivity, large Seebeck coefficient, and low thermal conductivity. These transport characteristics are internal properties, which are completely determined by the electronic structure of the materials and the limiting carrier and phonon scattering processes. We explore effective strategies based on a synergistic theoretical/computational and experimental approach to design suitable systems for thermoelectricity. Our emphasis is on systems composed of earth-abundant elements. Detailed microscopic understanding of advantageous features in several materials will be presented in order to formulate common trends for predicting beneficial thermoelectric behavior. Useful analytical models for transport in composites will also be discussed. Novel experimental results in terms of synthesis and measurements will be utilized to propel our modeling and theoretical understanding as well as for validation purposes. Future directions for thermoelectric and other energy applications development will also be discussed.

3:20 PM

(ICACC-S6-021-2015) Thermoelectric and structural modifications induced by the cation substitution on the new thermoelectric system Mn3-xCrxSi4Al2

T. Barbier*[1]; R. Funahashi[1]; E. Combe[1]; R. O. Suzuki[2]; E. Guilmeau[3]; T. Takeuchi[1]; 1. AIST, Japan; 2. Hokkaido University, Japan; 3. CRISMAT, France

Over the last decade, the increase in global interest in research on thermoelectric (TE) materials has been due to the need to find a sustainable future source of energy. Indeed, several sectors, could take advantage of thermoelectric materials capacity to directly convert the waste-heat into electrical energy. These technologies could be available only if performing and cheap thermoelectric materials, operating at temperatures well beyond room temperature, are available. For low temperature range applications (i.e. below 200°C), best performances are obtained by the well-known Bi2Te3 with optimum ZT values around 1 (or higher) at 120°C. However, it is well known that Te is toxic and scarce which prevents the use of this bulk thermoelectric material for large-scale applications and the necessity need to find alternative thermoelectric materials. In this context, we have recently shown that Mn3-xCrxSi4Al2 is an attractive candidate, which possesses high power factor values. In order to optimize the thermoelectric performance of this system, different cationic substitutions were carried out. The structural modifications induced by these substitutions were systematically investigated and correlated to the thermoelectric properties observed. A summary of the different series of substitution realized will be described and discussed in this presentation.

3:40 PM

(ICACC-S6-022-2015) Bandgap Engineering of Fe-doped (Bi1/2Na1/2)TiO3-0.06BaTiO3 ferroelectric ceramics for photovoltaic applications

L. Chen*[1]; J. Hart[1]; S. Li[1]; D. Y. Wang[1]; 1. University of New South Wales, Australia

Perovskite-type ferroelectric (FE) oxides have recently attracted increased attention as a candidate for use in photovoltaic devices because of their potentially large photovoltage outputs. However, the photocurrents generated from the FE oxides have been impeded by their wide bandgaps (Eg = 3 - 4 eV), which allows the use of only a small fraction of the solar spectrum, thus significantly reducing the photovoltaic efficiency. To achieve higher energy conversion efficiency, it is highly desired to have FE oxides that possess bandgaps in the visible range. In this study, we engineered the band structures of lead-free ferroelectric (Bi1/2Na1/2)TiO3-0.06BaTiO3 (BNBT) ceramics through Fe substitution. The calculation from density functional theory (DFT) revealed that their bandgap is substantially narrowed and intermediate states/bands appear within the forbidden gap due to the incorporation of Fe. Pure and 12.5% Fe doped BNBT ceramics were fabricated by solid state reaction route. The ceramics were characterized by XRD and XPS, respectively, to confirm the perovskite structure and orbital energy levels. The red shift of the optical absorption edge into the visible-light range and the presence of secondary absorption edge, as evidenced by the diffuse reflectance spectra, are in good agreement with our DFT calculated results.

4:00 PM

(ICACC-S6-023-2015) The CuO/Co3O4 system as thermochemical storage material

T. Block*[1]; H. Simon[1]; M. Schmücker[1]; 1. DLR, Germany

Transition metal oxides have been studied in view of their applicability as redox-materials in thermochemical storages, e.g. for solar plants (800-1100°C) to counteract discontinuities like passing clouds or day/night-cycles. Redox-based thermochemical storages absorb thermal energy during the reduction-reaction while oxygen is delivered. The reduced metal oxide later becomes re-oxidized in air and delivers thermal energy below the equilibrium temperature. Experimental investigations by STA demonstrate that the CuO/Co3O4-system is of special interest as thermochemical storage material due to its fast reaction-kinetics, high enthalpies (mass-changes) and its long-term cycling stability. Microstructural changes and phase transformations were investigated by SEM, TEM and (HT-)XRD. The composition of x=0.2 (x=Cu/(Co+Cu)) show a reduction-reaction of Co3O4+CuO→3(Cu,Co)O+O2 associated with a mass-change of 4.4%. By cooling down this reduced material in nitrogen atmosphere a further reduction of Cu2+ to Cu1+ occurs together with an additional energy conversion step. Depending on the cooling rate the value of the detected mass change from CuO/Cu2O (30K/min–mass change=0.4%; 1K/min–mass change=2.7%) as well as the microstructure of the material changes significantly. These additional energies and the influence of microstructural changes on long-term cycling stability are positive effects for use as thermochemical storage material.

4:20 PM

(ICACC-S6-024-2015) Realizing high thermoelectric figure of merit bulk nanomaterials through directed nanostructure synthesis, assembly and doping (Invited)

G. Ramanath*[1]; R. J. Mehta[1]; D. Devender[1]; T. Cardinal[1]; A. Gaul[2]; T. Borca-Tasciuc[2]; 1. Rensselaer Polytechnic Institute, USA; 2. Rensselaer Polytechnic Institute, USA

Realizing novel thermoelectric nanomaterials and tailored hetero-interfaces with metals is key for future applications in solid-state refrigeration and energy harvesting. I will discuss the synthesis and properties of a new class of doped bulk nanothermoelectric materials obtained by surfactant-directed sculpting and doping using a scalable microwave-solvothermal approach. Bulk pellets made from these nanocrystals exhibit 25-250% superior figures of merit than their non-nanostructured and non-alloyed counterparts. While nanostructuring leads to ultralow thermal conductivities, doping-induced alterations in defect chemistry and electronic band structure of the materials lead to high electrical conductivities and high Seebeck coefficients. Atomistic and electronic structure level property enhancement mechanisms will be discussed based upon a variety of microscopies, spectroscopies, and density functional theory calculations. I will conclude by demonstrating how interfacial nanolayers of coupling agents with suitably chosen termini are attractive for tailoring the electrical and thermal transport and other properties across metal-thermoelectric heterointerfaces.

S7: 9th International Symposium on Nanostructured Materials: Innovative Synthesis and Processing of Nanostructured, Nanocomposite and Hybrid Functional Materials for Energy, Health and Sustainability

One-dimensional Nanostructures for Energy Applications

Room: Coquina Salon B

Session Chairs: Alberto Vomiero, Institute of Metal Research; Alessandro Martucci, Università di Padova

1:30 PM

(ICACC-S7-009-2015) Physicochemical Interplay in Electrode Processing for Energy Storage (Invited)

P. P. Mukherjee*[1]; Z. Liu[1]; 1. Texas A&M University, USA

Recent years have witnessed a critical imperative to accelerate innovation toward improved performance, safety and life of energy storage devices for vehicle electrification, renewable energy integration and grid storage. Lithium-ion batteries (LIB), in particular, are the front runners for electric drive vehicles. The LIB performance is dictated by the electrode microstructure and properties which, in turn, are profoundly influenced by the processing conditions. Nanomaterials and nanostructures have spurred the recent innovation and breakthroughs in the development of LIB high-performance electrodes. However, the underlying interactions that take place during electrode processing and the influence on the resulting microstructure – property – performance characteristics of the electrodes are not well understood. In this presentation, a mesoscale perspective of the underlying physicochemical interactions in electrode processing will be discussed.

2:00 PM

(ICACC-S7-010-2015) Synthesis and characterization of silicon nitride nanowires

Y. Chung*[1]; J. Koo[2]; S. Kim[2]; E. Chi[2]; J. Hahn[2]; C. Park[1]; 1. Seoul National University, Korea (the Republic of); 2. OCI company Ltd., Korea (the Republic of)

Inorganic nanotubes and nanowires have recently received much attention because they usually exhibit unique optical, electrical, magnetic, and mechanical properties which are distinctive from those of bulk materials. Among these materials, silicon nitride is particularly noticeable owing to their excellent properties, such as wide band gap, high strength, high hardness, and good resistance to thermal shock and oxidation. As a result, various chemical and physical routes have been proposed for the synthesis of silicon nitride nanowires. In this study, silicon nitride nanowires were synthesized from the amorphous silicon nitride powder which was produced by low temperature vapor phase reaction method. The effect of processing parameters on the growth of silicon nitride nanowires was investigated. The silicon nitride nanowires were characterized by X-ray diffraction, Fourier transform infrared spectroscopy, scanning electron microscopy, and transmittance electron microscopy and their physical and mechanical properties were measured.

2:20 PM

(ICACC-S7-011-2015) Enhanced critical currents by flux pinning by 1D nanostructures in superconducting tapes

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

High temperature superconductor (HTS) thin films grown epitaxially on biaxially-textured oxide films on metal substrates have been developed for energy applications. These tapes have a 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. For this purpose, we have used a self-assembly process to create nanocolumnar defects of BaZrO3 simultaneously during growth of HTS films by metal organic chemical vapor deposition (MOCVD). Flux pinning by such BaZrO3 nanocolumns has resulted in a 3X improvement in the performance of the HTS tapes at the operating conditions of superconducting devices. We have also developed a chemical vapor deposition (CVD) process to prefabricate SnO2 nanowires on biaxially-textured oxide films on metal substrate which are then embedded in a subsequently grown HTS film. Since the HTS film has to be epitaxially grown, it is imperative that only out-of-plane SnO2 nanowires are present without in-plane nanostructures. The latest progress in growth of BaZrO3 self-assembled nanocolumns and CVD-grown SnO2 nanowires and their influence on the critical current of HTS thin film tapes will be discussed in this presentation.

2:40 PM

(ICACC-S7-012-2015) Electrospinning of Composite Nanofibers and Their Applications

M. Bueyuekyazi*[1]; R. Mueller[1]; S. Mathur[1]; 1. University of Cologne, Germany

Nanoscale materials (e.g., nanowires, nanotubes and nanofibers) are extensively investigated for lithium ion batteries due to their high surface-to-volume ratio and short radial lithium ion diffusion length, which results in faster charge/discharge processes. Metal oxides have drawn attention as anode materials in lithium ion batteries due to their high theoretical capacity (>800 mAh/g), which can in principle deliver a charge/discharge capacity, that is about 3 times larger than that of commercial graphite (372 mAh/g). Especially, 1D composite nanofibers such as Co3O4/C, Fe3O4/C and MnO2/C fabricated by the simple method electrospinning, have attracted increasing attention in lithium ion batteries due to high electrical conductivity of carbon and guided electron transport in axial direction. The composite nanofibers show the ability to accommodate strain through volume expansion without capacity fading resulting in better cycling performances. Additionally, the fibers form three dimensional networks which can be directly implemented into devices as self-supporting building units to greatly improve the electrochemical performances. This work presents electrospinning synthesis of metal oxide composite materials such as LiFeO2/C, Co3O4/C and TiO2/C nanofibers and the analysis of their structural and electrochemical properties as anode materials in lithium ion batteries.

Nanostructures Thin-films and Composites for Energy Applications

Room: Coquina Salon B

Session Chairs: Partha Mukherjee, Texas A&M University; Venkat Selvamanickam, University of Houston

3:20 PM

(ICACC-S7-013-2015) Synthesis and characterization of ZnO nanostructures/graphene oxide composites and its application in devices (Invited)

H. P. Nogueira[1]; N. V. Dias[1]; N. T. Azana[1]; P. J. Shieh[1]; T. Mazon*[1]; 1. Center for Information Technology Renato Archer, Brazil

The development of composite materials that combine the superior properties of graphene with the functionality of ZnO nanostructures is highly desirable and can improve the efficiency of optic and electronic devices. We have successfully synthesized ZnO nanostructures/Graphene Oxide and ZnO nanostructures/Reduced Graphene Oxide composites as powder or perpendicular aligned nanorods on rigid and flexible substrates by using chemical bath deposition. XRD, Raman spectroscopy, SEM and TEM analyses showed the growth of ZnO nanorods supported in GO or RGO sheets and have suggested that the presence of GO sheets during the synthesis is favorable to grow ZnO nanorods with smaller diameter. Application of the developed materials in dye sensitive solar cells (DSSCs), piezoelectric for energy harvesting and field emission displays will be present. The high electric mobility of ZnO and the good electrical conductivity of the RGO sheets leading to DSSCs with higher efficiency. ZnO nanostructures/GO composites on flexible substrate showed average output power density better than available commercially flexible devices and could replace batteries on RFID devices. Efficient field emission indicates that the cathods ZnO nanorods/GO composites possess good performance with low turn on and threshold fields.

3:50 PM

(ICACC-S7-014-2015) Exciton dynamics in quantum dots / metal oxide semiconductor composites

A. Vomiero*[1]; 1. CNR, Italy

Due to their unique optical features, semiconductor QDs are presented as the ultimate frontier as sensitizers 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 (a wide bandgap semiconductor). The control of exciton dynamics is critical in determining the performance of the device by regulating charge generation, separation and collection, and researchers are optimizing the matching between QDs and wide bandgap semiconductors. The most interesting results in terms of device performances were obtained by using poly-dispersed, in situ generated QDs by means of successive ionic layer absorption and reaction technique. 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 systems. 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.

4:10 PM

(ICACC-S7-015-2015) Nanostructured thin films from nanocrystalline inks (Invited)

A. Martucci*[1]; 1. Università di Padova, Italy

Solution-processing is a rapidly growing area in the field of materials science owing to the potential to reduce production costs of high-quality thin films at relatively low temperatures. Of the different wet chemistry techniques, the preparation of nanoparticles (NPs) by colloidal chemistry and their use as nanocrystal inks permit control of the particle size, size distribution, and shape; crystallinity; and surface states. This approach has been used to obtain plasmon-based optical gas sensors, transparent conductive oxide coatings and high refractive index biocompatible nanocomposites based on silk fibroin. Au NPs dispersed in a porous TiO2 matrix represent an effective design for a gas sensor's active material owing to their catalytic and localised surface plasmon resonance properties. Al-doped ZnO (AZO) or Ga-doped ZnO (GZO) represent inexpensive alternatives to indium tin oxide. AZO and GZO nanocrystals that show transparency in the visible range and absorption in the near-infrared range have been synthesized by colloidal chemistry obtaining coating with comparable properties of those prepared by physical techniques. Silk Fibroin, the protein extracted from the silk fiber, has been used successfully during the last few years as a platform for optics. Here we report on the synthesis of easy tailored refractive index nanocomposite made of silk and titanate nanosheets.

4:40 PM

(ICACC-S7-016-2015) ZnO/WO3 Bi-layered Thin Films for Efficient Solar Water Splitting

S. Sharma*[1]; B. Kumari[1]; A. Verma[1]; V. R. Satsangi[2]; S. D. Kaura[1]; R. Shrivastav[1]; 1. Dayalbagh Educational Institute, India; 2. Dayalbagh Educational Institute, India

Abstract: This study deals with the synthesis of ZnO/WO3 bi-layered thin film nanostructures, grown over glass substrate and investigated for possible use in photo-electrochemical (PEC) splitting of water to produce renewable hydrogen energy. Bi-layered structures, synthesized through sol-gel followed by sintering in air offered synergistic effect of the two oxides with regard to the absorption of light and the transport of photo-generated charge carriers. Film samples were characterized for micro-structural, surface and optical characteristics. In photo-electrochemical measurements current-voltage (I-V) characteristics were recorded under darkness and illumination, using films as working electrode. XRD pattern established dominant evolution of hexagonal Wurtzite ZnO and Monoclinic WO3, with average crystallite size varying from 45 to 60 nm. AFM analysis indicated preferential growth of nanocrystallites along c-axis, while SEM analysis confirmed films having uniform morphology. Bi-layered films yielded significant gain in photocurrent, compared to mono-layered pristine samples.

S8: 9th International Symposium on Advanced Processing and Manufacturing Technologies for Structural and Multifunctional Materials and Systems (APMT9)

Novel Ceramic Processing III

Room: Coquina Salon A

Session Chairs: Eugene Medvedovski, Endurance Technologies Inc.; Yiquan Wu, Alfred University

1:30 PM

(ICACC-S8-020-2015) Colloidal processing of ceramic oxides containing carbon nanodispersoids (Invited)

A. Rincón[1]; V. Carrillo[1]; A. S. Chinelatto[2]; M. Nieto[1]; R. Moreno*[1]; 1. Institute of Ceramics and Glass-CSIC, Spain; 2. Universidade Estadual de Ponta Grossa, Brazil

Laminated microstructures have been designed for improving the performance and mechanical behavior of ceramic matrix composites. The incorporation of carbon nanofibres (CNFs) or graphene oxide (GO) into a ceramic matrix has demonstrate its suitability to obtain new properties such as enhanced toughness or conductivity. The colloidal processing approach allows obtaining well dispersed concentrated suspensions containing carbon derivatives as nano-dispersoids. The aim of this work was to study the colloidal processing of ceramic oxides (ZrO2, Al2O3) aqueous suspensions to produce laminates comprising thick layers fabricated by either sequential slip casting or tape casting. The rheological behavior of the different suspensions prepared to different solid loadings and different sonication times was optimized. On one hand, these suspensions were slip cast to produce monolithic materials or sequentially slip cast to produce green laminates. On the other hand, binders were added and suspensions were optimized for producing laminates by tape casting. The laminates were sintered by SPS at different temperatures. The results showed that colloidal processing allowed us to obtain monolithic or multilayer structures with carbon nanofibers and graphene oxide with homogeneous microstructures and sharp interfaces.

2:00 PM

(ICACC-S8-021-2015) Consolidation and conversion of powders by RCVI

O. Ledain[1]; S. Jacques*[1]; L. Maille[2]; 1. CNRS, France; 2. University of Bordeaux, France

The main processing routes to manufacture ceramic matrix composites reinforced with long woven fibers are the gas phase route (Chemical Vapor Infiltration – CVI) and the liquid phase routes (Polymer Impregnation/Pyrolysis or Melt Infiltration). The former allows high-purity carbide matrices to be obtained at moderate temperature, however macropores still remain. The latter allow a rapid fabrication but the shrinkage or the required high temperature and the final low purity are drawbacks. The slurry route allows the easy preparation of fiber-containing high-density green bodies comprising submicron powder but the final consolidation by CVI is difficult in the core. In this work, it is proposed for this last route that a variation of the CVI method, called RCVI (reactive CVI), be used to facilitate the consolidation in the core of the powder. In RCVI, the CM carbide is obtained by reacting a carbon-bearing powder with the gas, which carries the M element but not the C element. The carbide growth involves the conversion of the powder and slows down with increase in carbide thickness. This self-limitation allows a self-regulation of the growth between the core and the periphery of the sample and thus a better homogeneity. The chosen carbide was TiC obtained by reacting H2 and TiCl4 with a carbon powder. The conversion rate of carbon into carbide was studied as a function of time and depth into the sample at various temperatures.

2:20 PM

(ICACC-S8-022-2015) Spectroscopic properties of (Mn,Nd) co-doped zinc sulfide powder

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

A study concerning the co-doping of Mn and Nd into ZnS ceramic nanopowders was performed to investigate the influence of Mn-Nd co-doping on the crystallite size, band gap and luminescence characteristics of ZnS. ZnS ceramic nanoparticles doped with Mn and Nd were synthesized using a wet chemical precipitation method utilizing (NH4)2S as the sulfur source. X-Ray Diffraction (XRD) was used to study the phase composition and crystallite size of the co-doped ZnS powder. The microstructure of the ZnS nanoparticles was characterized to understand the effect of co-doping on powder morphology. UV-Vis spectroscopy was applied to determine the relationship between the dopants and the band gap of the co-doped ZnS. In addition, the effect of Mn2+ and Nd3+ on the photoluminescence (PL) properties of ZnS was investigated through the use of PL spectrometry. The study also provides some preliminary results on the sintering of co-doped ZnS ceramics.

2:40 PM

(ICACC-S8-023-2015) Fabrication of Si3N4 ceramics by post-reaction sintering using Si-Y2O3-Al2O3 nanocomposite particles prepared by mechanical treatment

K. Jeong*[1]; J. Tatami[1]; M. Iijima[1]; T. Takahashi[2]; 1. Yokohama National University, Japan; 2. Kanagawa Academy of Science and Technology, Japan

In order to expand an application target of Si3N4 ceramics, the reduction of production cost and the improvement of mechanical reliability are desired. Post-reaction sintering technique is one of the solution to reduce the production cost, in which a powder compact of powder mixture of inexpensive Si and sintering aids is nitrided, followed by densification at higher temperatures. In this research, Si3N4 ceramics were fabricated by the post-reaction sintering technique using Si-Y2O3-Al2O3 nanocomposite particles prepared by mechanical treatment. The prepared nanocomposite particles were molded by uniaxial pressing and cold isostatic pressing. The green body thus obtained was calcined at 1390°C for 2 h in 0.15 MPa, N2 gas to form Si3N4. Nitridation in the green body produced from the nanocomposite particles prepared by mechanical treatment were more uniform than ball-mill method. This means that nitridation was enhanced by using the nanocomposite particles while abnormally exothermic reaction between Si and N2 was inhibited. Nitridation ratio also increased by mechanical treatment with an increase in the applied power. After densification at 1800°C for 2 h in 0.9 MPa, N2 gas, the Si3N4 ceramics prepared by mechanical treatment had more homogeneous microstructure and higher density than that by ball milling.

3:20 PM

(ICACC-S8-024-2015) Synthesis of superconducting MgB2 nanopowder

N. Bansal*[1]; J. Goldsby[1]; R. B. Rogers[1]; M. A. Susner[2]; M. D. Sumption[2]; 1. NASA Glenn Research Center, USA; 2. The Ohio State University, USA

Superconducting MgB2 nanopowder has been synthesized through chemical reaction between lithium borohydride and magnesium hydride at relatively low temperatures. From quantitative Rietveld analysis, the average crystallite size of MgB2 powder was evaluated to be 32 nm. The superconducting transition temperature of the MgB2 nanopowder was found to be 38.8-38.9 K from magnetization and DC susceptibility measurements. Powder morphology has been evaluated by scanning electron microscopy.

3:40 PM

(ICACC-S8-025-2015) Synthesis of nano structural WC-Co powders from water soluble precursors: effects of tungsten source and synthesis atmosphere on chemical and phase structure evolutions

U. Kanerva[1]; M. Karhu*[1]; J. Lagerbom[1]; A. Kronlöf[1]; E. Turunen[1]; 1. VTT, Finland

Thermal sprayed cemented carbides such as WC-Co(Cr) and Cr3C2-NiCr coatings are widely used in wear protection purposes. Submicron and multimodal carbides in cermets showed promising results in wear performance. Presented study is a part of the research aiming to create a new novel powder manufacturing route for homogenous nano WC + Co matrix powder for thermal spraying. Goal of this study was to compare the effects of raw materials (tungsten source) and synthesis atmospheres on synthesis steps and on chemical and phase structures of the final products. Powders were manufactured via spray drying from water based solution with raw materials APT or AMT as a tungsten source, glycine as a carbon source and cobalt acetate as a cobolt source. Dried products were heat treated in Ar and Ar-4H2 atmospheres at different temperatures. The thermal decomposition was studied by using Thermogravimetry (TGA) and evolved gas analysis with mass spectrometer. The morphology and particle size were analysed with scanning electron microscopy (SEM) and an X-ray diffractometer (XRD) was used for phase structure analysis. Results suggest that AMT is a better raw material as a tungsten source for this method. Heat treatment atmosphere have effects on the chemical and phase structure for raw materials but not for the final product.

4:00 PM

(ICACC-S8-026-2015) Facile Hydrothermal Synthesis of Sub-10 nm Ultrafine BaTiO3 Nanopowder

C. Baek*[1]; S. Moon[1]; K. Park[2]; C. Choi[2]; D. Kim[1]; 1. Korea Advanced Institute of Science and Technology, Korea (the Republic of); 2. Samsung Electro-Mechanics, Korea (the Republic of)

BaTiO3 has been widely used as a primary material in various electronic devices including thermistors, electro-optical devices, and multilayer ceramic capacitors(MLCCs) due to its prominent dielectric properties. The advances in portable devices necessitate the fabrication of miniaturized MLCCs maintaining high capacity. BaTiO3 nanoparticles are embedded in both dielectric layers and electrode layers. The BaTiO3 nanoparticles in electrode layers act as a sintering additive to mitigate the shrinkage mismatch between Ni electrode particles and BaTiO3 dielectric particles which is caused by different sintering temperatures of those layers. As the thicknesses of layers decrease, the sizes of the active dielectric BaTiO3 powders and the Ni powders are essential to be reduced below 100nm. Moreover, the size BaTiO3 powder for sintering retardation of Ni layers should be minimized for better coverage on Ni particles. In this study, sub-10nm-sized BaTiO3 nanopowders are synthesized via facile hydrothermal process with addition of polar aprotic solvents. The phase and morphology of resulting BaTiO3 nanoparticles were characterized using XRD, SEM, and TEM. The specific surface areas of the synthesized powders were measured byBrunauer-Emmett-Teller to estimate the sizes. The shrinkage behavior of Ni nanopowder mixed with the synthesized ultrafine BaTiO3 nanopowder was measured.

4:20 PM

(ICACC-S8-027-2015) Novel Ti3SiC2 Reinforced Metal Matrix Multifunctional Materials

R. Johnson[1]; T. Hammann[1]; S. Gupta*[1]; 1. University of North Dakota, USA

Mn+1AXn (MAX) phases (over 60+ phases) are thermodynamically stable nanolaminates displaying unusual, and sometimes unique, properties. These phases possess a Mn+1AXn 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 Wd (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 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 multifunctional metal matrix composites by adding MAX phases as additives.

4:40 PM

(ICACC-S8-028-2015) Synthesis of high purity SiC powders by a carbothermal reduction using a SiO2-C hybrid precursor fabricated by a sol-gel process

M. Youm*[1]; S. Youn[1]; S. Park[1]; 1. Korea Institute of Science and Technology, Korea (the Republic of)

SiC powders were synthesized by a carbothermal reduction process using SiO2-C precursors fabricated by a sol-gel process using phenol resin and TEOS as starting materials for carbon source and Si source, respectively. TEOS was mixed with the phenol resin solution in ethanol and then continuously stirred to gelation with keeping temperature at 40oC. Additional process for the homogenoization of carbon in SiO2-C hybrid gel was used to activate the synthesis of SiC during a carbothermal process. SiC powders were synthesized by both carbothermal reduction and modified carbothremal reduction of SiO2-C precursor at 1200 to 2300 oC in Ar or vaccum atmosphere. The synthesized SiC powders with various particle sizes and particle size distributions were synthesized by controlling the synthesis process as well as the C/Si mole ratios in SiO2-C precursors. It was found that the C/Si mole ratio of SiO2-C precursors used affected much on the synthesis temperature of β-SiC powders as well as the particle size of synthesized β-SiC powders. The size of synthesized SiC powders were varied from tens nano meter to several hundred micrometer. The contents of impurities of synthesized SiC powders in this study were less than 5 ppm. With increasing the C/Si mole ratio in SiO2-C precursors, the synthesis temperature of β-SiC powders was found to be reduced to 1300 oC.

S9: Porous Ceramics: Novel Developments and Applications

Innovations in Processing Methods and Synthesis of Porous Ceramics I

Room: Coquina Salon H
Session Chair: Paolo Colombo, University of Padova

1:30 PM

(ICACC-S9-001-2015) Monolithic porous silsesquioxanes and ceramic derivatives from sol-gel chemistry and carbothermal reduction (Invited)

K. Kanamori*[1]; 1. Kyoto University, Japan

As a typical organic-inorganic hybrid material, sol-gel-derived silsesquioxanes with the ideal formula of $RSiO_{1.5}$ form a unique class of materials. Silsesquioxanes from trialkoxysilanes such as methyltrimethoxysilane offer attractive features in functionalities, surface characters, and mechanical properties. However, such trialkoxysilanes-derived silsesquioxane monoliths based on random networks are not popular because of the high tendency to form polyhedral oligomeric silsesquioxanes or hydrophobic precipitates without a defined structure. Another important precursors to silsesquioxanes are bis(trialkoxysilane)s with an organic bridging moiety such as bis(triethoxysilyl)benzene. These are generally regarded as convenient precursors to functional porous materials, because of the high tendency to form random networks with six possible reactive sites in a molecule. We have been studying on the porous silsesquioxane monoliths based on random networks (such as aerogels and hierarchically porous gels) through careful controls over fundamental sol-gel chemistry and phase separation. Some examples of porous silsesquioxanes with reactivity on the pore surface and mechanical flexibility will be presented. The formation of silicon carbide ceramics from bridged silsesquioxanes through carbothermal reduction will also be discussed.

2:00 PM

(ICACC-S9-002-2015) Microcapsules from pickering emulsions stabilized by clay particles

G. Lecomte*[2]; V. Niknam[2]; A. Aimable[3]; M. Bienia[3]; D. Kpogbemabou[2]; J. Robert-Arnouil[1]; A. Lajmi[2]; 1. ENSCI, France; 2. ENSCI, France; 3. ENSCI, France

The objective of the present work was firstly preparing stable Pickering emulsions with the aid of phyllosilicate particles as stabilizers. The obtained stable clay-based Pickering emulsions were characterized and used for the elaboration of microcapsules. Kaolin, halloysite and hectorite wnich differer regarding the clay mineral nature and/or the particle morphologies, (platelet or tubular), were used as stabilizers while the deionized water and dodecane were used as the aqueous and oil phases, respectively. Stable clay-based Pickering emulsions were also prepared in the presence of low concentrations (0.5 to 1 mass %) of Span80 and Tween80. Emulsions are of oil-in-water type for all clay-stabilized Pickering emulsions. The most stable Pickering emulsions were utilized as templates to prepare microcapsules with encapsulating agents such as tetraethoxysilane (TEOS), an alkoxide monomer for the mineralization of the emulsion interface, and two biopolymers: chitosan (CS) and sodium alginate (SA). The effect of encapsulating agent nature and drying method on their encapsulating performance was investigated using aqueous electrophoresis, infrared spectroscopy and scanning electron microscopy characterizations. Results showed that the microcapsules obtained by CS exhibited the best desired morphology while TEOS and SA were less efficient as encapsulating agents in terms of the related microcapsules morphology.

2:20 PM

(ICACC-S9-003-2015) Fabrication of ceramic preforms with channels aligned in multiple directions

E. Hammel*[1]; O. I. Okoli[1]; 1. Florida State University, USA

While ceramic materials offer many desirable properties, they are hindered by their brittle nature and lack of reliability. Composite materials may be used to mitigate these issues. Ceramic-metal interpenetrating composites (IPCs), where both phases are continuously distributed, deserve further investigation. Often ceramic-metal IPCs are fabricated by infiltrating a porous ceramic preform with metal. Since the architecture and properties of the preform are transferred to the composite, the preform is an important feature. In this study, a threefold objective was initiated. First, a preform was created by casting an alumina-based slip around a sacrificial mesh. The effect of the channel architecture on the properties of the ceramic was investigated. The diameter and spacing of the channels was altered based on the geometry of the sacrificial phase. Additionally, the composition of the ceramic slip was optimized to produce a high green density and homogeneous microstructure. Finally, a method for investigating the cracks caused during the drying of the slip around the sacrificial phase was also developed. The purpose of this project was to create a more reliable ceramic preform with repeatable mechanical properties through the optimization of the slip composition and sacrificial phase architecture. The strategic placement of channels will allow the properties of the component to be tailored as desired.

2:40 PM

(ICACC-S9-004-2015) Effect of microstructure on thermal conductivity and compressive strength of thermal insulators prepared by gelation freezing method

M. Fukushima*[1]; T. Ohji[1]; Y. Yoshizawa[1]; 1. National Institute of Advanced Industrial Science and Technology (AIST), Japan

Thermal insulators are gaining energy-saving importance, as they have been utilized in many applications ranging from building products, steel plants, shipping container of molten metal to industrial furnace. Traditional firebricks have been generally employed as the most conventional insulators; however, their thermal conductivities are relatively high due to low porosities. On the other hand, fibrous insulators exhibit low thermal conductivities less than 0.1W/mK, though they lack sufficient mechanical strength. Thus, critically required are thermal insulators which have the adequate structural reliabilities as well as the low thermal conductivities equivalent to the fibrous insulators. In this study, we will discuss various characteristics of mullite based thermal insulators prepared by gelation freezing route. Ice growth in gel bodies during freezing could lead to the formation of honeycomb shaped cellular morphology without any dendritic structures and defects. Depending on the processing factors, very low thermal conductivities and improved compressive strength could be achieved, together with very high porosity around 80-90vol%. The effect of antifreeze protein additives on the grain growth of ice will also be discussed.

Membranes and High SSA Ceramics I

Room: Coquina Salon H

Session Chair: Gian Domenico Soraru, University of Trento

3:20 PM

(ICACC-S9-005-2015) Design of pores in inorganic membranes for efficient separation of liquids and gases (Invited)

I. Voigt*[1]; 1. Fraunhofer Institute for Ceramic Technology and Systems IKTS, Germany

Inorganic membranes for microfiltration, ultrafiltration as well as nanofiltration consisting of alumina, titania or zirconia are commercially available. The transport of liquids in these membranes is well understood. There are many applications in food and beverages, sterilization and waste water treatment. The sizes of gas molecules are below 1 nm and are close to each other. Therefore, the separation by size exclusion is challenging. On the other hand, transport in this dimension is not any more determined by poiseuille flow but by diffusion. Different inorganic materials are used for membrane preparation as well as membrane separation. The principle of pore size formation and the possibilities of pore size design is different: - Free volume in amorphous oxides like silica, titania or zirconia. The pore size can be designed by the composition as well as the temperature treatment. - Cages and channels in zeolites. Pore size and stability are determined by the type of the zeolite. - Lattice plane distances of carbon. The distance can be designed by a post treatment of the carbon. The paper will compare the different types of materials and pores concerning their ability for gas separation. Permeances and permselectivities from single gas as well as mixed gas measurements will be reported. Results from lab scale up to pilot testing will be presented.

3:50 PM

(ICACC-S9-006-2015) Thermally stable organosilica membranes derived by in-situ hydrosilylation for gas separation at high temperatures

M. Kanezashi*[1]; H. Sazaki[1]; H. Nagasawa[1]; T. Yoshioka[1]; T. Tsuru[1];
1. Hiroshima University, Japan

Thermally stable organosilica amorphous membranes were fabricated by in-situ hydrosilylation of vinyl and hydrosilyl groups in Si precursors for the formation of Si-C-C-Si unit, as well as the Si-O-Si unit via the conventional hydrolysis and condensation of silanol groups. SiOC structures prepared by vinyltrimethoxysilane (VTMS) and triethoxysilane (TRIES) consisted of a Si-C-C-Si unit created by the hydrosilylation of vinyl and hydrosilyl groups in a Si precursor were fabricated at temperatures higher than 400 oC under N2. Single-gas permeation properties for SiOC membranes at temperatures ranging from 100-500 oC were examined to determine the effect of a silica precursor on the size of an amorphous network. A SiOC membrane fabricated at 400 oC under N2 showed a H2 permeance of 3.0 x 10-7 mol m-2 s-1 Pa-1 with H2/CH4 and H2/CF4 permeance ratios of 50 and 400, respectively, at 400 oC. After heat treatment at 550 oC under air for 1h, a membrane showed little change in permeances, indicating thermal stability under air at 550 oC.

4:10 PM

(ICACC-S9-007-2015) Improved OTM mechanical properties controlling pore architecture

J. Seuba Torreblanca*[1]; C. Guizard[1]; A. J. Stevenson[2]; 1. CNRS, France;
2. Saint Gobain, France

Oxygen Transport Membranes (OTM) are promising and cost effective means of O_2 production. However, their lifetime is limited by the high thermomechanical stresses over long times. These thermomechanical stresses are born by the OTMs' porous supports which must exhibit high creep resistance, high strength and low resistance to gas flow. However, it is difficult to design a support that is simultaneously creep resistant, strong, and permeable. Our strategy to improve OTM support performance focuses on structured, directional porosity that maximizes both thermomechanical properties and gas flow. We produce model pore geometries in OTM supports using ice-templating, and study the effects of pore volume, size, shape and directionality on mechanical performance and gas flow. These results are compared with porous supports made by conventional processing routes (pore formers and extrusion) to understand the effects of structured porosity and demonstrate improved performance relative to currently industrialized materials.

4:30 PM

(ICACC-S9-008-2015) Synthesis and characterization of amorphous silica-based inorganic-organic hybrid materials for CO2-selectve ceramic-based porous membranes

Z. Mouline*[1]; K. ASAI[1]; T. ONISHI[1]; Y. DAIKO[1]; S. Honda[1]; Y. Iwamoto[1];
1. Nagoya Institute of Technology, Japan

Amorphous silica-based hybrid materials having alkylamino groups were designed and synthesized to develop CO2-selectve membranes having facilitated transport mechanism. Silicon-based polymers such as perhydropolysilazane (PHPS) were chemically modified with an aminosilane coupling agent, or alkyl amine derivatives, and subsequently oxidized in air at room temperature. The conversion behaviors of polymeric precursor into amorphous silica-based hybrid material were studied by FT-IR and NMR spectroscopic analyses. The hybrid materials were characterized by measuring the mico-/meso-porosity using the conventional N2 sorption technique, while their CO2 affinity were investigated by measuring weight gain under CO2 flow from 40°C up to 80°C. The non-functionalized PHPS-derived amorphous silica showed a slight weight gain by the physisorption of CO2, while the alkylamino group-functionalized amorphous silica exhibited an enhanced weight gain which could be achieved by the interaction between CO2 and the alkyl amino groups. At the presentation, the results of further study on the interaction by an in-situ monitoring using the DRIFTS technique, and evaluation of CO2 chemisorption properties will be shown and discussed from a viewpoint to develop CO2-selectve ceramic-based porous membranes.

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

Materials Design, New Composition and Composites II

Room: Ponce DeLeon
Session Chair: Bai Cui, University of Nebraska–Lincoln

1:30 PM

(ICACC-S12-020-2015) A novel Ti3AlC2-derived composite with unexpectedly excellent wear resistance and anomalous flexural strength (Invited)

X. Wang*[1]; H. Zhang[1]; Z. Li[1]; M. Liu[1]; Y. Zhou[2]; 1. Institute of Metal Research, China; 2. Science and Technology of Advanced Functional Composite Laboratory, ARIMPT, China

A novel twinning plateletes strengthened TiC/Ni2AlTi composite is designed and fabricated by in situ reactive hot pressing of blended powders of nanolaminated Ti3AlC2 and Ni. Upon de-intercalation of Al from Ti3AlC2 during the heating, TiC twinning platelets with width in submicrometer size are introduced in the composite. The obtained composite exhibits excellent wear resistance, which is comparable to commercial Co-cemented WC. It is demonstrated that the novel wear resistance results from the strong heterophase interfaces in the as-prepared composite. Close studies on the interfacial microstructure by high resolution transmission electron microscopy indicate that the observed two types of TiC/Ni2AlTi interface are semi-coherent, while the TiC/NiAl and Ni2AlTi/NiAl interfaces are coherent. These strongly bonded interfaces impede the failure of the heterophase boundaries, hinder the pullout of the hard carbide particles, accounting for the wear performance. In addition, the flexural strength of the composite unexpectedly increases with temperature rising from 500 to 800 degree C, reaching a maximum of 936 MPa at 800 degree C. A possible mechanism for this anomalous phenomenon is proposed.

2:00 PM

(ICACC-S12-021-2015) An Infiltration Approach for Producing High-Performance Metal/MAX Phase Composites with Customizable Microstructures

L. Hu*[1]; M. O'Neil[2]; V. Erturun[3]; R. Benitez[2]; G. Proust[4]; I. Karaman[1]; M. Radovic[1]; 1. Texas A&M University, USA; 2. Texas A&M University, USA; 3. Erciyes University, Turkey; 4. University of Sydney, Australia

The prospect of extending fabrication methods to develop new, highly reactive ceramic-metal composite materials is examined. Customizable microstructures are obtained in ceramic-metal composites using ceramic foams with controlled pore structures for metal infiltration. The resulting composites are lightweight and display exceptional mechanical properties at both ambient and elevated temperatures. Specifically, aluminum alloy 6061 (AA6061)/Ti2AlC composites with metal contents of approximately 40 vol.% and different metallic phase sizes, i.e. 42–83 um, 77–276 um, and 167–545 um, were processed and characterized. These structures achieve a compressive strength that is 2 times of peak-aged AA6061 at ambient temperature and 4 times at 400 oC (0.7 of the melting point of aluminum). Strengthening mechanisms are described together with further strengthening strategies.

2:20 PM

(ICACC-S12-022-2015) Structure characterization, formation mechanism and thermal stability of (Cr2/3Ti1/3)3AlC2

Z. Liu*[1]; M. Li[1]; Y. Qian[1]; J. Wang[1]; E. Wu[1]; L. Zheng[1]; 1. Institute of Metal Research, China

A new MAX compound, (Cr2/3Ti1/3)3AlC2, was synthesized and reported. The formation of (Cr2/3Ti1/3)3AlC2 was revealed to be the result of reaction between Cr2AlC and TiC. Its crystal structure was systematically characterized by various techniques. The space group of (Cr2/3Ti1/3)3AlC2 is determined to be P63/mmc by a combination of selected area and convergent beam electron diffraction techniques. The Rietveld refinements of neutron diffraction and X-ray diffraction show that in (Cr2/3Ti1/3)3AlC2, Ti and Cr are orderly arranged with Ti in 2a and Cr in 4f Wyckoff sites of a M3AX2 lattice. The formation of (Cr2/3Ti1/3)3AlC2 with uniquely ordered crystal structure may be related to the electronegativtiy and covalent radius of Cr and Ti atoms. As a typical M3AX2 compound, it exhibits good thermal stability in highly purified flowing argon (≥ 99.999%) during the DTA analysis for up to 1450oC. In contrast, when oxidized in air, it decomposed into Cr2AlC and TiC, inversely. The ambient-dependent stability of (Cr2/3Ti1/3)3AlC2 can be attributed to the different bonding strength levels in the crystal structure of M3AX2.

2:40 PM

(ICACC-S12-023-2015) Interaction of selected MAX Phases with pyrolytic carbon and silicon carbide

G. Bentzel*[1]; M. W. Barsoum[1]; 1. Drexel University, USA

Herein we report on the diffusion of both pyrolytic carbon (PG) and silicon carbide (SiC) with selected MAX phases – Ti2AlC, Ti3AlC2, Ti3SiC2, and Cr2AlC. Heated to 1300 °C under pressure for four, ten, and thirty hours in a hot press, samples were examined using Scanning Electron Microscopy, Energy-dispersive X-ray Spectroscopy, X-ray Diffraction, and Orientation Image Microscopy. All MAX phases showed little to no interaction with SiC. In the case of PG, both Ti2AlC and Ti3AlC2 were found to form TiC and Al4C3, Ti3SiC2 was found to form TiC and SiC, while Cr2AlC was found to form Cr3C2 and Al4C3, all of which agree well with their system's ternary phase diagrams.

Methods for Improving Damage Tolerance, Oxidation and Thermal Shock Resistance

Room: Ponce DeLeon
Session Chair: William Fahrenholtz, Missouri University of S & T

3:20 PM

(ICACC-S12-024-2015) Alumina-Forming MAX Phases in Turbine Material Systems (Invited)

J. L. Smialek*[1]; B. J. Harder[1]; A. Garg[1]; J. A. Nesbitt[1]; 1. NASA Glenn Research Center, USA

Coatings for high temperature turbine components are based on low conductivity YSZ thermal barriers and protective NiAl, NiCoCrAlY bond coats. Good oxidation/ hot corrosion resistance, intermediate CTE, and strain tolerance of Ti_2AlC and Cr_2AlC MAX phases are thus of special interest. Their alumina scale growth follows a cubic law in accord with FeCrAlY alloys, with oxygen grain boundary diffusivity: $D_{gb} = 1.8x10^{-10}exp(-375\ kJ/mole)\ m^3/s$. Protective cubic kinetics are also found in high pressure burner rig (6 atm., 25 m/s) and TGA tests of MAXthal 211©Ti_2AlC. The initial portion (0.1 hr) is dominated by fast TiO_2 growth. There was little evidence of scale volatility in high pressure water vapor, as found for SiO_2 scales on SiC. Bulk Ti_2AlC and Cr_2AlC substrates show promise as potential bond coats for YSZ TBCs in 1000-1200°C furnace life (500 h) tests. Cr_2AlC is proving to be very resistant to 700-900°C Na_2SO_4 hot corrosion and is of interest for disk alloys. Preliminary diffusion bonded Cr_2AlC-superalloy hybrid couples have survived 1000 hr interrupted furnace tests at 800°C with no indication of cracking or debonding. Diffusion zones of β-NiAl+Cr_7C_3 were produced here above 1000°C, but did not grow to any great extent after 1000 hr at 800°C. Processing as coatings presents challenges, however the basic properties of MAX phases provide novel opportunities for high temperature turbine components.

3:40 PM

(ICACC-S12-025-2015) Stress Generation in Oxide Scale during High-Temperature Oxidation of Ti2AlC Ceramics

B. Cui*[1]; W. E. Lee[2]; 1. University of Nebraska–Lincoln, USA; 2. Imperial College London, United Kingdom

Excellent oxidation resistance of Ti2AlC ceramics below 1400 °C relies on formation of a protective Al2O3-rich scale on the substrate, possibly due to selective oxidation of Al in its structure. However, at or above 1400 °C this oxide scale becomes cracked leading to loss of oxidation protection. In this study, we have examined possible mechanistic mechanisms responsible for the stress generation in the oxide scale during high-temperature oxidation of Ti2AlC ceramics. Thermal stresses generated during cooling from the high temperature may result from thermal expansion mismatch of phases in the oxide scale, the high anisotropy of thermal expansion in Al2TiO5 and thermal expansion mismatch between the oxide scale and substrate. Growth stresses generated during isothermal oxidation treatment may arise from volume changes associated with oxidation reactions. Improved understanding of the stress generation in the oxide scale may indicate potential methods to protect MAX phase ceramics from oxidation at high temperature.

4:00 PM

(ICACC-S12-026-2015) Contact Damage Characterisation of Composite Zirconium Diboride Ceramics using Vickers Indentation, Hertzian Indentation and Drop-Weight Testing

J. Wade*[1]; M. Xiang[1]; H. Wu[1]; H. Liu[2]; J. Liu[2]; G. Zhang[2]; 1. Loughborough University, United Kingdom; 2. Shanghai Institute of Ceramics, China

Compared to monolithic zirconium diboride ceramics, zirconium diboride composites have recently been demonstrated to have significantly improved fracture strength and toughness. Being used as thermo-structural components, these materials are likely exposed to various harsh environments, where mechanical contact damage is unavoidable. Such occurrences are likely to happen across a broad regime in temperature and loading speed. Up to now, there has been very limited knowledge on the contact damage of these materials. Under mechanical contact conditions, plastic deformation and brittle fracture are typical damage formats observed in ceramics. In this paper, we have used Vickers indentation, Hertzian indentation and drop-weight impact testing to quantitatively study the damage of monolithic and composite zirconium diboride ceramics at room temperature. Based on the experimental measurements, we have tried to establish how cracking and plastic deformation contribute to the observed overall damage of each material tested. Through comparative studies, we have demonstrated the possible responsibilities of zirconium carbide/silicon carbide reinforcements in constraining the damage of composite zirconium diboride ceramics.

4:20 PM

(ICACC-S12-027-2015) Effect of hyperthermal, plasma, and thermal oxygen beams on oxidation behavior of ultra-high temperature ceramics at low temperatures

M. Miller-Oana*[1]; W. Pinc[1]; L. Walker[1]; V. Murray[2]; T. Woodburn[2]; T. Minton[2]; E. L. Corral[1]; 1. University of Arizona, USA; 2. Montana State University, USA

We investigate the influence of high energy and low energy oxygen beams on oxidation behavior of ultra-high temperature ceramics in order to understand the effect of atomic oxygen and energy on the oxidation process. Hyperthermal, plasma, and thermal beams of oxygen and argon are used to expose ZrB2-SiC ceramics at 25 and 300°C for ~14 hours and the exposed surfaces are characterized using scanning electron microscopy (SEM), Raman spectroscopy, and X-Ray photoelectron spectroscopy (XPS). The hyperthermal oxygen exposure at 300°C results in the most oxide formation on ZrB2 and SiC as detected by SEM, Raman, and XPS, which is due to the high energy of the beam and most reactive oxygen species. The initial stages of oxidation at low temperatures under high vacuum result in dark spots of B2O3 formed on ZrB2 grains and white spots of SiO2 formed on SiC grains.

4:40 PM

(ICACC-S12-028-2015) Dynamic non-equilibrium thermal gravimetric analysis of the isothermal oxidation behavior of ultra-high temperature ceramics

M. Miller-Oana*[1]; L. S. Walker[1]; E. Corral[1]; 1. University of Arizona, USA

In order to investigate the oxidation behavior of ultra-high temperature ceramics, oxidation rate measurements are obtained using purely isothermal rate measurements. The oxidation behavior of ZrB2-SiC composites is examined by investigating the temperature dependence from 1000-1600°C and the pressure dependence from 0.2-19 kPa oxygen partial pressure and compared to non-isothermal results. Mass gain from isothermal methods is up to 3 times more and oxide scale thicknesses are up to 5 thicker than those of non-isothermal methods in thermal gravimetric analyzer furnace at the same temperatures and oxygen pressure. Isothermal oxidation is more aggressive than non-isothermal thermal oxidation for 15 minutes due to oxygen diffusing farther into the bulk of the specimen over this short time period.

S13: International Symposium on Advanced Ceramics and Composites for Sustainable Nuclear Energy and Fusion Energy

Joining Technology for Nuclear Ceramics II

Room: Tomoka B

Session Chair: Charles Henager, Pacific Northwest National Lab

1:30 PM

(ICACC-S13-019-2015) Precursor Derived Composite Ceramic Joints for Ceramics and Ceramic Matrix Composites (Invited)

R. K. Bordia*[1]; M. M. Stackpoole[2]; K. Wang[3]; 1. Clemson University, USA; 2. NASA Ames Research Center, USA; 3. University of Washington, USA

Pre-ceramic polymers filled with active fillers can be used to make a range of in-situ ceramic matrix composites. The fillers can be used to control the pyrolysis shrinkage. In this presentation, after a brief background on the versatility and limitations of this approach, results from one specific study conducted in our group will be presented. We will present results on the processing and properties of high temperature joints prepared from preceramic polymer systems filled with reactive metals and intermetallics. When pyrolyzed in reactive environments these systems form in-situ composites with low shrinkage and porosity. Using analytical models for constrained pyrolysis, we have shown that there is a critical joint thickness such that if the joint thickness is less than the critical value, crack free joints can be formed. We have also developed model guided processing approaches to make joints of controlled thickness. Using theses analyses, we have demonstrated that this is a feasible approach to form high performance composite ceramic joints at low processing temperatures (1000 to 1400oC). The mechanical properties of joints have been investigated including the fracture toughness of the interface. Results on these properties and the performance of the resultant high temperature ceramic joints will be presented.

2:00 PM

(ICACC-S13-020-2015) Pressure-less joining of silicon carbide based components (Invited)

M. Ferraris*[1]; M. Salvo[1]; V. Casalegno[1]; S. Rizzo[1]; M. Reece[2]; S. Grasso[2]; P. Tatarko[2]; 1. Politecnico di Torino, Italy; 2. Nanoforce Technology, United Kingdom

Joining of SiC-based materials for nuclear applications is of interest in particular if the joining process can be done without using any pressure. Pressure-less joining offers greater possibilities for joining dissimilar materials and for on-site or in the field joining processes and repairs. Several materials and techniques have been tested for pressure-less joining of SiC-based materials within an international cooperation involving EU, USA, and Japan. Surface modification of SiC-based materials has been tested in order to increase the shear strength of joints. One non-silica based glass-ceramic and several non-oxide joining materials based on Ti-Si-C have been used to join SiC and SiC/SiC by pressure-less joining techniques such as slurry methods and spark plasma sintering.

2:20 PM

(ICACC-S13-021-2015) Silicon carbide joints formed by pressureless transient eutectic-phase process

T. Koyanagi*[1]; J. Kiggans[1]; Y. Katoh[1]; 1. Oak Ridge National Laboratory, USA

Robust and radiation-tolerant joining technology is required to facilitate the use of silicon carbide (SiC) materials for nuclear structural applications such as fusion blanket structures and fission fuel cladding. A transient eutectic-phase (TEP) process has been used to produce dense and robust SiC-based joints. The excellent radiation-resistance of pressurized TEP joints has been demonstrated following neutron irradiation to intermediate fluences; however, the requirement to apply pressure during heating is a factor that potentially limits the applicability of this method. This paper presents the processing and characterization of newly developed SiC joints formed by a pressureless TEP route. The TEP joints were produced using SiC nano-powder and small amounts of oxide additives. The mixed powders were sandwiched between SiC plates and cold pressed. The sandwich materials were then heated without external loading. Dense microstructures with small amounts of second phases were achieved for the joint layer. Robust mechanical properties of the joints were demonstrated by shear strength tests. The effects of the processing conditions and starting materials on the microstructure and the strength will be discussed to details. This work was supported by Office of Fusion Energy Sciences and Office of Nuclear Energy, US Department of Energy, under contract DE-AC05-00OR22725 with UT-Battelle, LLC.

2:40 PM

(ICACC-S13-022-2015) Reactive Surface Wetting Method For Joining Select Fusion Candidate Materials

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

Currently materials such as silicon carbide fiber reinforced-silicon carbide composites (SiCf/SiC), RAFM steels, vanadium alloys, carbon fiber reinforced-carbon composites and tungsten (W) are some of the leading candidate materials for fusion reactor components to take advantage of their properties such as high melting points, low activation, irradiation and chemical stability, and good thermo-mechanical and thermo-physical properties. Although these materials have proved their worth in terms of properties, some of the main challenges to fabricating actual scale components using these materials include: gaseous transmutation, hermetic behavior (in SiC/SiC and C/C), thermal conductivity and lack of reliable materials joining technology. This work focuses on the joining technology issues for fusion related materials currently listed under TRL-3 of fusion materials science and technology. In view of some of the major limitations of traditional joining methods, especially joining of dissimilar materials, this work investigates reactive wetting of surfaces to achieve graded transition joints between SiC and W. Surface reactive wetting is achieved by disposition of thick films followed by reactive alloying of select interlayer materials such as Cu, W, V and Cr. The processing methods and the microstructure along with some simple tests to assess the strength of the joints will be discussed.

Accident Tolerant Nuclear Fuels

Room: Tomoka B

Session Chair: Gokul Vasudevamurthy, Virginia Commonwealth University

3:20 PM

(ICACC-S13-023-2015) Compatibility in Advanced/Accident Tolerant Nuclear Fuels (Invited)

T. M. Besmann*[1]; S. Voit[2]; 1. Oak Ridge National Laboratory, USA; 2. Oak Ridge National Laboratory, USA

A number of alternative nuclear fuel systems are under study to improve fuel performance and accident tolerance in light water reactors (LWRs) over that of the current urania clad in zirconium alloy configuration. These range from urania containing second phases to uranium nitrides/silicides for fuels, and to FeCrAl alloys and SiC ceramic composite for cladding. These systems require extensive testing both out of reactor and under irradiation before they can be accepted as practical fuel systems. Initial screening using thermochemical analysis and small scale testing was used to provide information as to whether to proceed to more costly and elaborate experimental efforts. The current presentation reports on the results of the analysis on a number of alternative fuel systems, projecting behavior under irradiation, including potential design basis and beyond design basis accident conditions. This work was supported by the US Department of Energy Office of Nuclear Energy, Fuel Cycle Research and Development Program.

3:50 PM

(ICACC-S13-024-2015) Enhanced Thermal Conductivity of Uranium Dioxide-Diamond Composite Fuel

Z. Chen*[1]; G. Subhash[1]; J. S. Tulenko[2]; 1. University of Florida, USA; 2. University of Florida, USA

In an effort to enhance the safety and efficiency of commercial light water reactors, innovative accident tolerant UO_2-diamond composite fuel pellets were produced. Pellets were processed by mixing UO_2 powder with between one and ten volume percent of monocrystalline diamond powder and sintered by means of spark plasma sintering (SPS). It is shown that the use of SPS allows high density (96.5% theoretical density) pellets to be made on the order of minutes compared to conventional sintering which takes several hours. The microstructure (grain size and interfacial contact) of sintered pellets were investigated using Scanning Electron Microscopy (SEM). The chemical stability during sintering were characterized using X-Ray Diffraction (XRD) and Raman Spectroscopy. In addition, thermal diffusivity measurements at 100ºC, 500ºC, and 900ºC were conducted. An increase of up to 58% in thermal diffusivity has been measured at 900ºC when compared to pure UO_2.

4:10 PM

(ICACC-S13-025-2015) Batch Processing of Accident Tolerant Composite UO2 Fuel Fabricated by Spark Plasma Sintering

J. A. Kuntawala*[1]; G. Subhash[2]; J. S. Tulenko[1]; 1. University of Florida, USA; 2. University of Florida, USA

This study was conducted to prove the industrial viability of Spark Plasma Sintering (SPS) of nuclear fuel. Spark plasma sintering is an advanced manufacturing process which allows for the fabrication of high density, accident tolerant, composite uranium-dioxide (UO2) nuclear fuels. These fuels utilize high thermal conductivity additive

materials to UO2 to increase the overall thermal conductivity of the fuel pellet. Both silicon carbide (SiC) and diamond powders at the 10 volume percent level have proven to be viable additives to increase the thermal conductivity of the fuels by up to 40% relative to that of pure UO2. The increased thermal conductivity of the fuel pellets decreases the fuel centerline temperature, radial temperature gradients, and gaseous fission product release. In addition, during a loss of active cooling high thermal conductivity fuel can release the stored thermal energy quicker making it able to withstand the accident sequence for longer. To be commercially viable UF has developed specially tooled dies to prove various batch processing concepts for composite UO2 fuel. Both pellet stacking and multiple cavity pellet processing were investigated and shown to successfully produce high quality and high density fuel pellets. A 3 stage SPS system is proposed using these batch processing concepts to lead to the commercial viability of SPS for nuclear fuel applications.

4:30 PM

(ICACC-S13-026-2015) Structural and Mechanical Properties of Multiphase Oxide Ceramics as Model Composites for Nuclear Fuel

M. Mecartney*[1]; 1. UC Irvine, USA

Multiphase ceramics offer several advantages that can be used to design safer nuclear fuel. Creating a stable sub-micron grain size will provide higher room temperature fracture strength, while allowing for high temperature plasticity. Thermal conductivity can be enhanced by the inclusion of high thermal conductivity phases. Thermal shock can also be improved by including second and third phases. This talk will focus on results from three phase systems with Al2O3, MgAl2O4, and 8YSZ. 8YSZ acts as a surrogate for UO2 with a similar fluorite structure and low thermal conductivity. Alumina and spinel are phases with higher thermal conductivity. Our initial results on creating a range of grain sizes for these multiphase ceramics and the corresponding mechanical properties at room temperature and high temperature will be reported. (This work is funded by DOE grant DE-NE0000711.)

4:50 PM

(ICACC-S13-027-2015) Evaluation of Novel Composite Nuclear Fuels for Light Water Reactor Applications

J. T. White*[1]; A. T. Nelson[1]; J. T. Dunwoody[1]; D. D. Byler[1]; K. J. McClellan[1]; 1. Los Alamos National Laboratory, USA

Uranium silicide fuels have received renewed interest due to the higher thermal conductivity and hypothesized oxidation resistance relative to currently employed fuel forms in light water reactors. Practical deployment of uranium silicide fuels will likely be in the form of composite fuels, which integrate UO_2 or UN, another advanced fuel candidate. Characterization of the thermal transport in the composite fuels is critical to evaluate the fuel forms prior to insertion into a test reactor. For this study, composites were fabricated with UN while individually varying the U_3Si_5 and U_3Si_2 concentrations from 5-30 volume percent. Heat capacity, thermal expansion, and thermal conductivity were characterized for the silicide compounds as a function of temperature to 1673 K. Oxidation performance of the candidate composite fuels during representative off-normal conditions in a light water nuclear reactor were evaluated using a thermogravimetric analyzer with water vapor generator attachment to maximum temperatures of 1273 K. Discussion of the data will focus on microstructural evolution under highly oxidizing environments and application of these composite fuels to present and future reactor designs.

FS1: Geopolymers, Chemically Bonded Ceramics, Eco-friendly and Sustainable Materials

Composites II and Conversion to Ceramics I

Room: Oceanview

Session Chairs: Henry Colorado, Universidad de Antioquia; Dinesh Medpelli, Arizona State University

1:30 PM

(ICACC-FS1-007-2015) Microstructures, mechanical properties and electrical and thermal conductivities of graphene nanoplatelet-reinforced, potassium geopolymer

S. Cho*[1]; T. A. Carlson[2]; C. Marsh[2]; W. M. Kriven[3]; 1. University of Illinois at Urbana-Champaign, USA; 2. US Army Engineering Research and Development Center (ERDC) – Construction Engineering Research Laboratory (CERL), USA; 3. University of Illinois at Urbana-Champaign, USA

Graphene nanoplatelets have high mechanical, electrical and thermal properties that can significantly improve the desired properties of composites at even low contents. 1, 2 and 3 wt% of graphene nanoplatelet-reinforced, potassium geopolymers (GNP KGP) were prepared and their microstructures were investigated by SEM, XRD and Raman spectroscopy. The mechanical properties such as flexure strength, Weibull modulus, Vickers hardness and Young's modulus were measured by four-point flexure, microindentation and impulse excitation (IE) testing. In addition to mechanical properties, the electrical and thermal properties of GNP KGP were investigated by measuring electric resistances and thermal conductivities. Moreover, silicon functionalized graphene nanoplatelets (sGNP) were prepared in order to enhance interfacial bonding between GNP and geopolymer matrix. The various mechanical properties of sGNP KGP were measured and compared with GNP KGP, in order to investigate the effect of silicon functionalization.

1:50 PM

(ICACC-FS1-008-2015) Ceramic Felt Reinforced Geopolymer Composites

E. Koehler*[1]; W. M. Kriven[1]; 1. University of Illinois at Urbana Champaign, USA

Geopolymers are a Group I, charge balancing alumino-silicate, soild gel made by dissolution, polycondensation and precipitation under ambient conditions. Their nominal chemical composition is M2O. Al2O3.4SiO2.11H2O where M is a Group I cation. The ceramic-like, cross-linked product shares the brittle nature of ceramics, but can be reinforced with chopped or unidirectional fibers, or fiber weaves, yielding a strong and tough composite which has additional properties of fire and corrosion resistance. Geopolymers also have refractory adhesive properties up to 1,000°C whereupon they crystallize into a ceramic. Fibers are commonly used as reinforcements to improve the mechanical performance of many materials because they are effective in strengthening and toughening these materials. This paper will describe the fabrication and microstructure (SEM, EDS) of two different felt weaves, fiberglass and basalt, reinforcing geopolymer composites. The mechanical properties including flexure strength, tensile strength and impact resistance of metakaolin-based geopolymer composites will be measured and analyzed by Weibull statistics.

2:10 PM

(ICACC-FS1-009-2015) Green Composite: Potassium Geopolymer Reinforced with Curaua Fibers

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

Lignocellulosic fibers obtained from the curaua plant (Ananas erectifolius) can be used as suitable reinforcements for geopolymers owing to their high strength and biodegradability. In this work, the tensile and flexure strength as well as impact properties of as-received and alkali-treated curaua fiber reinforced potassium geopolymer composites were measured according to ASTM standards and analyzed by Weibull statistics. Thermogravimetric analysis (TGA) was used to study the behavior of fibers and the composites at high temperatures. X-ray diffraction (XRD) was used to confirm the formation of geopolymer and scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) were used to examine the fiber-matrix interface.

2:30 PM

(ICACC-FS1-010-2015) Green Composite: Sodium Geopolymer Reinforced with Malva Fibers

K. Sankar*[1]; W. M. Kriven[1]; R. K. Vieira[2]; 1. University of Illinois at Urbana-Champaign, USA; 2. Federal University of the Amazonas, Brazil

Plant fibers from the Amazon have excellent mechanical properties in comparison with some ceramic fibers. This makes them suitable candidates as reinforcements for geopolymers. In this work, the tensile and flexure strengths as well as impact properties of as-received and alkali-treated malva (Malva sylvestris) fiber reinforced sodium geopolymer composites were measured according to ASTM standards and the data was analyzed by Weibull statistics. Thermogravimetric analysis (TGA) was used to study the behavior of fibers and the composites at high temperatures. X-ray diffraction (XRD) was used to confirm the formation of geopolymer and scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) were used to examine the fiber-matrix interface.

3:10 PM

(ICACC-FS1-011-2015) Portland Cement-reinforced with luffa fibers

H. A. Colorado*[1]; S. A. Colorado[2]; J. M. Velez[3]; 1. Universidad de Antioquia, Colombia; 2. Instituto Tecnologico Metropolitano, Colombia; 3. Universidad Nacional de Colombia, Colombia

Luffa (also spelled loofah) fiber is a green renewable resource with traditional uses such as scrubbing sponge or in modern art. In this research, luffa fibers from Colombia are used as reinforcement material for cement. Fibers are used as-received and with a treatment that prepares them to be placed in the alkaline Portland cement matrix. The effect of fiber contents on the compressive strength, density, and microstructure is presented. Thermal and water weakening properties and stability were also evaluated. Microstructure is evaluated by optical and scanning electron microscopy.

3:30 PM

(ICACC-FS1-012-2015) Sodium Geopolymer Reinforced with Cordgrass Fibers

D. S. Roper*[1]; K. Sankar[1]; J. Crawford[1]; D. Lee[2]; W. M. Kriven[3]; 1. University of Illinois at Urbana-Champaign, USA; 2. University of Illinois at Urbana-Champaign, USA; 3. University of Illinois at Urbana-Champaign, USA

Prairie cordgrass (Spartina pectinata) is a natural fiber resource which is highly accessible in Illinois and the Midwest region in United States. Lignocellulosic fibers extracted from cordgrass can be used as suitable reinforcements for geopolymers. The goal of this design was to create a sustainable organic fiber-reinforced geopolymer composite utilizing resources found locally in the Midwest. Its properties and viability were determined through tensile, flexure and impact testing according to ASTM standards and analyzed by Weibull statistics. Thermogravimetric analysis (TGA) was used to study the behavior of fibers and the composites at high temperatures. X-ray diffraction (XRD) was used to confirm the formation of geopolymer and scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) were used to examine the fiber-matrix interface.

3:50 PM

(ICACC-FS1-013-2015) Influence of halloysite nanotubes on the microstructure and mechanical resistance of textured ceramic substrates shaped by tape-casting (Invited)

N. Houta*[1]; G. Lecomte[1]; N. Tessier-Doyen[1]; C. Peyratout[1]; 1. GEMH-CEC, France

Ceramic layers shaped by tape-casting allowed the development of filtration membranes or multilayer ceramic capacitors (thickness between 25 μm and 1500 μm). This shaping process manufactures laminated tapes with a regular surface, thickness, and microstructure. Phyllosilicates offer a wide range of applications, from traditional to high-added value ceramics. The present work aims at understanding the influence of halloysite nanotubes on microstructure and mechanical resistance. The sintering conditions were determined using thermogravimetric, differential thermal and dilatometric analyses. The structural characteristics of green and sintered tapes were performed using scanning electron microscopy, interferometric microscopy, X-ray diffraction. Mechanical properties were determined by biaxial bending tests. Results (for kaolin/hallloysite mixture) indicated that dolaflux B was the most suitable dispersant for the studied clay suspensions. Concerning the shaping process, the binder/plasticizer ratio equal to 1 allowed reaching the required viscosity. The texturation of tapes, due to the shape of clay particle and organic phase distribution, leads to structural anisotropy (before and after sintering) between the upper and the basal surfaces of tapes. The mechanical stress to rupture was increased from 20 to 130 MPa after sintering at 1150°C.

FS5: Single Crystalline Materials for Electrical, Optical and Medical Applications

Semiconductor II

Room: Tomoka C
Session Chair: Koichi Kakimoto, RIAM

1:30 PM

(ICACC-FS5-015-2015) Preparation and properties of bulk aluminum nitride (AlN) crystals and substrates (Invited)

M. Bickermann*[1]; 1. Leibniz Institute for Crystal Growth (IKZ) Berlin, Germany

Wafers cut from aluminum nitride (AlN) bulk single crystals are most promising substrates for deep UV optoelectronic or power electronic devices based on high Al content AlGaN epitaxial layers, due to their chemical stability, low thermal and lattice mismatch, and compressive strain to AlGaN layers. AlN bulk crystal growth is performed by physical vapor transport at temperatures of about 2200°C. We will present our status and progress in AlN bulk crystal growth on N-polar basal plane AlN seeds prepared from spontaneously nucleated freestanding AlN crystals. The crystals show excellent structural quality which is inherited in subsequent seeded growth runs. The current technological challenges, enabling efficient single-crystalline diameter enlargement as well as preventing seed backside evaporation, crystal cracking, and parasitic nucleation adjacent to the seed, are discussed in the presentation. Optical and electrical properties of AlN substrates are critical for their application. Residual impurities such as C, O, and Si, as well as intrinsic defects, do not only govern the materials properties, but also influence crystal growth. We will present means to control impurity content during growth and to influence optical properties by

compensation and Fermi level effects. Finally, we show examples of proper surface preparation, MOVPE growth results, and first AlGaN/AlN test devices.

2:00 PM

(ICACC-FS5-016-2015) Development of single-crystal AlN for high performance, ultraviolet (UVC) LEDs (Invited)

L. J. Schowalter*[1]; 1. Crystal IS, USA

Ultraviolet light-emitting diodes, designed to emit at wavelengths shorter than 280nm, are attractive light sources for chemical analysis and disinfection applications. Their small size, robustness, ability to turn on and off instantly, stability, and ability to fabricate tuned to a specific wavelength are inherent advantages over alternate sources such as mercury, deuterium and xenon lamps. Recent improvements in efficiencies and lifetimes from the light-emitting diodes opened up new applications. Much of the improvement has been driven by improved quality of the epitaxial nitride semiconductor layers that are used to fabricate the LEDs. Crystal IS has pursued an approach where the device structure is formed by using OMVPE to grow pseudomorphic (fully strained to the substrate) epitaxial layers on a suitably prepared, bulk AlN single crystal wafer. This approach achieves dislocation densities lower than 105 cm-2 in the active device region. This results in a significant improved internal efficiency over devices with higher dislocation densities. The low dislocation density also leads to long operating lifetimes for the devices even at high current operation. This approach has been used in the recently released Optan LED product which represents the first commercial product based on AlN substrates.

2:30 PM

(ICACC-FS5-017-2015) New Challenges for Transparent Conducting and Semiconducting Oxides (Invited)

E. M. Fortunato*[1]; R. F. Martins[1]; 1. FCT-UNL, Portugal

Transparent electronics has arrived and is contributing for generating a free real state electronics that is able to add new electronic functionalities onto surfaces, which currently are not used in this manner and where silicon cannot contribute [1,2]. The already high performance developed n- and p-type TFTs have been processed by physical vapour deposition (PVD) techniques like rf magnetron sputtering at room temperature which is already compatible with the use of low cost and flexible substrates (polymers, cellulose paper, among others). Besides that a tremendous development is coming through solution-based technologies very exciting for ink-jet printing, where the theoretical limitations are becoming practical evidences. In this presentation we will review some of the most promising new technologies for n- and p-type thin film transistors based on oxide semiconductors and its currently and future applications.

Ferro/piezo-electric I

Room: Tomoka C

Session Chair: Mario Maglione, ICMCB-CNRS

3:20 PM

(ICACC-FS5-018-2015) Materials Design for Enhancing Piezoelectric Properties of High-Quality Bi-based Ferroelectric Single Crystals (Invited)

Y. Noguchi*[1]; M. Ogino[1]; K. Hirano[1]; Y. Kitanaka[1]; M. Miyayama[1]; Y. Yoshida[2]; T. Ishigaki[2]; 1. The University of Tokyo, Japan; 2. Ibaraki University, Japan

Ceramics of ferroelectric materials (1−x)Bi0.5Na0.5TiO3−xBaTiO3 [BNT−BT] and (1−x)Bi0.5K0.5TiO3−xBi0.5Na0.5TiO3 [BKT−BNT] have been intensively studied because these ceramics show superior piezoelectric properties around their morphotropic phase boundaries (MPBs). Few studies on ferroelectric and piezoelectric properties of the single crystals of BNT−BT and BKT−BNT, however, have been reported to date, because of a difficulty in growing high-quality single crystals. The objective of this study is to establish materials design of BNT−BT and BKT−BNT by investigating crystal and domain structures, and polarization/piezoelectric properties of high-quality single crystals obtained by the high-oxygen-pressure crystal growth method.1) It is demonstrated that the tetragonal phase in space group P4bm plays an important role in the formation of the MPB and in an enhancement of the piezoelectric properties.

3:50 PM

(ICACC-FS5-019-2015) Piezoelectric single crystals excluding polar axis for high temperature sensor application (Invited)

H. Takeda*[1]; K. YOSHIDA[1]; M. HAGIWARA[2]; T. HOSHINA[1]; S. FUJIHARA[2]; T. TSURUMI[1]; 1. Tokyo Institute of Technology, Japan; 2. Keio University, Japan

Aim of this study is to find a new promising material for combustion pressure sensor directly placed in automobile engines. For such the sensor, piezoelectric single crystals excluding polar axis has been paid attention because the crystal does not possess pyroelectricity, that is electric charge is not generated by temperature fluctuation. Typical examples are quartz and related material GaPO4, but the former cannot be used at high temperature because of its phase transformation and the latter has difficulty of its crystal growth. Under this situation, we focused on calcium aluminate silicate Ca2Al2SiO7 (CAS) single crystal, which belongs to tetragonal system, point group -42m. The CAS single crystals can be grown by the Czochralski method. We grew the single crystals with one inch in diameter and more than 50 mm in length. By the resonance method, we determined the two independent piezoelectric moduli (d14 and d36) and evaluated their low temperature dependence up to 500 degC. In this study, we have constructed measurement system of direct piezoelectric effect at high temperature and characterized the crystals under pseudo combustion environment in the engine cylinder. Output charge signal against applied stress was properly detected at 700 degC. These observations suggest that CAS crystals are superior candidates for sensing pressure at high temperatures.

4:20 PM

(ICACC-FS5-020-2015) Application of Langasite Family Crystals in Piezoelectric Devices (Invited)

A. Medvedev*[1]; S. Sakharov[1]; A. Zabelin[1]; O. Buzanov[1]; V. Alenkov[1]; 1. OAO"Fomos-Materials", Russian Federation

Langasite family crystals are promising piezoelectric materials for new generation acoustoelectronic devices, as they can successfully replace the traditionally used ceramics and quartz. Resonators, wide bandwidth BAW and SAW filters, and high-temperature sensors operating at up to 1000°C have been developed and manufactured using these crystals. In this work, a collation of piezoelectric characteristics of devices using different crystals, as well as the influence of design and technology on these characteristics are given. The crystals were grown by CZ method. The obtained crystals were oriented using X-ray diffraction. Ag or Ir electrodes were deposited. Measurements of the frequency characteristics of devices using the inverse piezoelectric effect have been made. The influence of vacuum annealing on crystal conductivity for sensors using direct piezoelectric effect was investigated. It was shown that resonators operating on thickness-shear mode have the following capacitance ratio and temperature coefficients of the frequency of the second-order: about 88 and −58 ppb/°C2 for langasite, 57 and −62 ppb/°C2 for langatate, 47 and −26 ppb/°C2 for catangasite, respectively. Also, the conductivity vacuum annealed langatate crystals is about a hundred times less than of those annealed in air. Langasite family crystals have good prospects for application in piezoelectric devices working in a wide temperature range.

2nd European Union - USA Engineering Ceramics Summit

Advanced Ceramic Technologies: Current Status and Future Prospects III

Room: Coquina Salon F
Session Chairs: Pavol Sajgalik, Institute of Inorganic Chemistry; Surojit Gupta, University of North Dakota

1:30 PM

(ICACC-PRECS-015-2015) Advanced Ceramics for Automotive Industry (Invited)

M. J. Hoffmann*[1]; 1. Karlsruhe Institute of Technology (KIT), Germany

Ceramic materials are widely used in automotive industry as structural or functional components such as pump seals, catalyst supports, particulate filters, spark plugs, sensors or piezoelectric actuators, and more recently in high performance batteries. Many other ceramic parts had been developed in the past, but never used in mass production. Reasons are often due to high costs, insufficient reliability or only minor benefits for the performance of the entire system. To open new markets for ceramic components in automotive industry, feasibility studies are required and the development of prototypes to demonstrate the potential of an enhanced efficiency. Another driver for new products is legislation that makes ever greater demands on the environmental impact. The paper will give examples for a potential use of engineering ceramics as local strengthening of light weight metal parts with porous ceramic performs or corrosive and tribologically highly stressed pump components. In terms of functional ceramics, the current status of piezoelectric actuators for fuel injection systems and PTC heaters is reviewed. Finally, challenges are discussed to develop new materials for all solid state batteries for hybrid drives and electric vehicles.

2:00 PM

(ICACC-PRECS-016-2015) Processing of graded ceramic-metal composites for functional applications (Invited)

F. Cambier*[1]; D. Hautcoeur[1]; S. Hocquet[1]; Y. Lorgouilloux[2]; A. L. Leriche[2]; B. Nait-Ali[4]; D. Smith[4]; M. Gonon[3]; V. Lardot[1]; 1. Belgian Ceramic Research Centre, Belgium; 2. University of Valenciennes, France; 3. UMons, Belgium; 4. ENSCI - University of Limoges, France

Graded ceramic-metal composites were prepared by liquid metal infiltration into porous ceramic structures for thermal flux management applications. The aim was to shape parts showing thermal anisotropy, able to conduct the heat in one direction and be insulating in the perpendicular direction. The potential use of such materials is in automobiles to protect electronic components against heat excess and conduct it to energy transforming devices. The porous ceramic matrices were prepared by two techniques: 1/ the impregnation of a polymeric skeleton made of bonded PMMA beads by slurries, allowing the control of the spherical pore size and their interconnection. By such a technique, it is possible to make samples with a gradient of pore sizes and volume 2/ the freeze casting of aqueous ceramic slurries leading to the formation of ellipsoidal elongated pores. Alumina and zirconia porous scaffolds were post-infiltrated by an aluminium based alloy. The various obtained structures infiltrated by the metal are compared from the point of view of directional thermal conductivity and mechanical properties. The measured conductivity values are in good agreement with numerical modelling. The remaining porosity after impregnation also influences the thermal conductivity values. By using zirconia as the ceramic matrix, while keeping a residual porosity, a large anisotropy (>10x) was achieved.

2:30 PM

(ICACC-PRECS-017-2015) Developing novel strategies for enhancing materials education

S. Gupta*[1]; D. Bose[2]; M. Cavalli[1]; 1. University of North Dakota, USA; 2. Boise State University, USA

During part A, we will report an innovative approach for creating senior design projects for better understanding of sustainable materials manufacturing for both online and campus based students. The authors will present a case study with engineering students located in regions of the United States. Some of the major challenges during the design of online senior design projects are, (a) establishing online communication between students, (b) teaching online students in real time, and (c) creating a project where different online students can participate and contribute synchronously as well as asynchronously. During part B, the authors will report specific types of best-practice online strategies, which may be used to enhance Undergraduate (UG) student learning experiences. We also propose a Modified Flipped Learning Approach (MFLA). Different aspects of MFLA will be discussed in the presentation. In addition, the effect of formative evaluation through SGID (Small Group Instruction Design) on course development will be discussed. It is expected that these online strategies may further support student learning and have wider pedagogic applications.

3:20 PM

(ICACC-PRECS-018-2015) GB chemistry of silicon nitride based nano-composites – implications to mechanical, tribological and chemical properties (Invited)

P. Sajgalik*[1]; M. Hnatko[1]; Z. Lences[1]; M. Gall[1]; J. Dusza[1]; P. Tatarko[1]; Z. Chlup[2]; 1. Institute of Inorganic Chemistry, Slovakia; 2. Institute of Physics of Materials, Czech Republic

Six different sintering aids (Lu2O3, Yb2O3, Y2O3, Sm2O3, Nd2O3 and La2O3) were used for the processing of dense Si3N4/SiC micro/nano composites. Formation of SiC nano–inclusions was achieved by in situ carbothermal reduction of SiO2 by C during the sintering process. Room temperature fracture toughness, hardness and strength showed increasing tendency when the used rare-earth element in the oxide additive changes from a large to a small rare-earth cation (i.e. from La3+ to Lu3+). Besides the highest hardness and reasonably high fracture toughness and strength of composite material with Lu2O3 sintering additive. 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. Besides mechanical properties composites containing luthecia expose the excellent oxidation resistance and wear resistance.

3:50 PM

(ICACC-PRECS-019-2015) Resilience, Sustainability ad Robustness in Ceramic Processing (Invited)

R. D. Sisson*[1]; 1. WPI, USA

In the future ceramic processing enterprises will thrive only if they are resilient. Resilience is the ability to rapidly adapt to changes in the processing and business environment. While all ceramic processes need to robust and sustainable, the ability to adjust to the changing environment in terms of supply chain, materials shortages, energy supply and cost, environmental and safety compliance as well as litigation will be mandatory for survival in our new global environment. In this paper the key issues robustness, sustainability and resilience will be presented and discussed. Strategies to create a resilient enterprise will also be discussed.

4:20 PM

(ICACC-PRECS-020-2015) Influence of porous scaffolds structure on their mechanical properties and cell colonization ability (Invited)

A. L. Leriche*[1]; J. Hornez[1]; F. Bouchart[1]; E. Meurice[1]; D. Hautcoeur[2]; V. Lardot[2]; F. Cambier[2]; 1. University of Valenciennes, France; 2. Belgian Ceramic Research Centre, Belgium

For nearly twenty years, calcium phosphate ceramics like hydroxyapatite (HA) or β-tricalcium phosphate (TCP) have been largely used as bone substitutes because of their chemical composition close to bone mineral phase. Today, research is more focused on the development of biomimetic structures. In this study, the behavior of structures obtained from 3 processes are compared: (1) impregnation by ceramic slurries of a polymeric skeleton made of bonded PMMA beads which allows to control the size of spherical porosity and the interconnection between pores, (2) freeze casting of aqueous ceramic slurries and (3) 3D-printing of ceramic viscous inks; these two last techniques lead to columnar porous structures. The freeze-cast porous material shows ellipsoidal channels of a few ten microns whereas the material prepared from 3D printing presents regular continuous channels with bigger size and square shape. The as-obtained porous architectures are compared according to cell colonization ability along with their mechanical properties. An additional microporosity can also be obtained by adding a microporogenous agent, allowing besides the cell colonization, the loading of implants with anti-bacterial and host biological agents. The drug and phage releasing kinetics, as a function of the type of porous structures, are compared according to time and ceramic porosity.

4th Global Young Investigator Forum

Ceramic Composites

Room: Coquina Salon C

Session Chair: Marta Quintanilla Morales, Institut National de la Recherche Scientifique

1:30 PM

(ICACC-GYIF-020-2015) Effect of Surface Modification of Boron Nitride Nanomaterials in the Preparation of Nanocomposites

D. Santiago*[1]; C. Puleo[1]; J. Hurst[1]; C. Hung[1]; M. Lebron-Colon[1]; 1. NASA Glenn Research Center, USA

Boron nitride nanotubes and nanosheets (BNNT and BNNS) have been attracting attention due to interest in providing improvements to thermal conductivity and insulation properties of thin film nano-polymer composite materials. Dispersing boron nitride nanomaterials in polymer matrices becomes very difficult for high filler content. Therefore, surface functionalization of boron nitride is imperative to avoid agglomeration in the preparation of thin films. Nanocomposites prepared using functionalized and non-functionalize boron nitride nanomaterials are evaluated by different characterization techniques: FTIR, Raman, SEM, UV-Visible and thermal conductivity.

1:50 PM

(ICACC-GYIF-021-2015) Polyethyleneimine Functionalized with Oleic Acid as Polymer Dispersants for Non-aqueous Si3N4 Suspensions

M. Iijima*[1]; N. Okamura[1]; S. Sueyasu[1]; J. Tatami[1]; 1. Yokohama National University, Japan

Tuning the stability of non-aqueous suspensions that comprises from multiple species of particles are critically essential to control the final properties of ceramic products through wet processing, typically for materials, such as Si3N4 and AlN, those needs addition of various sintering agents and prevention of major contact with aqueous content. In this study, a complex of oleic acid (OA) and polyethyleneimine (PEI) was simply designed and applied as polymer dispersants in order to improve the stability of non-aqueous suspension of Si3N4 and Si3N4/sintering additive mixtures. While PEI itself was not soluble in toluene, it became soluble with addition of oleic acid and an assistance of ultra-sonication. FTIR analysis revealed that the carboxyl group of oleic acid had associated with amine segments of PEI. It was found that the designed PEI-OA complex can effectively adsorb on various types fine particles in toluene, such as Si3N4, AlN, Al2O3, MgO, and TiO2. While the dense Si3N4 and Si3N4/sintering additive suspension (~35vol%) of toluene solidified without dispersant addition, they became flowable and their stability has drastically improved when the additive content of designed PEI-OA has increased to reach the saturated adsorption content on these particles.

2:10 PM

(ICACC-GYIF-022-2015) Structure and ionic conductivity of Meixnerite modified with mono butyl ether ethylene glycol (mbeeg)

M. J. Paulo*[1]; E. Tchomgui[1]; A. Benyounes[1]; S. Ntais[1]; A. Tavares[1]; 1. INRS, Canada

Meixnerite (Mg6Al2(OH)18(OH)2.4H2O) is an anionic clay from the family of the Layered Double Hydroxides (LDH) whose conductive properties are exploited in this work for fuel cells applications. For this purpose we investigate the effect of meixnerite's interlayer distance, water content and type of water on its ionic conductivity. Thus a water miscible compound, monobutyl ether ethylene glycol (mbeeg) is added during the meixnerite synthesis in different ratios. This organic molecule is used to induce structural and textural modifications in meixnerite, through the interaction of its hydrophilic part with the meixnerite's hydroxide layers. The effect of this ethylene glycol on the LDH's textural properties was investigated by means of X-ray diffraction, transmission electron microscopy, nitrogen sorption and thermogravimetrical analysis. The ion conductivity is determined by electrochemical impedance spectroscopy at 98% RH from 21 to 180 °C and correlated with the LDHs intrinsic properties.

2:30 PM

(ICACC-GYIF-023-2015) Effects of type and amount of silicon nitride filler on thermal conductivities of epoxy resin/silicon nitride composites

A. Shimamura*[1]; Y. Hotta[1]; N. Kondo[1]; H. Hyuga[1]; K. Hirao[1]; 1. National Institute of Advanced Industrial Science and Technology (AIST), Japan

Epoxy resin, most frequently utilized thermosetting polymer, has been widely employed as electrical insulation substrates. Such resin substrates have advantages in cost and workability, but have low thermal conductivity. In order to improve its thermal conductivity, addition of high thermal conductive ceramic fillers such as BN and AlN has been investigated. Although silicon nitride (Si3N4) possesses high intrinsic thermal conductivity as well as high chemical stability, there have been few reports on the use of Si3N4 as a filler. In this study, we examined the effects of type and amount of Si3N4 filler on the thermal conductivity of Si3N4 / epoxy resin composites. Two types of silicon nitrides, α- and β-Si3N4, with about the same average particle size of 3.5 μm were used, and the amount of Si3N4 was varied in the range from 0 to 70 vol%. Thermal conductive behavior of α- and β-Si3N4 loaded composite could be divided to two region below and above 50 vol%. Below 50 vol% of Si3N4 filler content, the type of Si3N4 filler hardly affected to thermal conductivity of the composite material. On the other hands, it had strong impact on thermal conductivity of composite above 50 vol.% of Si3N4 filler content. The β-Si3N4 loaded composite at 68 vol% showed 1.6 times higher thermal conductivity than the α-Si3N4 loaded composite

2:50 PM

(ICACC-GYIF-024-2015) Exfoliation of Laminated h-BN Particles by Wet-Jet Milling

Y. Tominaga*[1]; D. Shimamoto[1]; K. Sato[1]; Y. Imai[1]; Y. Hotta[1]; 1. National Institute of Advanced Industrial Science and Technology, Japan

Plate-like ceramics, such as hexagonal boron nitride (h-BN), have been widely used as filers for polymer ceramics, which are lightweight materials, with high electrical and thermal conductive properties. Because the performance of its polymer ceramics is strongly dependent on the aspect ratio of plate-like fillers, the exfoliation development of laminated particles is of importance for improvement of polymer ceramic properties. In this study, we will demonstrate to exfoliate h-BN efficiently by using various mechanical high shear devises, such as vortex fluid device, planetary homogenizer, ultrasonication and wet-jet milling (WJM) with effective shear flow. The sedimentation test indicated that WJM process led to exfoliation of the laminated h-BN effectively. Also, the particle size distributions showed that the particle size of wet-jet milled h-BN was as similar as the initial particle size, whereas the particle sizes of h-BN treated by other mechanical devices were less than 70% of the initial particle size. These results suggested that the difference of particle size were based on the method of applying shearing force on the mechanical methods. In WJM, h-BN must be uniformly aligned in the thickness direction by pushing the slurry out at a high pressure, and the large impact energy is applied in the direction of the thickness of the h-BN particles. Therefore the exfoliation of h-BN effectively is progressed by WJM.

3:10 PM

(ICACC-GYIF-025-2015) Structure-property-processing relationships in modified BiScO3 – PbTiO3

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

In recent years there has been an intense push for high temperature piezoelectrics for applications in both terrestrial and aerospace territories. For years the operating temperature limit, usually taken as ½ the Curie temperature (Tc), has been ~200°C for one of the most widely used commercial piezoelectrics, Pb(Zr,Ti)O¬3 (PZT). Subsequent research into Bi(B'B")O3 – PbTiO3 piezoelectrics led to the discovery of the morphotropic phase boundary (MPB), high-Tc system BiScO3 – PbTiO3 (BS-PT) with a Tc of 460°C and a d33 of 460 pm/V. While the Tc marks the boundary between the ferroelectric-paraelectric state, it is also necessary to determine the depoling temperature (Td) which dictates the actual working temperature range. By modifying the B-site cations [Zn or (Zn0.5¬Zr¬0.5) for Sc] and adjusting processing parameters the Td can be increased as much as 25°C while also tuning the electromechanical properties. The effect of B-site modification on various relevant properties as a function of temperature has been explored through the characterization of microstructure and weak/high field measurements.

Biomaterials and Biophotonics

Room: Coquina Salon C

Session Chairs: Diana Santiago, NASA Glenn Research Center; Maria Paulo, INRS

3:30 PM

(ICACC-GYIF-026-2015) Biofunctional polymer modification on ceramic nanophosphors for near-infrared biophotonics (Invited)

M. Kamimura*[1]; K. Soga[1]; 1. Tokyo University of Science, Japan

Fluorescence bioimaging is an important technique in biomedical research fields because of the advantages such as high sensitivity and resolution. Recently, the imaging in the over-1000 nm (OTN) near infrared (NIR) wavelength range is attracting interests because of the much deeper penetration depth of the both excitation and emission lights in the OTN-NIR range. Especially, the low loss is advantageous for an in vivo imaging. Rare-earth doped ceramic nanophosphors (RED-CNPs) are known to emit efficient fluorescence in the OTN-NIR range under an NIR excitation. The authors have studied to use the RED-CNP to as the fluorescent material for the OTN-NIR fluorescence bioimaging under the NIR excitation. For using the CNP, the conjugation of the CNP and a biofunctional polymer is inevitable to control the biodistribution of the fluorescence probe in a small animal. In this study, biofunctional poly(ethylene glycol) (PEG) based block copolymers were introduced on the surface of RED-CNPs to utilize the nanoparticles for the OTN-NIR fluorescence bioimaging. PEG is well known as a biocompatible polymer, to improve the biocompatibility and dispersion stability of RED-CNPs under physiological conditions. This presentation will report recent progress of the development of PEG modified RED-CNPs for OTN-NIR fluorescence bioimaging.

3:50 PM

(ICACC-GYIF-027-2015) Highly Porous Wollastonite-Hydroxyapatite Scaffolds For Bone Ingrowth From Preceramic Polymers

L. Fiocco*[1]; E. Bernardo[1]; S. Li[2]; P. Colombo[1]; J. R. Jones[2]; 1. University of Padova, Italy; 2. Imperial College, United Kingdom

A novel strategy was employed to synthesise porous wollastonite-hydroxyapatite ceramic scaffolds with open pores for bone regeneration. A commercial liquid preceramic polymer filled with micro-CaCO3 powders was foamed into a highly porous structure at low temperature (at 350°C), using the decomposition of hydrazine additive, and then converted into ceramic by a treatment at 700°C. Hydroxyapatite was later developed by application of a novel treatment, based on the phosphatization of ceramized foams in a P-rich solution, while wollastonite was obtained by a second firing, at 900°C. The effectiveness of the method was proven by X-rays diffraction analysis, showing the presence of the two expected crystalline phases. Porosity, interconnect size distribution and mechanical strength were measured and found to be suitable for cell penetration and for bone regeneration in non-load bearing sites (crushing stregth ≈ 3 MPa, porosity ≈ 90 %, interconnect size ≈ 130-200 μm). In particular, bioactivity and ion release rate were assessed by 3 weeks dissolution study in SBF. 3 weeks cell culture tests with osteoblasts showed the the cells colonized the pores, perfectly following the surface architecture of the pores. The preceramic mixture was also successfully 3D-printed.

4:10 PM

(ICACC-GYIF-028-2015) Lanthanide-doped $NaGdF_4$ Nanoparticles as Promising Probes for Nanothermometry

E. Hemmer*[1]; F. Légaré[1]; F. Vetrone[1]; 1. INRS, Canada

Lanthanide (Ln^{3+}) containing compounds are promising candidates for cellular nanothermometry. Their outstanding optical properties include narrow absorption and emission bands, high emission efficiency and long lifetime of excited states. The use of near-infrared (NIR) light for the excitation of the Ln^{3+}-based biomarkers may overcome the drawbacks of conventional organic dyes such as photobleaching, autofluorescence, and phototoxicity. Besides, biomedical applications require small nanoparticles in the range below 20 nm, non-toxicity, and water dispersibility. Efficient emission at such small size is provided by doping Ln^{3+}-ions into a fluoride matrix. Thus, upconverting $NaGdF_4$:Ln^{3+},Yb^{3+} (Ln^{3+}: Er^{3+} or Tm^{3+}) nanoparticles that convert invisible NIR light into visible light are synthesized by thermal decomposition. Ln^{3+}-ions 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. However, further surface modification with a thermoresponsive polymer opens new pathways towards efficient cellular nanothermometers. The combination of Ln^{3+}-based upconverting nanoparticles with an organic dye provides potential donor-acceptor-pairs allowing for a temperature-dependent energy transfer, whereas the light emitted by the Ln^{3+}-ions (donors) is absorbed by the organic dye (acceptor).

4:30 PM

(ICACC-GYIF-029-2015) Growth of graphene and Ag nanoparticles doped TiO2

M. Barberio[1]; S. Veltri*[1]; F. Stranges[1]; F. Xu[1]; P. Antici[2]; 1. University of Calabria, Italy; 2. INRS-EMT, Canada

In recent years, the use of nano materials in many fields (medicine, biochemistry, nanoelectronics, energetics, etc.) has become very popular due to their intrinsic properties of being able to improve the macromaterials without changing their chemical composition. Strong effort has been made to study the growth of nanostructured films with properties of optical transparency, super-hydrophobicity and bactericidal activity. Carbon-based nanomaterials (graphene and carbon nanotube) are often hydrophobic and exhibit strong antibacterial activity. On the other hand, silver (Ag) has been known as an antibacterial agent for centuries due the capability of the Ag+ ions destroying the cell membrane. Finally, TiO2 is characterized by chemical stability, non-toxicity, high photo-reactivity, broad-spectrum antibiosis and cheapness, and it has been used extensively as biocide against various microorganisms. Moreover the wettability of titanium dioxide can be tuned by irradiation. In this work, we report a study on the growth and characterization of a thin hybrid film of titanium dioxide nanoparticles doped with graphene nano-flakes and/or silver nanoparticles. The aim is to realize new materials combining and enhancing the properties of each component. Varying the ratio of components in the nano-hybrids, we can tune the properties of hydrophobicity, bactericidal and transparence of materials adapting each material to a specific application

4:50 PM

(ICACC-GYIF-030-2015) Coupling of gold nanorods with upconverting nanoparticles: heat releasing and temperature monitoring

S. Rohani*[1]; 1. INRS, Canada

Gold Nanorods (GNRs) have a strong absorption linked to the surface plasmon resonance in the Near Infrared (NIR) region, resulting in radiative emission as well as heat release, making them interesting for applications such as photothermal therapy. Lanthanide doped upconverting nanoparticles (UCNPs) can absorb NIR radiation and re-emit it in the visible range. These visible emission bands, for a commonly used UCNPs composition which is NaGdF4:Er3+/Yb3+, are known to be intrinsically dependent on environmental temperature, making these nanoparticles potentially applicable in nanothermometry. In this project, we coupled the GNRs and UCNPs in order to combine the functionalities of both types of nanostructures. Both nanostructures were tuned so that they can be excited at the same NIR wavelength (980 nm). It was demonstrated that the samples temperature can be controlled after optical pumping by GNRs, and this increase was sensed and monitored by changes in the emission spectra of UCNPs. The limitations of the combined system have been analyzed to provide a reliable heat and sensing probe for nanothermometry.

5:10 PM

(ICACC-GYIF-031-2015) How dark is the dark side of lanthanide-based upconversion: quantum yield and possibilities of enhancement (Invited)

M. Quintanilla Morales*[1]; S. Rohani[1]; J. Marques-Hueso[2]; E. Hemmer[1]; B. Richards[3]; L. Razzari[1]; F. Vetrone[1]; 1. Institut National de la Recherche Scientifique, Canada; 2. Heriot Watt University, United Kingdom; 3. Karlsruhe Institute of Technology, Germany

Upconversion (UC) energy transfer offers an interesting excitation scheme for lanthanide-doped nanoparticles (NPs), since it allows access to the visible and ultraviolet emitting energy states of lanthanides through excitation in the near infrared. Such excitation strategy is finding applicability in a wide range of fields (photovoltaics, imaging, theragnostics) yet UC in the most favorable case is a second order process. This, together with the additional depopulation routes of the energy states, strongly limit UC efficiency. Here we chose one of the most widespread materials for UC, NaGdF4:Er3+/Yb3+, as an example to study both quantitatively and qualitatively how the phase and shape of the NPs can alter UC quantum yield. Next, we explore the effect that the presence of gold nanorods (GNR) can have on the optical properties of UCNPs. The extremely localized electric field created by GNR can modify the transition probabilities of lanthanides, so enhancement or quenching of the UC-emissions can occur in their proximity. This is indeed a promising option to overcome UC limits but is not the only advantage of coupling GNR with UCNPs. Upon optical excitation GNR are known to be efficient heaters, yet to monitor the achieved temperature is complex due to the lack of an intrinsic thermal probe. UCNPs can help also here, further confirming the potential of the GNR/UCNP couple.

Posters

Session A

Room: Ocean Center Arena

(ICACC-PRECS-P001-2015) A Study of the $CuAlO_2$ - Pt Interface After High Temperature Electrical Measurements

S. Mudenda*[1]; G. Kale[1]; Y. S. Hara[1]; 1. University of Leeds, United Kingdom

The use of platinum as an electrical contact has always been unconciously chosen because of its reliable stability at a wide temperature range disregarding other ruinous effects it can cause on materials it is connected to. This investigation reports on the possible reactions at the interface of Pt–$CuAlO_2$ after AC impedance measurements and repercussions to the overall conductivity of the material. Both XRD and SEM/EDX revealed a new phase of $CuAl_2O_4$ at the interface which is believed to hinder charge transport. EDX also revealed that Pt acted as a driving force in the conversion of $CuAlO_2$ to $CuAl_2O_4$ by absorbing Cu^{2+} and O^{2-}. This happened on both samples fired in air and argon indicating that Pt was the driving force in the formation of the high resistant phase. AC impedance results show a decrease in conductivity after each run of measurement indicating a continous growth of the $CuAl_2O_4$ layer. When Pt is used as a coating on any ceramic sample that contains metals that can form alloys with Pt, there is a likelihood of the metal ion diffusing into the Pt coating and this will change the structural stoichiometry of the ceramic at the interface giving inaccurate and irreproducible results. A careful selection of electrical contact is then crucial.

(ICACC-S1-P002-2015) Porous Graphite From Pitches in Sandwich Composite Construction: Manufacturing and Mechanical Characterization

H. Hosseini*[1]; S. Ghaffarian[2]; M. Teymouri[3]; A. Moeini[3]; 1. University of Missouri- Columbia, USA; 2. Amirkabir University of Technology (Tehran Polytechnic), Iran (the Islamic Republic of); 3. National Iranian Oil Company, Research Institute of Petroleum Industry, Iran (the Islamic Republic of)

Porous graphite has been synthesized by two step polymerization of coal tar pitch under heat and pressure. First step is attributed to the Meso Carbon Micro Bead (MCMB) formation in the pitch matrix via heating to the maximum fluidity temperature and applying pressure to maintain stability in MCMB production. XRD and optical microscopy results showed the formation of stacking aromatic carbon sp2 layers and enhanced graphitization degree. MCMB formation is essential for the next step due to its graphite transformation in the matrix. Second step belongs to foam production based on internal bubble formation, as a result of pyrolysis reactions and releasing of remaining volatile matters restricted by external pressure. XRD presented magnified peaks of graphite crystals formed on the ligaments of pore walls. SEM and OM depicted the formation of pores throughout the mesophase pitch media. Mechanical properties proved the capability of synthesized porous structure to use as a

core in sandwich composite construction (Compressive modulus of 0.175 GP and ultimate compressive strength of 12.5 MPa), furthermore, low density and light weight features (ρ < 1g/cm3 and higher specific weight) are another brilliant characteristics of these noble materials, making them favorable to be utilized in light weight material constructions.

(ICACC-S1-P003-2015) Electrical resistance and acoustic emission during fatigue testing of SiC/SiC composites

Z. Han*[1]; E. Maillet[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, ER of both HNS and SA specimens, were measured under cyclic loading conditions at both room and elevated temperature (815oC). 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. Three different cyclic loading rates, ranging from 0.01 Hz to 1Hz, were applied on HNS and SA specimens respectively. Mechanical and electrical-mechanical models are considered and compared with the experimental data.

(ICACC-S1-P004-2015) International Standards for Properties and Performance of Advanced Ceramics

M. G. Jenkins*[1]; J. Salem[2]; J. Helfinstine[3]; G. D. Quinn[4]; S. T. Gonczy[5]; 1. Bothell Engineering and Science Technologies, Inc., USA; 2. NASA Glenn Research Center, USA; 3. Corning Inc Retiree & Consultant, USA; 4. Government Retiree & Consultant, NIST, USA; 5. Gateway Materials Technology, Inc, USA

Mechanical and physical properties and performance of brittle bodies, including advanced ceramics and glasses, can be difficult to measure correctly unless the proper techniques are used. 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 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 and continually update, as well as validate through round robin test programmes, more than 45 standards 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 that might be 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-P005-2015) Mecahnical Properties of Bioceramics

M. Umair Farrukh*[1]; K. Ghauri[1]; 1. UET Lahore, Pakistan

Strength of bioceramics is important mechanical property because they are brittle in nature. In the brittle bioceramics crack are easily propagate in tensile load therefore, it is more critical than the compressive load. Fatigue is defined as failure of a material due to repeated/cyclic loading or unloading (tensile or compressive stresses). Hardness is one of the most important parameters for comparing properties of bioceramics. Fracture toughness is required to alter the crack propagation in ceramics. It is help to evaluate the serviceability, performance and long term clinical success of bioceramics.

(ICACC-S1-P006-2015) Ceramic Matrix Composites: Effect of Defects on Fatigue and Nondestructive Evaluation

G. Ojard*[1]; I. Smyth[2]; N. Magdefrau[1]; U. Santhosh[3]; J. Ahmad[3]; Y. Gowayes[4]; 1. United Technologies Research Center, USA; 2. Pratt & Whitney, USA; 3. Structural Analytics, USA; 4. Auburn University, USA

As the interest keeps growing on insertion of ceramic matrix composites for engineering use, the effect of defects needs to be known. Defective samples were introduced via stopping the polymer infiltration pyrolysis at different number of cycles. Past work by the authors showed that increasing mechanical and physical properties could be correlated with increasing thermal diffusivity (lower defects) within a full gauge area of the sample. Accordingly a thermographic investigation of these samples was carried out, but tests performed did not shed insight into the effect of localized defects. A limited number of samples were fully interrogated via micro-focus X-ray CT in the full gauge section of the sample. After interrogation, the samples were fatigue tested at 982C to failure. The localized effects of the defects on the performance will be presented.

(ICACC-S1-P007-2015) Ceramic Matrix Composites: Residual Testing After Intermediate Temperature Oxidation

G. Ojard*[1]; I. Smyth[2]; U. Santhosh[3]; Y. Gowayed[4]; D. jarmon[1]; 1. United Technologies Research Center, USA; 2. Pratt & Whitney, USA; 3. Structural Analystics, USA; 4. Auburn University, USA

As ceramic matrix composites evolve past their current point design approach and application, additional understanding of changes due to exposure and the resulting properties need to be understood. This is especially true when materials are exposed at an Intermediate Temperature Oxidation (ITO) point. Any additional insight will give designers greater flexibility into working with the material at various design points. A series of three panels were fabricated via a polymer infiltration process: 8 harness satin (HS) balanced symmetric layup, 8 HS bias weave, and angle interlock (bias). From these panels, a series of durability tests were done at an ITO point as well as its maximum use temperature. From this series of testing, some samples achieved either the fatigue or creep run-out condition. Residual room temperature tensile testing was then done on these samples. Before testing, the samples were nondestructively interrogated to see if effects of the ITO exposure could be comprehended. The tensile data will be compared against the baseline data and idealized stress-strain curves to understand the effect of exposure on the samples. The results and analysis of the testing done will be presented.

(ICACC-S1-P008-2015) Effect of Particle Loading on Properties, Damping, and Wear of Al/SiC MMCs

S. Salamone*[1]; B. Givens[1]; K. Kremer[1]; M. Aghajanian[1]; 1. M Cubed Technologies, Inc., USA

Al/SiC metal matrix composite (MMC) castings offer significant advantages over traditional unreinforced Al castings and monolithic ceramics. There are many applications that require increased specific strength and stiffness, vibration-damping, improved wear resistance and toughness. These enhanced performance goals are difficult to obtain without the ability to tailor physical and mechanical properties. Particulate reinforced metal matrix materials are well suited for engineering of specific properties. This study measures the effect of particle loading on cast Al/SiC MMCs. Composites with reinforcement loadings of 0, 30, 55 and 70 volume percent were fabricated then characterized with respect to static and dynamic mechanical properties (density, Young's modulus, compressive strength, fracture toughness, vibration-damping behavior and wear). The results are correlated to microstructure and particulate loading.

(ICACC-S1-P009-2015) Temperature Dependence of Electrical Resistivity Measurements of SiC/SiC MiniComposites

A. Almansour*[1]; E. Maillet[1]; G. N. Morscher[1]; 1. The University of Akron, USA

Ceramic Matrix Composites (CMCs) are viable and attractive candidates for use in a spectrum of temperature-critical applications such as aerospace and nuclear. Electrical Resistivity has been shown to be very sensitive to damage in CMCs, and although, it is highly dependent on temperature, this temperature dependence is still not well understood. Therefore, this work aims on establishing the influence of temperature on the electrical resistance using three different mini-composites systems, i.e., Hi Nicalon, Hi Nicalon Type S and Tyranno ZMI reinforced minicomposites with BN interphases and different fiber volume fractions. The thermal cycles were achieved by heating specimens to 1200C and cooling them down to room temperature: with or without applied stress on fibers. The effects of different constituents (e.g. interphase type, fiber volume fraction) on the temperature dependence of electrical resistance has been studied as well.

(ICACC-S1-P010-2015) Mechanical Strength and Thermal Conductivity of Reaction-bonded Silicon Carbides with a Variety of Casing Processes

S. Kim*[1]; Y. OH[1]; S. LEE[1]; Y. HAN[1]; H. SHIN[2]; Y. KIM[2]; 1. Korea Institute of Ceramic Engineering and Technology, Korea (the Republic of); 2. Inocera Inc., Korea (the Republic of)

Reaction-bonded silicon carbide (RBSC) represents a family of composite ceramics processed by infiltrating with molten silicon into a skeleton of SiC particles and carbon, in order to fabricate a fully dense body. RBSC has been commercially used and widely studied for many years, due to its advantages such as relatively low temperature for fabrication and easier to form components with near-net shape and high density, compared with other sintering method. In this study, RBSC is fabricated with a forming process of centrifugal casting. Microstructure, mechanical strength, and thermal conductivity are examined with the reaction-sintered samples and compared with a commercial RBSC formed by slip casting. The relation between microstructures and physical properties are also discussed.

(ICACC-S1-P011-2015) The influence of particle size and sintering temperature on sinterability of SiC powders prepared from solar cell wafer sludge

Y. Kim*[1]; H. Shin[1]; B. Yoon[1]; 1. Inocera inc., Korea (the Republic of)

This study is designed to investigate effects of particle size and sintering temperature on the sinterability of SiC powders prepared from solar cell wafer sludge. The sludge were consist 10um SiC and Si powders and were heat treated with carbon black in vacuum in order to transform Si to SiC. Powders with different particle size were prepared by ball milling times. Granules for sintering experiments were spray-dried with sintering aids of B4C and carbon resin. Granules are pressed with uniaxially pressed at 50MPa to make formed bodies, then they are pressed by CIP at 200MPa. The formed bodies were sintered at near 2100C for 1hr in Ar purging atmosphere. Particle size distribution, flexural strength, hardness and toughness were measured and the microstructures of sintered specimen were observed using SEM.

(ICACC-S1-P012-2015) Diffusion bonded oxide ceramics via mixed hydride nano powders

N. Hosseinabadi*[1]; H. Dehghanian[2]; 1. I. Azad University, Shiraz branch, Iran (the Islamic Republic of); 2. Shiraz University, Iran (the Islamic Republic of)

Mixed hydride/alanate nano powders in Al - Sr - Mg system were used as the interlayer for low temperature diffusion bonding of dense alumina parts. Decomposition of hydride nanopowders at bonding temperatures in-situ formed metals and alloys nano particles with oxide free surfaces and high sinter-ability in the interlayer. Nano powders sintering behavior in the interlayer and formation of compounds in the reaction layer during diffusion bonding were studied. Mixture of 50-50 molar ratio of AlH3 and Mg(AlH4)2 and SrAl2O4, as the interlayer improved bond strength of the joints. Diffusion bonding products were formed in MgO-Al2O3 and SrO-Al2O3 spinel systems with different stoichiometries. Bond strength improved up to 202 MPa by induction hot pressing alumina parts at low bonding temperature of 400 oC under pressure of 20MPa during 30 min bonding period.

(ICACC-S1-P013-2015) Mechanical properties of sealants and cells

J. Wei*[1]; G. Pećanac[1]; J. Malzbender[1]; 1. Forschungszentrum Jülich GmbH, Germany

The reliable long-term operation of solid oxide fuel cell stacks depends critically on the robustness of sealants and cells. The current work focuses on the room and elevated temperature properties of these materials, in particular fracture strength, fracture toughness and creep properties. Available mechanical testing methodologies are improved and new tests are developed. Different mechanical testing methods are compared by means of advantages and disadvantages and assessability of mechanical parameters. The fracture and elevated temperature deformation results are supported by advanced microstructural characterizations along with fractography to gain insight into the relationship of properties and microstructure and failure origins. To assess the influence of non-linear effects onto the experimental results, the work is supported by finite element structural simulations of the deformation behaviour.

(ICACC-S1-P014-2015) Preparation and mechanical properties of YSZ/MnZn ferrite composites

Z. Qu*[1]; Q. Wang[1]; L. Zhang[1]; C. Han[1]; 1. Beijing University of Technology, China

Magnetic materials have been widely used in the field of electromagnetic compatibility. With the development of electronic devices to be more compact, integrated and multi-functional, it is a feasible way to functionalize the structural ceramic components with electromagnetic shielding or interference suppression capabilities through adding magnetic particles into ceramic matrix, which can improve the electromagnetic compatibility of the device without any additional accessories. Meanwhile, the good mechanical properties of ceramics should be retained as much as possible for structural applications. In this paper, a series of the composites with different volume ratio of yttria stabilized zirconia 3mol%YSZ and MnZn ferrite Mn0.5Zn0.5Fe2O4 were prepared by solid-state sintering. The density, phases, microstructure and mechanical properties of the composites were characterized, and the effect of the composition and particle size of the starting materials on the microstructure and mechanical properties was investigated. The results show that the mechanical properties of the composites certainly decrease with the increasing content of MnZn ferrite. However, the decrease shows a slighter slope at the beginning of the curve. This suggests that the composites can retain the good mechanical properties in certain composition range for the addition of the magnetic particles.

(ICACC-S1-P015-2015) Experimental Demonstration for Continuum Damage Mechanics Model of SiC/SiC Composites Using Digital Image Correlation Technique under UV light

R. Maeno[1]; T. Ogasawara[2]; S. Ogihara*[1]; 1. Tokyo University of Science, Japan; 2. Japan Aerospace Exploration Agency, Japan

SiC fiber reinforced SiC matrix composites (SiC/SiC) exhibits nonlinear stress-strain behavior due to matrix crack propagations. The objective of this study is to measure the full-field strain (displacement) of SiC/SiC composite specimens using digital image correlation (DIC) technique. To apply the DIC method to the full-field strain measurement at elevated temperature (> 1000 C), the effect of black body radiation has to be eliminated. This study examined the strain measurement using DIC under UV light. On-axis tension, off-axis tension and Iosipescu shear tests were carried out at room temperature. The full-field strain measurement was successfully conducted using DIC method under UV. The average strain measured using DIC agreed with those measured using electrical resistance strain gauges below the proportional limit stress (SPL), however some discrepancies were observed above SPL. This is due to the local damages. Continuum damage mechanics (CDM) model was adopted to representing nonlinear stress-strain behavior of the SiC/SiC composite, and the effect of multi-axial stress (shear / tension coupling) was taken into consideration. The numerical result showed good agreement with the experimental results of on-axis tension, off-axis tension and Iosipescu shear tests.

(ICACC-S1-P016-2015) Thermal stability of steel/titanium carbide composites

A. Miriyev*[1]; N. Frage[1]; 1. Ben-Gurion University of the Negev, Israel

Metal matrix composites reinforced with hard particles of titanium carbide are widely used in many engineering applications owing their high level of wear resistance. High temperature applications, such as tooling for metals treatment, require high thermal stability of the tooling material. The reported data on thermal stability of the steel/titanium carbide composite materials is limited. In the present work, the thermal stability of the carbon steel/titanium carbide composite with various steel to TiC ratios in the 800-1000°C temperature range was evaluated using thermodynamic analysis of the Fe-Ti-C system. The analysis enables to predict the altering composition of titanium carbide and steel as a function of temperature and initial volume ratio of steel and reinforced particles within the composite. It was established that titanium carbide phase is extremely stable in a steel matrix in the 800-1000°C temperature range.

(ICACC-S1-P017-2015) Novel Application of the Fractal Method in the Ceramic Composites Surface Flaws Characterization

A. Terzić[1]; Z. Radojević[1]; M. Arsenović[1]; V. Mitić*[2]; S. Pašalić[3]; 1. Institute for Material Testing, Serbia; 2. Institute of Technical Sciences, Serbian Academy of Science and Art, Serbia; 3. Ministry of Education, Science and Technological Development, Serbia

Fractal dimensions theory employed in surface analysis as a means of structural defects origin explanation was studied. This paper proposes new method of roughness peaks curvature radii calculation and its application to glazed ceramic composites surface tribological analysis. Fractal dimensions method is introduced via asperity radius calculation by fractal concept of surfaces curvature radii. Dependence of calculated radii on fractal dimension of studied curves was established and notion of peak is mathematically formulated. The method efficiency was tested by fractal curves simulations described by Brownian motions. Microstructural investigations were conducted using SEM equipped with EDS. Correlation between defects microstructure and ceramic composite properties, based on fractal geometry and contact surface probability, has been developed. Using fractals and grains contact surface statistics a reconstruction of microstructure configurations has been successfully performed. Obtained results indicated that fractal analysis and statistics model for contact surfaces of different shapes were important for prognosis of ceramics properties and identifying defects origin.The novel statistical approach to investigation of ceramic defects was successfully conducted, as a result introducing fractal identification as means of evaluating performance of ceramic composites.

(ICACC-S1-P018-2015) FTIR spectroscopy of sodium silicate glasses containing iron oxide

B. Mehdikhani*[1]; 1. 1Standard Research Institute, Iran (the Islamic Republic of)

In this study, the effect of iron oxide on crystallization of sodium disilicate glasses has been investigated by fourier transform infrared spectroscopy (FTIR) in 4000-400 cm-1, X-ray diffraction analysis (XRD), and scanning electron microscopy (SEM). In these glasses, iron has two forms of Fe2+ and Fe3+ ions. Presence of high iron content in mixture and formation of two different valence results tendency toward phase separation and crystallization. More increscent of iron oxide and annealing of samples in higher temperatures cause nucleation and crystallization took place in glasses. In this study, changing of infrared transmitted spectrum in samples led to appearance of a new sharp peak in 550-600cm-1 region. Crystal phase has been investigated by X-ray scattering pattern and microstructure morphology by SEM microscopy.

(ICACC-S1-P019-2015) Ceramic nano pigment prepared by mechanochemical; Fe–Cr–Ti-(Al2O3)

B. Mehdikhani*[1]; 1. Standard Research Institute, Iran (the Islamic Republic of)

The present work relates to a process for the production of nano particles pigment and relates particularly to the production of nano composite powders consisting of individual particles with sizes in the range of 10 nm to 100 nm. This process involves the mechanically activated chemical reduction of reducible metal compounds during milling, to refine and manufacture nano composite powder. Nano particle pigment for ceramic glazes was obtained by mechano-chemical insertion of Fe–Cr–Ti in an α-Al2O3 host matrix. Iron, chromium and titanium oxides were reduced by milling with metallic aluminium with subsequent formation of additional Al2O3 by oxidation of aluminium. XRD and BET has been used for investigation of phases and particle size of powder.

(ICACC-S1-P020-2015) Mechanical properties of tantalum carbide-boride

B. Mehdikhani*[1]; S. Bakhshi[1]; G. Borhani[1]; 1. Malek-e-ashtar University of Technology, Iran (the Islamic Republic of)

Tantalum carbides/boride composite were synthesized by spark plasma sintering (SPS), using the powder mixtures of TaC and B4C as the starting materials. In this work densification, phase formation, microstructures, and mechanical properties of the materials were investigated.The densification of tantalum carbide (TaC) was enhanced by adding 2.0 wt% B4C, reaching 97% relative density by spark plasma sintering at 1900 degree centigrade using a 30MPa applied pressure. X-ray diffraction analysis identified two phases, TaC and tantalum diboride (TaB2), with no peak shifts, indicating a solid solubility was not significant at these temperatures. Densification of TaC was enhanced while the grain growth was suppressed by adding 2 wt% B4C,which allowed mechanical properties to be analyzed. A relative density of >97% was achieved for TaCwith B4C additions by SPS at 1900 degree centigrade. By comparison, additive-free TaC could be sintered to only 76% relative density at 1900 degree centigrade.The results are compared to hot pressing conducted under similar settings.

(ICACC-S1-P021-2015) Unlocking the Mystery Behind the Oldest Fort in the United States Using Compression and Impact Experiments

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

The Castillo de San Marcos Fort in St. Augustine, FL was built over 330 years ago and has endured numerous wars between the Spanish and the British. During these wars, cannonballs were fired at the fort walls, but interestingly, the cannonballs became embedded in the coquina— the walls did not shatter, nor did large cracks form. The fort was constructed from a native rock called coquina, found only on the east coast of Florida and the west coast of Australia. Coquina is a highly porous sedimentary rock, consisting of crushed shells, fragmented fossils and coral, limestone, sand, minerals and clay. Despite the fort's long existence, there are no scientific studies illustrating its ability to withstand cannonball impacts. This research focused on testing specimens of coquina and two other similar materials (sandstone and a commercial foam) in uniaxial compression and high velocity impact, which mimics a cannonball impact. The compression experiments revealed that coquina had 2-3 times the specific energy compared to the other materials. In the impact experiments, the ball became embedded in the coquina, whereas the sandstone shattered into several fragments. The research revealed that the microstructure of coquina allows impact to be absorbed by progressive crushing and hence possesses a high energy absorption capability compared to the other two materials.

(ICACC-S1-P022-2015) Ti-Based Ceramic Composite Processing using Hybrid Centrifugal Thermite Assisted Technique

R. Mahmoodian*[1]; M. Bin Abd Shukor[1]; M. Hassan[1]; 1. University of Malaya, Malaysia

A fundamental study was conducted to investigate Ti-C system when it is exposed to a hybrid reaction between thermite and elemental powders of titanium and carbon under centrifugal acceleration. A pellet of Ti+C was fixed in an offset position relative to the surrounding steel tube in the reaction chamber, which was filled with thermite mixture. The aluminothermic mixture was ignited; it generated a massive amount of heat and was able to initiate a secondary reaction. The secondary Ti+C reaction was affected by the high temperature. Several byproducts were formed, including intermetallics contents. A microstructure and phase analysis of the synthesized product are investigated in this paper, revealing 27% formation of a new product with 796 MPa hardness. The study explains how the Ti+C behaved at the time of short and sudden heating environment.

(ICACC-S4-P023-2015) Measuring the Equibiaxial Flexure Strength of Soda-Lime Silicate Glass: Further Experimental Results

S. Kilczewski*[1]; P. Patel[1]; T. Talladay[2]; J. Swab[1]; L. Gilde[1]; 1. Army Research Laboratory, USA; 2. TARDEC, USA

The engineering applications associated with glass are to be considered ubiquitous. Strength is one of the important properties of interest for these applications. However, it has been well documented that determining the actual strength of glass is considered very challenging. Compositional variation, manufacturing techniques, surface quality, and test methods all contribute to influence the mechanical strenght of glass. ASTM C1499 addresses a standardized testing method for the equibiaxial flexure strength of advanced ceramics at ambient temperatures, but this standard allows some latitude when addressing the testing of glass specimens. Previous studies have shown the variations in specimen dimension coupled with load/support ring diameters leads to the variation in the reprted strength values. A study was initiated to further understand the role of plate size on the strength of glass plates using a biaxial flexural test method. At a constant plate thickness, the plate area was increased 125%. To gain a better understanding of whether these variants in the actual glass specimen size have an effect, experiments will be conducted to determine if a strength/size scale effect can be realized for glass. This presentation will describe the material, methods, and the results of the mechanical testing for Soda-Lime-Silicate glasses.

(ICACC-S4-P024-2015) Preparation, characterization and development of TiB2 hard ceramic materials

A. M. Celik*[1]; 1. Rutgers University, USA

Titanium diboride (TiB2) is one of the hardest materials known. It has a high melting temperature and high hardness, and also low theoretical density. Those properties make TiB2 an important hard material which can be used as ballistic armor, crucibles, coating for cutting tools, and wear resistance parts. TiB2 was produced by rapid carbothermic reduction process (RCR). The reaction for TiB2: 2TiO2 (s) + B4C (s) + 3C (s) $\rightarrow$ 2TiB2 (s) + 4CO (g). Mixture of raw powders was reacted at various temperatures and TiB2 was produced. Chemical composition and phase determination were done on final product, and it was determined that phase pure TiB2 was synthesized. Micron size particles were produced and SPS sintering on powder was performed.

(ICACC-S4-P025-2015) Incorporation of silicon in boron carbide for the mitigation of high pressure amorphization

A. M. Etzold*[1]; R. Haber[1]; W. Rafaniello[1]; T. Munhollon[1]; Y. Gao[1]; 1. Rutgers University, USA

Boron carbide is known to suffer from a loss in compressive strength in high pressure events due to amorphization. However DFT simulations indicate that the introduction of silicon into the boron carbide lattice could mitigate this amorphization. Using rapid carbothermal reduction (RCR), within a temperature range of 1800-2000°C, the production of boron carbide powders lacking free carbon is possible. Using this method, incorporating silicon into the boron carbide lattice without the immediate production of silicon carbide becomes feasible. This incorporation is done via the addition of silicon from multiple sources, ranging from fumed silica to borosilicate xerogels, into the boron carbide precursor. 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. This study will show that not only is the incorporation of silicon possible but, in agreement with the computational modeling, the addition will work to improve the performance of the boron carbide.

(ICACC-S4-P026-2015) The application of computational thermodynamics in the sintering of B4C

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

Boron carbide has a lot of critical usages because of its interesting properties such as high hardness, low density and good chemical stability. It is, however, it is difficult to sinter. The sintering mechanism in pressureless sintering, hot press, SPS are not clear. In this research, we plan to investigate the sintering mechanism based on the prediction from computational thermodynamics. We will try to explore the effect of sintering aid and the impurities in the raw powder to the sintering behavior of B4C.

(ICACC-S4-P027-2015) Reaction Bonded SiC/Diamond Composites: Properties and Impact Behavior in High Strain Rate Applications

S. Salamone*[1]; M. Aghajanian[1]; S. Horner[2]; J. Zheng[2]; 1. M Cubed Technology, Inc., USA; 2. US Army, USA

Composites of reaction bonded silicon carbide (RBSC) with diamond particles have a huge potential as an armor material because of the high hardness of both the SiC and diamond phases. The SiC matrix particles were varied from an average size of 12μm to 50μm and the diamond content, incorporating a 22μm particle, was increased from 0 to approximately 20vol%. The current study relates SiC grain size and diamond particle content to microstructure, properties and impact behavior of the SiC/Diamond composites. It is shown that increasing the diamond content, for all SiC grain sizes, improves impact behavior.

(ICACC-S4-P028-2015) Synthesis and Processing of Nanostructured BN and BN/Ti Composites

R. S. Horvath*[1]; B. Kear[1]; S. Tse[1]; O. Voronov[1]; J. Al Sharab[1]; 1. Rutgers University, USA

Cubic boron nitride (cBN) is widely used in machine tools, drill bits, and grinding wheels. Recently, interest has developed in its potential for lightweight armor applications. cBN is a candidate for next generation personnel and vehicular armor. To ensure superior ballistic-impact performance for superhard cBN, its fracture toughness must be improved. We have targeted for development a new class of nanostructured cBN/Ti composites, in which a high fraction of superhard cBN particles are cemented together with a tough Ti binder. Under high pressure/high temperature (HPHT) processing conditions, Ti can bond directly to cBN particles to form Ti-bonded cBN or react with cBN particles to form Ti-bonded TiB2/TiN. Similar reactions between mixed Ti and hBN powders under HPHT conditions have also been observed as a low cost alternative. Progress has been made in: (1) HPHT synthesis of cBN powders using Mg as activator; (2) HPHT consolidation of cBN powders to form superhard cBN; (3) reactive-HPHT consolidation of mixed cBN/Ti powder to produce Ti-bonded cBN; (4) reactive-HPHT consolidation of mixed hBN/Ti powder to produce Ti-bonded TiB2/TiN; and (5) reactive-HPHT processing of multi-layered structures, comprising alternating layers of superhard Ti-bonded cBN, hard

TiB2/TiN, and tough Ti. As noted above, such a layered composite structure should provide superior ballistic performance.

(ICACC-S4-P029-2015) Nano-crystalline boron carbide powder synthesized via carbothermal reduction reaction

S. M. El-Sheikh*[1]; Y. M. Ahmed[1]; E. M. Ewais[1]; A. A. Abd-Allah[2]; S. A. Sayed[2]; 1. Central Metallurgical Research and Development Institute, CMRDI, Egypt; 2. Faculty of Science,Helwan University, Egypt

In this study, we aimed to develop a cost effective and low-temperature manufacturing process to synthesize boron carbide from cheap raw materials. Nanocrystalline boron carbide was successfully synthesized via hydrothermal method followed by the carbothermal reduction reaction (CRR). Boron carbide (B4C) powder has been prepared by using an aqueous solution of boric acid and lasts, which transferred to outcalve and heated at 280oC for 24 h. Then the produced materials were calcined and followed by CRR under argon atmosphere. Several parameters such as molar ratios of boron to carbon, time and temperatures of carbothermal reduction reaction were also investigated. The produced materials were examined with the help of XRD, XPS, Raman, FT-IR, FE-SEM,TEM, PL and thermal analysis. XRD data of calcined materials show a precursor powder consisting of boron oxide and carbon. The results of XRD and FT-IR studies after carbothermal reduction reaction at 1500oC for 3h indicate that the product consists of pure nano-crystalline B4C. Raman spectra revealed that B4C was formed according to Raman peaks at 270, 320, 481, 531, 728, 830, 1,000 and 1,088cm-1. FE-SEM images show that a hexagonal nanocrystalline boron carbide is formed with a particle size around 60 nm and it is fused together to form a tubes and sword shapes depending on the time and temperature of carbothermal reduction reaction.

(ICACC-S4-P030-2015) Synthesis of Complex Microstructures for Mesoscale Finite-Element Analysis Using the Potts Model

M. C. Golt*[1]; 1. TKC Global, USA

The Monte Carlo-based Potts model is often used to synthesize liquid phase sintered (LPS) microstructures due to its ability to accurately simulate Ostwald ripening. The model has been applied to the generation of 3D microstructures consisting of two phases (solid and liquid). However, some ceramic microstructures such as aluminum-doped silicon carbide (SiC) are known to contain a complex core/rim structure (intrinsic core, doped rim, and grain boundary phase) which formed through solution and reprecipitation. In an effort to create finite-element models of SiC microstructures, this work details a multi-step approach based on the Potts model to simulate LPS- intrinsic SiC (cores) surrounded by a liquid phase, followed by reprecipitation of the rims through simulated epitaxial growth onto the SiC nucleation sites. The resulting microstructures resemble a more accurate representation of the core/rim SiC, consisting of multiple finite-element analysis domains and boundaries to which model parameters can be applied.

(ICACC-S4-P031-2015) Liquid phase sintering of silicon carbide ceramics with the addition of alumina and yttria

H. Lee*[1]; G. Kim[1]; K. Oh[1]; B. Kim[2]; T. Chung[1]; 1. Andong National University, Korea (the Republic of); 2. Wonik QnC, Korea (the Republic of)

SiC ceramics has high hardness, corrosion resistance, and wear resistance, so it can be an ideal armor material. But, the strong covalent boding nature of SiC requires high sintering temperatures and additives to be properly densified. In this study, the liquid phase of sintering of SiC is revisited to fabricate large SiC for industrial and armor application. Al2O3 and Y2O3 and other sintering additives are used to sinter SiC under the ambient pressure. The optimum sintering condition is identified by changing sintering variables, such as green composition, temperature, etc., and the mechanical properties are characterized. Further, two-step sintering (sintering at the higher temperature and then quenched to the lower temperature) is applied and the results show that it can improve mechanical properties of SiC significantly.

(ICACC-S4-P032-2015) Developing damage-resistant ceramics by mimicking natural materials

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

Even though ceramics exhibit interesting thermo-mechanical properties, because of their inherent brittleness, catastrophic failure is unavoidable. The main limitation of ceramic components is the lack of plasticity which often results in unpredictable failure during service. Damage-resistant ceramic components are thus in great demand for use in a range of applications including armor. Although naturally occurring materials are promising with improved toughness, mimicking the structure is extremely difficult and combining polymeric materials with ceramics sometime limits the use of the components. In this research, we employed a well-established ceramic processing route, tape casting, to fabricate a bio-inspired, bulk ceramic laminate. Upon dynamic impact, the energy was dissipated through fracture in parallel orientation (0°) or transmitted in perpendicular (90°) orientation. The dynamic impact of the layered ceramics with respect to two different orientations and the microstructure will be discussed and supplemented with high-speed camera images.

(ICACC-S4-P033-2015) Predicting the Light Transmittance of Multi-layer Transparent Armor

B. S. Aldinger*[1]; 1. Ibis Tek, LLC, USA

Unlike standard architectural or automotive glazing, thick multi-layered transparent armor (TA) absorbs a large fraction of impinging light, perceptibly dimming the view. Stringent light transmittance requirements therefore play an important role in TA material selection, but constructing prototypes to test the optical properties of every proposed TA formula can be cost-prohibitive—especially with experimental materials. To predict the light transmittance of novel TA designs, the spectra of common TA materials were analyzed, including clear glass, low-iron glass, borosilicate glass, PVB interlayer, urethane interlayer, and polycarbonate. After obtaining the materials' transmittance and reflectance properties, the optical constants were incorporated into a linear model to predict the light transmittance of arbitrary TA formulae. Measured transmittances of physical TA laminates were typically within ±2% of the predicted values in both the visible and NVG-relevant spectral regions. Assumptions of the model and major sources of error, such as strongly-colored materials, will be addressed.

(ICACC-S4-P034-2015) Limits of accelerating numerical analysis study of the failure mechanism of ceramics during low velocity impact used in protective systems

C. G. Fountzoulas*[1]; R. E. Brennan[1]; 1. U.S. Army Research Laboratory, USA

The rapid advancement of computing power and recent advances in numerical techniques and material models have resulted in accurate simulation of ballistic impacts into multi-layer armor configurations. For both transparent and opaque protective systems, low velocity impact damage can compromise structural integrity. Modeling and simulation of material impact by various threat types has proven to be a significant analysis tool in the identification of damage mechanisms and the failure process. Drop-tower experimentation is used to assess the damage of low velocity impact of ceramics. However, numerical simulations at impact velocities between 2 and 5 m/s take long to produce results. Our effort examines various ways of accelerating the numerical study, by (a) increasing the impact velocity of the current impactor; and (b) by keeping the impact kinetic energy constant while decreasing the impactor mass. The failure mechanisms of laminate targets were studied by numerical analysis and the results were compared to available experimental data from various nondestructive techniques. Successful output of this modeling effort will provide useful information of damage propagation through targets used in protective systems by establishing acceptance criteria for any future material prior to its fielding.

(ICACC-S4-P035-2015) Identification of Cleavage Planes of Single-Crystal Silicon Carbide Using Single and Sequential Knoop Indentations

C. Kunka*[1]; A. Trachet[2]; G. Subhash[1]; 1. University of Florida, USA; 2. University of Florida, USA

Due to its transparency, high hardness, and low density, single-crystal silicon carbide (SiC) is a candidate material for applications involving impact, such as armor and bullet-proof windows. Therefore, the fracture anisotropy must be investigated to optimize crystallographic orientation in intended applications. The experimental analysis provided here not only identifies, compares, and verifies the preferred cleavage planes in 4H-SiC and 6H-SiC but is also the first investigation to reveal how single-crystal silicon carbide performs under sequential indentation. These results have fundamental value in modeling the fracture behavior of single-crystal silicon carbide.

(ICACC-S4-P036-2015) Evaluation of Flaws in Composite Materials Using a Microwave Interference Scanning System

W. H. Green*[1]; J. M. Gardner[1]; 1. U.S. Army Research Laboratory, USA

Microwave frequency scanning is a relatively new NDE method that has undergone significant basic development and technical advancement over recent years. It has significant advantages of ease of use, one sided inspection, compactness, modularity, portability, applicability in varied environments, non-ionizing radiation, and lack of need of transferring medium between probe and specimen. A series of microwave scans using a probe with a 24.6 GHz emitter were performed on a polymer composite panel with engineered flaws both before and after being bonded to an aluminum plate. Engineered flaws included simulated delaminations of different sizes in the top, middle, and bottom of the composite panel, as well as bond line delaminations between the panel and plate. Microwave scans of the panel pre- and post bonding of the aluminum back plate will be shown. The quality and characteristics of the scans will be discussed, including the detectable feature size in the scan data.

(ICACC-S4-P037-2015) Investigation of the Kinetic Energy Characterization of Advanced Ceramics

T. L. Jones*[1]; 1. U.S. Army Research Laboratory, USA

The US Army Research Laboratory conducted an initial study to characterize the material properties and armor performance of low-density ceramic composite tiles manufactured by the Ukrainian National Academy of Science, under Army International Technology Center contract # NW911NF-11-1-0078. These ceramic formulations were compared to standard armor grade boron carbide and silicon carbide tiles versus the 12.7mm APM2 projectile.

(ICACC-S4-P038-2015) Operator Training and Performance Measurement for Nondestructive Testing of Ceramic Armor

K. Schmidt*[1]; J. R. Little[1]; W. H. Green[2]; L. P. Franks[3]; W. A. Ellingson[4]; 1. Evisive, Inc., USA; 2. US Army Research Laboratory, USA; 3. US Army Armored Brigade Combat Team, USA; 4. ERC Company, USA

Operator training and development of performance metrics are simultaneously implemented by a novel program for microwave nondestructive testing (NDT) of composite ceramic armor. A Portable Automated Microwave Scanning System (PAMSS) and accompanying Hand-Held Tool (HHT) were developed for efficient condition assessment of composite ceramic armor, in-situ on vehicles. Operator training for the simpler, HHT will be based on a self-study course available on the tool's operator interface computer. The course includes a library of examination samples, created using the more operator-controllable PAMSS, and validated by digital x-ray NDT. Operators will be able to study examples from the library on their own, and take a performance test using 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 microwave interference scanning technique can image the volume of most 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 who provided test panels and Evisive, Inc. internal development.

(ICACC-S4-P039-2015) Fracture Cone Formation in Brittle Materials due To Normal and Oblique Impact

B. Aydelotte*[1]; B. E. Schuster[1]; 1. U.S. Army Research Laboratory, USA

Ceramics undergo a complex failure process when subjected to impact by a projectile. Projectile impacts on thick ceramic targets produce varying levels of comminution, cone cracking, and radial cracking. Sphere impacts result in limited penetration and comminution relative to cylindrical projectiles, yet significant cone cracking is produced. This makes sphere impact a good validation problem to study the ability of hydrocodes to predict the formation and extent of radial and cone fractures in ceramic materials. Experimental results from normal and oblique sphere impacts on ceramic targets are reported. Similarities and differences in the growth and development of cone cracks from normal and oblique impacts on the different materials are discussed. The experimental results are compared with hydrocode predictions and discussed.

(ICACC-S6-P040-2015) $Na_2MnP_2O_7$ glass-ceramics cathode for sodium-ion batteries

M. Tanabe*[1]; T. Togashi[1]; K. Shinozaki[1]; T. Honma[1]; T. Komatsu[1]; 1. Nagaoka University of Technology, Japan

$Na_2MnP_2O_7$ pyrophosphate was prepared by glass-ceramics method. We examined crystallization behavior of precursor glass and its electrochemical properties. We found that $Na_2MnP_2O_7$ glass-ceramics can be used as cathode active materials for sodium-ion batteries with good cyclic performance as well as high columbic efficiency. Charge-discharge tests of the $Na_2MnP_2O_7$ glass-ceramics cathode exhibited efficient capacity of 95 mAh/g at 0.1C rate which is almost 100 % of theoretical capacity (97.5 mAh/g) and quite high stability with high redox potential of 3.6 V. $Na_2MnP_2O_7$ glass-ceramics has much possibility of being a new sodium-ion battery cathode material.

(ICACC-S6-P041-2015) A New Phenomenon in Sodium Batteries: Voltage Step Due to Solvent Interaction

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

A curious voltage step was observed during discharge (sodium insertion) in the galvanostatic cycling of the two-phase cathode material, $Na_3V_2(PO_4)_3$, when cycled against sodium metal with 1M $NaClO_4$ in EC:PC (1:1 v/v) acting as the electrolyte. Interestingly, if 1M $NaClO_4$ in PC was used as the electrolyte, this voltage step was not witnessed. Such observations were also reproduced in another two-phase electrode, $NaTi_2(PO_4)_3$(NTP). In order to investigate this phenomenon further, a three-electrode cell was constructed with sodium metal as the counter electrode (CE) and reference electrode (RE) and NTP as the working electrode (WE). Three-electrode galvanostatic cycling in EC:PC revealed the voltage step originating due to an increased polarization of the Na CE during discharge, with the WE's voltage profile being devoid of any voltage step. Electrochemical Impedance Spectroscopy (EIS) suggested a drastic increase in the resistance of the Na CE caused by this voltage step. Such observations were not made if the solvent was just PC. Hence, the sodium CE is covered with a passivation layer which can influence the galvanostatic cycling of a sodium battery, especially in EC:PC solutions. These observations are important since erroneous conclusions can be made about the sodium storage of the WE based on appearances of such voltage steps. More details about this phenomenon will be presented at the conference.

(ICACC-S6-P042-2015) Synthesis and electrochemical performance of nanostructured $NaVPO_4F$ for sodium storage

M. Law[1]; P. Balaya*[1]; 1. National University of Singapore, Singapore

Sodium-ion battery is suggested to replace lithium-ion battery for large-scale applications due to the existing challenges regarding safety, lifespan, and cost of the latter technology. Foreseeing issues associated with lithium-ion battery, we present herewith a high performance cathode material for sodium-ion battery. Nanostructured pure $NaVPO_4F$ was synthesised by a solution-based soft template approach. FESEM images recorded on the sample show that the particles are of spherical morphology, with size centred around 200 nm. This material tested against Na metal is capable of delivering an initial discharge capacity of 133 mAh g^{-1} at 0.1 C. At high rates of 10 and 20 C, it displays high discharge capacities of 86 and 77 mAh g^{-1}, respectively. The material exhibits good long term cyclabilty at high rates. Even after 10,000 cycles at 10 and 20 C, the $NaVPO_4F$ is able to retain 81 and 77 % of respective initial discharge capacities. We believe these findings are helpful for development of sodium-ion battery for grid storage applications.

(ICACC-S6-P043-2015) Synthesis and properties of LiMn1-x(Ni, Co)xBO3 as an cathode material for Li-ion batteries

H. Lee*[1]; J. Park[1]; T. Chung[1]; 1. Andong National University, Korea (the Republic of)

As a potential cathode material for Li-ion batteries, LiMnBO3 is expected to have large capacity and better safety. Unfortunately, the promise of LiMnBO3 has never been realized due to its intrinsic low electronic conductivity and structural instability. In this study, the cation mixing of Mn with Ni or Co is investigated to the effect of doped cations and resulting electrochemical behavior. The cation mixing with Co leads no structural change from LiMnBO3 up to Mn:Co = 0.5:0.5, however, the doping of Ni into LiMnBO3 more than Mn:Co = 0.7:0.3 results in the phase change. The charge-discharge behavior of LiMn1-x(Ni, Co)xBO3 also changes correspondingly to the phase change.

(ICACC-S9-P044-2015) Quasistatic and high-strain rate response of lightweight ceramics fabricated from hollow glass microspheres

D. Ghosh*[1]; G. Ravichandran[2]; R. D. Conner[3]; 1. Old Dominion University, USA; 2. California Institute of Technology, USA; 3. California State University, USA

Use of hollow ceramic spheres dispersed in a metal or polymer matrix has been found to be an effective route of producing low-density porous materials with high specific strengths and energy absorption capabilities. Very little attention, however, has been given on porous ceramics made directly from hollow ceramic microspheres and their mechanical properties, in particular high-strain rate behavior. An in-depth understanding of the strain rate sensitivity of the compressive behavior of porous structures made out of hollow glass spheres is essential for using such structures for energy absorption in impact loading applications. The current work thus investigates the fabrication of lightweight (highly porous) ceramics from commercially available hollow glass microspheres and their compressive mechanical properties under both quasistatic and high-strain rate loading conditions. The porous ceramics developed from the hollow glass microspheres possesses sufficiently high mechanical strength and has high specific energy absorption ability, which make them suitable for kinetic energy absorption applications.

(ICACC-S9-P045-2015) Kaolinite foams stabilized by strontium aluminate for high temperature application

E. Bartonickova*[1]; P. Ptacek[1]; R. Novotny[1]; J. Masilko[1]; M. Bohac[1]; F. Frajkorova[1]; J. Havlica[1]; 1. Brno University of Technology, Czech Republic

The research on the structure, behaviour and properties of kaolinite foams is strongly motivated by industrial demands for high-temperature applications. Sintered kaolinite foams stabilized by strontium aluminate are appropriate candidate for industrial refractory application under the elevated temperatures. The preparation technique is based on foaming of kaolinite slurry and on the stabilization of foam structure by strontium aluminate cement. Wet foam precursors were dried and treated to temperature of 1250°C. High-temperature behaviour and bulk properties of dried and sintered foams were studied by using of high temperature X-Ray diffraction analysis, thermal analysis and scanning electron microscopy. The mechanical properties and thermal conductivity of sintered ceramic foams were determined. The foams of bubble walls thickness within the nanometres scale can be prepared by this method hence the thickness of wall is considerably smaller than the median of particle size of original kaolinite.

(ICACC-S9-P046-2015) Preparation of high temperature stable Si-O-C Aerogels for foundry applications

E. H. Meyer*[1]; L. Ratke[1]; B. Milow[1]; 1. German Aerospace Center, Germany

Silica Aerogels are highly porous nanostructured materials with an open three-dimensional silica network. Their low density, high surface area and low thermal conductivity are interesting for several industrial applications. Casting of metals and alloys simply means the pouring of a liquid metal into a form which most often is made from resin bonded quartz sand. Replacing a fraction of sand by aerogels can improve the casting quality, since the contact of the hot melt leads to a huge gas evolution and induces many casting defects. The huge internal surface of aerogels helps to absorb this decomposition gases and thus improves casting quality. Unfortunately the thermal load on the aerogels can lead to a rapid sintering and shrinkage and then induce other casting defects. We therefore developed a new thermally stable Si-O-C aerogel. These are synthesized using a mixture of MTMS and TEOS as precursor materials in a conventional two-step acid-base sol-gel routine. After ambient drying of the aerogels these are transformed into to Si-O-C aerogels by pyrolysis at 1000 °C. A systematic variation of the TEOS: MTMS ratio allows to vary the Oxygen and Carbon content. The aerogels are characterized by envelope and skeletal density, nitrogen adsorption (BET, BJH) and SEM. Tests in foundries are on the way.

(ICACC-S9-P047-2015) Fabrication and characterization of high strength lightweight ablator using porous carbon materials

Y. Kubota[1]; S. Sasaki[1]; Y. Kogo*[1]; T. Aoki[2]; T. Ogasawara[2]; Y. Ishida[2]; 1. Tokyo University of Science, Japan; 2. Japan Aerospace Exploration Agency (JAXA), Japan

The existing lightweight ablators, such as PICA developed by NASA Ames research center, indicates low density and high thermal resistance. However, the mechanical properties of these are very low compared with fully densified ablators. In this study, a porous carbon material was used as a preform of an ablator instead of carbon fiber so as to develop a high strength lightweight ablator. Mechanical properties of the porous carbon material are ten times higher than those of carbon fiber preform applied for PICA. We expected that an application of the porous carbon as a preform of lightweight ablator would increase the mechanical properties. Before mechanical tests, arc wind tunnel heating tests were conducted in order to evaluate ablation-cooling performance. In these heating tests, the surface temperatures were lower than the radiative equilibrium temperatures. In addition, recession rates of the developed ablator were equivalent to that of the existing lightweight ablators. Accordingly, the developed ablator performed as an ablation material. The mechanical property of the developed ablator was evaluated by compression tests. The results indicate that the compressive strength was quite higher than that of the existing lightweight ablators. For example, the compressive strength of the developed material was 16 times higher than that of PICA in the in-plane direction.

(ICACC-S12-P048-2015) Tantalum carbide for application as ultra high temperature

B. Mehdikhani*[1]; G. Borhani[1]; S. Bakhshi[1]; 1. Malek-e-ashtar University of Technology, Iran (the Islamic Republic of)

Ultra-high temperature ceramics are a unique class of materials Extremely high melting temperatures (>3000°C). Stable in reactive environments UHTCs are needed for use in extreme environments, Reusable atmospheric re-entry vehicles, Hypersonic flight vehicles and Rocket propulsion. Hypersonic flights, re-entry vehicles, and propulsion applications all require new materials that can perform in oxidizing or corrosive atmospheres at temperatures in excess of 2000°C and sometimes over the course of a long working life. Ultra High Temperature Ceramics (UHTCs) are good candidates to fulfill these requirements. In this paper, we present TaC-TaB2-composites developed in the for use in high temperature applications.

(ICACC-S12-P049-2015) High temperature oxyacetylene torch testing and oxidation behavior of graphite, ZrB2, and ZrB2-SiC at temperatures greater than 1500°C under oxygen rich testing environments

M. Packard*[1]; P. K. Neff[1]; M. Miller-Oana[1]; E. L. Corral[1]; 1. University of Arizona, USA

Creating aerodynamic hypersonic flight vehicles requires thermal protective system (TPS) materials that can withstand high temperature and high heat flux while in oxidizing environments. Therefore, oxyacetylene torch testing is one method that has the potential to be used as an extensive screening tool for land based testing that allows replication of the high temperature, high heat flux and oxidizing environment these materials will experience in application. Characterization of the torch flame shows that it is capable of producing heat flux values up to 873 W/cm2, pO2 values of up to 11.85 kPa, and gas velocities from 50-230 m/s. Ultra-high temperature ceramics such as ZrB2 and ZrB2-SiC are tested for oxidation behavior above 1500°C where heat flux and ablation rates are recorded. Results from oxidation studies performed on the oxyacetylene torch show that ZrB2-SiC demonstrates enhanced oxidation resistance over ZrB2. Tests conducted at similar conditions are compared to results of thermogravimetric analysis (TGA). TGA tests conducted at 1600°C and low pO2 are used for comparison.

(ICACC-S12-P050-2015) Reactions between Ti_2AlC, B_4C and Al and Phase Equilibria at 1000 °C in the Quaternary Al-Ti-B-C System

M. T. Agne*[1]; B. Anasori[1]; M. W. Barsoum[1]; 1. Drexel University, USA

As automotive, aerospace and the power industries increasingly look to carbide and boride based aluminum composites for their high specific strengths and increased thermal stability, it is important to characterize equilibrium phase relations at temperatures common for processing Al matrix composites. Two composites were fabricated starting with Al, Ti_2AlC, and B_4C. The Ti_2AlC/B_4C powders were mixed in both 50/50 and 75/25 vol. % ratios and cold pressed into 53 % dense preforms. The preforms were pressureless melt infiltrated in the 900 to 1050 °C temperature range with Al. Ten hour equilibration experiments were also conducted at 1000 °C. X-ray diffraction and scanning electron microscopy were used to characterize the reaction products and equilibrium phases of each composite. Neither Ti_2AlC nor B_4C was found to be an equilibrium phase. A variety of reaction phases – AlB_2, Al_3BC, TiB_2, TiC, $TiAl_3$, Al_4C_3 – could be found from the non-equilibrated samples. The equilibrium phases were found to be Al, TiB_2, Al_3BC, and Al_4C3 for the more B-rich composite and Al, TiB_2, TiC, and Al_4C_3 for the Ti-rich composite. From these results, the 1000 °C quaternary phase diagram adjacent to the Al-TiB_2-Al_4C_3 triangle was developed for the first time. This study is a requisite first step for the development and use of advanced composites in the Al-Ti-B-C system.

(ICACC-S12-P051-2015) Towards joining micro tubular solid oxide fuel cells with the current collector: A solder barrier based approach

A. Stoeck*[1]; S. Mnich[1]; S. Kuehn[2]; 1. eZelleron GmbH, Germany; 2. eZelleron GmbH, Germany

One of the major issues in building stacks from single cell micro tubular SOFCs is to prevent fuel leakage. In the usual arrangement air surrounds the stacked tubes while fuel is flowing internally along the tubes. Thus fuel leakage can only occur at the extremities of the tubes. Hence a good brazing between the tubes and the current collector is a key feature determining the efficiency and operability of a stack. The most commonly used brazing material for this purpose is silver. Using silver for joining cathode and current collector creates a lot of different problems which have to be addressed. In this contribution we present an approach to overcome these problems by creating an electrically conducting solder barrier.

(ICACC-S12-P052-2015) Improvement of the thermal shock resistance performance for Ultra-high temperature ceramics

W. Li*[1]; D. Li[1]; R. Wang[1]; X. Shen[1]; 1. Chongqing University, China

The thermal shock resistance of ceramic materials depends on the mechanical and thermal properties. Component geometry and thermal environmental also affect thermal shock resistance performance. It is the comprehensive performances of their mechanical and thermal properties corresponding to various heating conditions and external constraints. In this paper, a temperature-damage-dependent thermal shock resistance model with the consideration of the effects of thermal environment and external constraints was established. The results show that introducing micro-cracks into ultra-high temperature ceramic material and controlling damage evolution as the nucleation mode through microstructure design method can significantly improve the thermal shock resistance, particularly in the corresponding initial thermal shock temperature dangerous range. The influences of constraints on the thermal shock resistance and critical fracture temperature difference also have been studied and an effective idea to improve thermal shock resistance for ceramic material and structure is found. Furthermore, the results are verified by finite element numerical calculation.

(ICACC-S12-P053-2015) High temperature interaction of metal oxides with molten Gd, Ti, Zr and its alloys

N. Sobczak*[1]; R. Nowak[1]; A. Siewiorek[1]; M. Homa[1]; G. Bruzda[1]; B. Korpala[1]; I. Kaban[2]; N. Mattern[2]; J. Eckert[2]; 1. Foundry Research Institute, Poland; 2. IFW, Germany

There is a strong need in a new generation refractory materials characterized by good chemical stability in contact with highly reactive metallic melts, both for practical purposes (melting, casting) as well as for fundamental research (high-temperature measurements of thermophysical properties by container-assisted techniques). A sessile drop method was applied for investigation of high-temperature interaction between oxide-based ceramics in contact with molten Gd, Ti, Zr and its alloys. In situ monitoring and recording of high-temperature behaviour of metal samples placed on ceramic substrates were performed upon their contact heating in protective atmosphere (Ar) by a high-speed and high-resolution CCD camera. Detailed characterization of structure and chemistry of interfaces formed in high-temperature tests were performed using optical, scanning and transmission electron microscopy. The results are discussed in terms of chemical interactions and high-temperature stability of selected metal oxides affected by aggressive metallic melts.

(ICACC-S12-P054-2015) Fire behaviour of composite materials made of ettringitic binders

M. Michel*[1]; L. Michel[1]; J. Ambroise[1]; E. Ferrier[1]; E. Prud'homme[1]; 1. Université LYON 1, France

The fireproof mineral materials marketed today are either in the form of projecting mortar or in the form of plates. Mortars used

in the manufacture of the plates are based on ordinary Portland cement, calcium aluminate cement or plaster or silicates, with or without light loads. The fire property is obtained through the thickness of the plate, which makes it heavy and difficult to handle. Furthermore, the setting time of these mortars is relatively long and therefore does not allow the application of facing on each side of the plate at the time of its manufacture. Under these conditions to make cosmetic plate and to enhance rigidity of the plate, the reported facings on either side of the plate, after it was manufactured, do not always have fire resistant properties. This paper presents the fire behavior of the facing which, when applied to a mineral or organic foam, give the composite properties of combustibility, flame resistance and fireproofing. Will set more precisely the characteristics of plates 2 mm thick, made with micro-mortar based on ettringitic binder and reinforcing glass fibers.

(ICACC-S12-P055-2015) Contribution of ettringitic binders in the fire resistance of composite materials

M. Michel*[1]; E. Prud'homme[1]; A. Limam[1]; A. Llosa[1]; E. Reyes[2]; 1. Université LYON 1, France; 2. MIHB, France

The fireproof mineral materials marketed today are plate-shaped. Mortars used for the manufacture of these plates are made from ordinary Portland cement or calcium aluminate cement, or plaster or silicates, with or without light loads. The fire property is obtained through the thickness of the plate, which makes it heavy and difficult to handle. This study is in the process of replacing the organic binder by inorganic binder. The interest of ettringitic binder compared with mineral binders conventionally used is based on the speed of setting of ettringitic binders. Indeed, the acceleration of the setting and hardening of ettringitic cement-based binders reduces an important phenomenon in thin layers, the phenomenon of drying which leads to poor hydration. On the other hand, rapid hardening allows the stability and the uniform repartition of air injected into the plate. Hence it becomes possible to obtain thinner plates of lower density (between 0.4 and 0.6), ensuring lightness and fire property. The results presented in this paper deal with the fire properties of plates and castings, established according to standard ISO 834.

(ICACC-S12-P056-2015) Polymer-derived ZrC-SiC Composite Ceramic Powders

X. Wei*[1]; M. Ge[1]; W. Zhang[1]; 1. State Key Laboratory of Mulitphase Complex systems, Institute of Process Engineering, Chinese Academy of Sciences, China

Zirconium carbide is one of the most promising candidates for many applications such as matrix and coating of ceramic matrix composites, thermostrucural ceramics for ultra-high termperature environments. For the latter application, it is suggested that silicon carbide should be introduced to form ZrC-SiC composite ceramics because ZrC-SiC composite ceramic has better oxidation and corrosion resistances than both monolithic ZrC and monolithic SiC at temperature higher than 1800°C. In this study, ultra-fine ZrC-SiC composite ceramic powders were synthesized by pyrolysis of novel hybrid polymeric precursors of polycarbosilane and polycarbozirconiane as sources of silicon carbide and zirconium carbide respectively. Pyrolysis process of the precursor, composition and microstructure of ceramic powders were characterized. It is indicated that ZrC phase initially forms at 1400°C and carbothermal reduction reactions are completely finished at 1500°C for 2h. ZrC-SiC composite ceramic powders on the order of 50-300nm posses a special nano-substructure: discrete ZrC-rich aggregations are surrounded with continuous SiC-rich phase. Characteristic dimension of ZrC-rich aggregations is less than 150nm. This special nano-substructure is thought to be greatly beneficial to oxidation and ablation resistance and makes ZrC-SiC powders a promising candidate for ultra-high temperature thermostructural application.

(ICACC-S12-P057-2015) Superconductivity in the M2AX phases

A. D. Bortolozo*[1]; M. Meireles[2]; C. M. dos Santos[3]; A. S. Machado[3]; 1. School of Applied Science of Unicamp, Brazil; 2. Federal University of Itajuba – campus Itabira, Unifei-Itabira., Brazil; 3. School of Engineering of Lorena - USP, Brazil

The modern superconductivity concept is based upon to 2D anisotropic materials. One of the most studied materials to exhibit 2D superconductivity is the MgB2. It has considerable impact on the superconductivity field due to Tc of 40 K. Another example of superconductivity in layered compounds is the family of the borocarbides. In the scenario, the MAX phases are similar to 2D other compounds. The M2AX compounds have a hexagonal lattice in which the lattice is composed of molecular M2X layers where each X atom has an octahedral coordination (XM6). Each M2X layer is separated from each other by an A atom which obeys the sequence X-M-A-M-X. The lamellar natures of these compounds give them 2D characteristics where the electric and thermal properties are anisotropic. In this work, it will be review about superconductivity in the M2AX phases: Nb2InC, Nb2SnC, Ti2GeC, Ti2InN and Ti2InC. All them were prepared by solid-state reaction and the superconductivity phenomena is strongly dependent of synthesis method. The results show critical temperature (Tc) among 3.1 to 9.5 K. The results about nitride compound of Ti2InN composition show more than twice from critical temperature of the carbide correspondent. This is suggesting that other nitride compound of this family can be exhibit High Superconducting Critical Temperature and it represents a new class of superconductor of high temperature.

(ICACC-S12-P058-2015) Effect of SiC addition on oxidation behavior and mechanical properties of TiB2 and NbB2

I. Akin*[1]; F. Sahin[1]; O. Yucel[1]; G. Goller[1]; 1. Istanbul Technical University, Turkey

Metallic borides (TiB2, NbB2, ZrB2, etc.) are candidate materials in many applications such as cutting tools, wear and high temperature applications, armour and electrodes due to their high melting temperature (>3000°C), high hardness (> 20 GPa) and wear resistance, good electrical and thermal conductivity, chemical stability and good high temperature mechanical properties. However, difficulties in densification, low fracture toughness and poor oxidation resistance of TiB2 and NbB2 limit the use of these materials. Recent studies have shown that addition of SiC enhances the oxidation resistance by forming a protective SiO2-rich layer and improve fracture toughness of borides. In this study, SiC-TiB2 and SiC-NbB2 composites having 10 and 20 vol% SiC 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, 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 will be discussed in this presentation.

(ICACC-FS1-P059-2015) Encapsulation of fluoride in wastewater by using dicalcium phosphate dihydrate (DCPD)

Y. Arioka*[1]; M. Tafu[1]; T. Toshima[1]; T. Chohji[2]; 1. National Institute of Technology, Toyama College, Japan; 2. National Institute of Technology, Kagoshima College, Japan

Fluoride is widely used in variety of industries. On the other hand, the industries generate a large amount of wastewater with high concentration of fluoride. Treatment of fluoride in the wastewater is one of the important issues in environmental engineering. Precipitation of fluoride to fluoroaptite (FAp) is widely used because of very low solubility of the FAp. However, precipitation consisit of FAp is difficult to separation because particle of the FAp is very small. Dicalcium phosphate dihydrate (DCPD) reacts with fluoride ion in aqueous solution and forms Fluorapatite (FAp). One of the characteristics is that particle morphology of obtained FAp is same of the DCPD. Utilization of the DCPD for water treatment seems to be one of technology for fluoride encapsulation. In this study, we aimed to find DCPD utilization for the fluoride removal treatment, and building a low-emission wastewater treatment method co-using conventional reagent and DCPD. Results of the study indicated that usage of DCPD was improved amount and property of the obtained sludge and release of fluoride from the sludge. From these results, obtained sludge after treatment wastewater using DCPD is seems to stable in the landfill. DCPD is applicable to encapsulation of fluoride in wastewater.

(ICACC-FS1-P060-2015) Flash Sintering of Geopolymer Composites

F. Trombin[2]; T. Dietz[1]; S. P. Letourneau[1]; P. F. Keane*[3]; G. P. Kutyla[1]; S. K. Jha[2]; R. Raj[2]; W. M. Kriven[1]; 1. Institute of Metal Research, USA; 2. University of Colorado, USA; 3. University of Illinois at Urbana-Champaign, USA

Geopolymer composites have been fabricated containing various reinforcements. These include chopped, Saffil® alumina fibers where 20 wt % of the alumina fibers were dispersed in Cs-based geopolymers and 66 wt % corresponding to 50 vol% of Microgrit® alumina platelets alumina platelets were dispersed in K-based geopolymers. These composites had dimensional stability upon dehydration at temperatures up to 400 °C. Cubed or rectangular samples of Cs-GP, of maximum dimensions 5 mm were exposed to constant heating rate tests and electric fields up to 2 kV/cm and currents up to 60 mA. Flash temperatures of 625 °C and 740 °C were observed. Similar samples underwent isothermal holds, but no flash effects were observed. The K-based composites were also examined under constant heating rates and isothermal heating under simultaneous electric field conditions, in order to determine the flash conditions. The resulting microstructures were examined by XRD, SEM/EDS and density measurements.

(ICACC-FS1-P061-2015) Sustainable design driven philosophy:case studies of sustainable materials and processing

M. Karhu*[1]; P. Kivikytö-Reponen[1]; 1. VTT Technical Research Centre of Finland, Finland

The amount of waste from primary mining and industrial side streams is huge and it is expected to increase in the near future. At the same time there is scarcity of some critical materials, and the specific high technology metals consumption is expected to increase considerably. New sustainable material solutions processed through refining from waste in order to substitute scarce or critical materials are under development. Furthermore, sustainable processing and manufacturing techniques are strongly needed to increase energy and material efficiency. New processing techniques (mechanical, thermomechanical and thermochemical processes) enable new material solutions refined from waste and industrial side stream based materials. The energy-saving alternatives are Self-propagating High-temperature Synthesis (SHS) or low temperature chemical (and chemically activated) processes. In this study the effect of sustainable choices in material selection, processing and manufacturing phases were discussed though case studies and novel methods for sustainable material design were introduced. In some cases material can be processed directly to 'ready' component which shortens dramatically the traditional manufacturing routes. Material selection software was utilized including database of commercial material properties, average material price and relevant indicators of material "eco" properties.

(ICACC-FS1-P062-2015) Effect of fly ash composition on geopolymer synthesis

J. Eichler*[1]; 1. Universal Technology Corporation, USA

Geopolymers are amorphous aluminosilicate materials made from an aluminosilicate source material (e.g., metakaolin (MK) or fly ash (FA)) and an alkaline activator solution. FA is retrieved as a by-product from coal plants making it an attractive, renewable, green, low cost alternative for concrete applications specifically geopolymers. The properties associated to FA are directly associated to the source of coal and firing process used by the coal plant. Different coal and firing yield differences in FA composition and properties resulting in inconsistent geopolymer formation and properties. A protocol for optimal geopolymer production would allow tailoring of the synthetic procedures regardless of FA composition helping to reduce production of waste and decrease costs associated with these methods.

(ICACC-FS5-P063-2015) The formation mechanism of defect and its effect on laser induced damage in DKDP crystal

B. Liu[1]; X. Sun*[1]; X. Xu[1]; Z. Wang[1]; 1. Shandong University, China

Deuterated potassium dihydrogen phosphate (DKDP) crystals are an important nonlinear optical material used in high power laser systems which are developing for inertial confinement fusion (ICF). However, the laser induced damage threshold of as grown crystal is one order of magnitude lower than that of theory calculation. This issue seriously limits the fluence of output laser and frequency conversion efficiency. And it seriously restricts the development of ICF. Thus it has attracted intensive attentions on how to improve the laser induced damage threshold of DKDP crystal. The damage initiation in DKDP has been attributed to either impurity particles incorporated during growth or clusters of intrinsic material defects that form during growth. However, the bulk damage mechanism is still not well explained. The characteristic of these defects and the growth parameters affecting their concentrations have not yet been identified. This paper will comprehensively research the formation of defects in DKDP crystal and the effect of growth conditions on it. Moreover, the influence of these defects on the optical absorption and the resistance to laser induced damage will be performed to optimize the growth conditions of DKDP crystal.

(ICACC-FS5-P064-2015) Phase Analysis of Atomic Layer Deposited VOx Thin Films

S. Wang*[1]; T. Singh[1]; N. Aslam[2]; H. Zhang[2]; S. Hoffmann-Eifert[2]; S. Mathur[1]; 1. University of Cologne, Germany; 2. Forschungszentrum Juelich, Germany

Vanadium oxides thin films of different thicknesses were deposited by ALD with vanadium tri-isopropoxide (VTIP) and water as precursors. XRD, Raman, XPS were employed to study their phase evolution after different post-growth-annealing processes in air. The as-deposited VOx thin film is amorphous, and it crystallizes after annealing above 300 °C. With increasing annealing temperature from 350 to 500 °C, a variation of phases from dominant V3O7 to dominant V2O5 is observed in 50-nm-thick films. However, V3O7 phase trace becomes faint in case of the films of 100 nm. Stable V2O5 phase appeared after the annealing temperature higher than 400 °C. Compared to the films of larger thicknesses (≥ 50 nm), thinner films (thickness ≤ 24 nm) tend to more difficult to crystallize and oxidize, and therefore no V2O5 was detected in these thinner films even after annealing at 450 °C. Furthermore, the effect of annealing time from 30 minutes to 5 hours was investigated. It is revealed that short annealing time also affects the oxidation of vanadium oxide, especially in cases of lower annealing temperatures.

(ICACC-FS6-P065-2015) Flash sintering of ceramic composites: thermal analysis of the incubation stage

M. Steil*[1]; E. Bichaud[1]; J. Chaix[2]; P. Carry[2]; 1. Université Grenoble Alpes & CNRS, France; 2. Université Grenoble Alpes & CNRS, France

Flash sintering is able to densify ceramic material in less than 5s, at much lower temperatures than conventional sintering. The capability of this sintering process has been reported for a large range of ceramic oxide materials and recently for composite materials. The flash sintering elementary mechanisms are not yet fully understood. It has been recognized that the application of a constant electric field under constant furnace temperature, leads to sudden abrupt increase in the material conductivity and to the flash, after an incubation period. In this communication, we report experimental results on this incubation period, obtained with Alumina-Zirconia composites. All the samples were prepared from pre-mixed Alumina-Tetragonal zirconia composite powders provided by Baikowski, France. The alumina contents were: 0, 20, and 40 vol. %. For the flash experiments, the following electrical parameters were maintained constant: the AC field E0 (1000Hz, 100V/cm); the maximum current density Imax (10 or 20 A/cm^2). The pre-heating temperatures T0 were 900, 1000 and 1100°C. The power density supplied to the sample is the key parameter. During this first heating stage, the incubation time depends on the heat losses by conduction through the electrode contacts, as evidenced by the marked influence of the sample geometry. A simple energy balance equation accounts for the observed conductivity variations.

Wednesday, January 28, 2015

S1: Mechanical Behavior and Performance of Ceramics & Composites

CMCs

Room: Coquina Salon D
Session Chair: Dileep Singh, Argonne National Lab

8:30 AM

(ICACC-S1-031-2015) C/SiC composites with a self-healing SiBC matrix fabricated by liquid silicon infiltration (Invited)

X. Yin*[1]; L. Zhang[1]; L. Cheng[1]; 1. Northwestern Polytechical University, China

Most researched continuous carbon fiber reinforced silicon carbide matrix composites (C/SiC) composites have porous matrix, which are fabricated by chemical vapor infiltration (CVI) or polymer infiltration and pyrolysis (PIP). The porous C/SiC composites exhibit higher fracture toughness, flexural and tensile strength but lower compression and shear strength. Liquid silicon infiltration is a quick and low-cost densification method to fabricate dense C/SiC composites. However, besides the issue of residual silicon, high process temperature results in large thermal residual stress (TRS) in the composites. TRS is released usually in the form of spontaneous matrix micro-cracks, which is not beneficial to the oxidation resistance of dense C/SiC composites at temperatures ranging from 600 to 1000C. In order to fabricate dense C/SiC composites with excellent oxidation resistance, it is necessary to design a crack self-healing matrix and relieve TRS in dense C/SiC composites by interphase thickness control. The synthesis mechanism of Si-B-C matrix and the effect of PyC interphase thickness on mechanical properties and oxidation behaviors of C/SiC-SiBC are analyzed in details with an emphasis on the crack self-healing mechanisms. This review might provide a directional guide for the optimization design of dense ceramic matrix composites for long term use in oxidizing atmosphere.

8:50 AM

(ICACC-S1-032-2015) Defect Evolution in Polymer Impregnation and Pyrolysis Derived CMCs

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 engine environments. It is widely recognized that, in order to utilize SiC/SiC composites at their full potential, new matrix processing routes need to be developed. The current study aims to investigate defect evolution and mitigation in polymer impregnation and pyrolysis (PIP) derived CMCs. Preliminary results on the pyrolysis kinetics and chemical evolution measured via thermogravimetric mass spectrometry (TGMS) and nuclear magnetic resonance (NMR) will be discussed. Finally, the pore structure in both unidirectional fiber composites and SiC particle composites is characterized at various stages in the PIP process. Possible mechanisms of defect formation in these composites will be discussed.

9:10 AM

(ICACC-S1-033-2015) Processing and evaluation of Re2Si2O7 fiber coatings for SiC/SiC composites

E. E. Boakye*[1]; P. Mogilevsky[1]; T. A. Parthasarathy[1]; K. Keller[1]; T. Key[1]; R. Hay[2]; M. Cinibulk[2]; 1. UES, Inc., Dayton, OH, USA; 2. Air Force Research Laboratory, USA

Rare-earth disilicates (RE2Si2O7) are potential oxidation-resistant coating alternatives to carbon or BN for SiC fibers. In our prior work, hardness values of 5.5-7 GPa were determined for α, β, γ-Y2Si2O7 and γ-Ho2Si2O7. SCS-0 fibers were incorporated into α-, β- and γ-Re2Si2O7 matrices and densified at 1050°C - 1200°C using FAST. The average sliding stress values 30 – 50 MPa were measured by fiber push-out. In our current work, Re2Si2O7 (Re = Y, Ho) coatings are formed on Tyranno SA fiber tows, using a two stage coating process, based on our earlier reported work of monazite coatings on Tyranno SA fibers. First, RePO4 coatings are formed on Tyranno SA fiber filaments using heteronucleation. Secondly, the RePO4 coatings are heat treated in argon at 1200°C/10h to convert them to Re2Si2O7. Fiber strength measurements were done for both RePO4 and Re2Si2O7 converted coatings. Coated and uncoated RePO4 were infiltrated with SMP-10 preceramic polymer to form minicomposites at 1100°C and 1200°C. Coating microstructure and phase evolution, as well as minicomposite tensile strength and fractography results will be presented.

9:30 AM

(ICACC-S1-034-2015) Interface behavior in Hi-Nicalon S/SiC composites

C. Chanson*[1]; S. Jacques[1]; E. Martin[2]; 1. LCTS-CNRS, France; 2. LCTS-Université Bordeaux I, France

SiC/SiC composites made of a SiC matrix reinforced with 3rd generation SiC fibers (Hi-Nicalon S) are promising materials for aerospace and aeronautic fields. Their behavior can be tailored thanks to a thin interfacial coating called "interphase" intercalated between the fiber and the matrix. The influence of the nature of the interphase material, pyrocarbon (PyC) or BN, on the mechanical behavior of HNS/SiC 1D minicomposites is studied. The surface of the Hi-Nicalon S fibers is modified by a proprietary treatment prior to the deposition of the interphases and the SiC matrix by chemical vapor infiltration in the fiber tows. The interfacial bonding is estimated through tensile mechanical tests with acoustic emission monitoring, in particular by determining the interfacial fracture energy. The mechanical results are discussed on the basis of the debonding location and the fracture surface observed by scanning and transmission microscopies. In the minicomposites with the PyC interphase, though limited, a debonding occurs preferentially at the fiber/PyC interface, which results in a low fiber/matrix bonding. In minicomposites with the BN interphase, outside debonding at the BN/matrix interface is observed. In this last case, the measured interfacial fracture energy is even lower.

10:10 AM

(ICACC-S1-035-2015) Development and Testing of a Low NOx Oxide Ceramic Combustor for Aero-Engines

S. Hackemann*[1]; T. Behrendt[2]; Y. Shi[3]; P. Mechnich[1]; T. Aumeier[2]; B. Kanka[1]; T. Richter[2]; S. Hofmann[3]; K. Artzt[1]; 1. DLR - German Aerospace Center, Germany; 2. DLR - German Aerospace Center, Germany; 3. DLR - German Aerospace Center, Germany

An all-oxide CMC combustor liner based on winding technique was developed for the application to aero-engines and tested at the German Aerospace Center. WHIPOX- CMCs (Wound Highly Porous Oxide) show good thermoshock resistance and toughness due to the embedding of alumina fibers into a porous matrix. Aim of the developments and investigations is the reduction of cooling air for combustor walls which is necessary to establish future lean combustion concepts in low NOx-combustors. The work comprised further development of CMC materials and TBC/EBC coatings as well as material characterization and testing. The development of CFD-based cooling concepts with variable cooling hole arrangements and the opportunity for detailed testing of flat samples by means of a high pressure cooling rig with optical access played a major role. A new attachment concept for the integration of the can type CMC combustor liners into the high pressure test rig was developed. The final test campaigns of two different liners will be conducted in autumn 2014. The presentation gives an overview to the joint project from 2009-2014.

10:30 AM

(ICACC-S1-036-2015) Structural Stress Analysis of an Effusive Cooled CMC Liner

S. Hoenig[1]; R. Jemmali[1]; S. Hofmann[1]; D. Koch*[1]; 1. Institute of Structures and Design, Germany

Oxide ceramic matrix composites (Ox-CMC) are reliable candidates for combustion purposes in gas turbine engines as they allow higher efficiency and environmental friendly use due to an increase of operation temperature. Within this scope the German project HiPOC (High Performance Oxide Ceramics) supported the development of Ox-CMC combustor liners as well as fluid dynamic and mechanical testing and analysis. This presentation reviews the structural stress analysis of an effusive cooled liner made of the Ox-CMC WHIPOX. The cylindrical liner with varying diameter is manufactured via oxide filament winding and ceramic slurry infiltration. After sintering effusion holes are drilled and their influence on the mechanical behaviour and temperature distribution was studied in finite element analysis (FEA). Then a complete model for the combustor liner with realistic boundary conditions representing attachment system and test facility is mechanically analysed. The experimental results from combustor test facility under real loading conditions and also from coupon testing are evaluated. Finally, a simple analytical method is presented which validates the FEA approach and the resulting hoop and axial stresses of the liner. Additional computer tomography analysis of as received state and after testing supports the interpretation of FEA and analytical evaluation of hoop and axial stresses of the thermally loaded combustor liner.

10:50 AM

(ICACC-S1-037-2015) Mechanical Behavior of Nextel™720/ Aluminosilicate Composite Under Combined Tension-Torsion Loading

S. Hilburn[1]; M. Ruggles-Wrenn*[1]; C. Ryther[2]; L. Zawada[2]; 1. Air Force Institute of Technology, USA; 2. Air Force Research Laboratory, USA

Mechanical behavior of an oxide-oxide ceramic composite under biaxial loading was explored in combined tension-torsion tests at room temperature in laboratory air. The composite (N720/AS) consists of a porous aluminosilicate matrix reinforced with laminated, woven mullite/alumina (Nextel™720) fibers, has no interface between the fiber and matrix, and relies on the porous matrix for flaw tolerance. Thin-walled tubular test specimens were fabricated using a novel involute ply lay-up technique. The deformation and failure behaviors under proportional tension-torsion loading were examined for several different ratios of normal stress to shear stress. Axial and shear failure stresses were measured. The tension-torsion tests were complemented with uniaxial compression tests designed to measure compressive strength of the composite. The failure stress levels determined in combined tension-torsion tests and in compression tests were used together with data from literature to construct a biaxial failure envelope. The efficacy of multiaxial failure theories developed for laminated composites in predicting failure of the N720/AS ceramic composite was explored.

11:10 AM

(ICACC-S1-038-2015) Coatings and Matrices Improving the Oxidation Resistance of Carbon Fiber Reinforced Composites for Ultra-High Temperature Applications

X. Zhang*[1]; S. Dong[1]; L. Gao[1]; H. Zhou[1]; Z. Wang[1]; Y. Ding[1]; P. He[1]; J. Hu[1]; Y. Kan[1]; 1. Shanghai Institute of Ceramics,Chinese Academy of Sciences, China

C/SiC and C/C composites are the prefferred carbon fiber reinforced composites for many high temperature applications because of their outstanding thermomechanical properties. However, owing to their instability in oxidizing environments at elevated temperatures, ultra-high temperature ceramics (UHTCs) coatings need to be developed to improve their oxidation resistance in extreme environments. Besides,introduction of UHTCs to the matrices of the carbon fiber reinforced composites is another potential solution. In this work, multilayered UHTCs coatings with different structures, comprising SiC,MC and/or MB2 (M=Hf or Zr), are developed. The structures and compositions of the coatings are characterized and the oxidation resistances of the materials at high temperatures are evaluated using static oxidation or are jet tests. The preliminary results obtained will be discussed in detail with the purpose of presenting an understanding of the effects of the coating structures on the oxidation resistance of carbon fiber based composites. Furthermore, carbon fiber reinforced composites with matrices consisting of UHTCs are prepared via hybrid CVI-PIP process.The high temperature resistances of the composites are evaluated using arc jet tests and the results are compared with that of the composite of which the matrix is not modified using UHTCs.

11:30 AM

(ICACC-S1-039-2015) Novel Hybrid Ceramic Nanocomposites

I. Ahmad*[1]; 1. King Saud University, Riyadh, Saudi Arabia, Saudi Arabia

Al2O3 is an attractive structural ceramic however; brittleness turns Al2O3 down for advanced applications. Development of muti-phase phase ceramics systems is promising to curtail the brittleness and the incorporation of strong/elastic graphene, as third phase, into dual phase (Al2O3-SiC) is striking for mechanical upgrading purpose. Thin graphene nanosheets were prepared by thermal exfoliation process and reinforced into dual phase ceramic system. The hybrid nanocomposites were consolidated by novel HF-IH (high-frequency induction-heating) sintering furnace at 1500 °C at of 50 MPa under vacuum. Structural features and grain size were analyzed by SEM and TEM whilst the mechanical properties were assessed by micro-hardness and nanoindentation techniques. The fracture toughness of the hybrid nanocomposites was appraised by direct crack measurement method. Electron microscopic investigation confirmed the preparation of thin (< 10 nm) graphene nanosheets (GNS). HF-IH sintering route condensed the three-phase hybrid nanocomposite system to > 99% relative densities. SEM of the hybrid nanocomposites fractured surfaces revealed even distribution of composite constituents and changed in fracture-mode. Structurally, 88% grain reduction into hybrid nanocomposite was obtained. Mechanically, enhanced fracture toughness (50%) and hardness (53%) were achieved for hybrid nanocomposites, than monolithic Al2O3.

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

Thermal Barrier Coatings: Characterization and NDE Methods

Room: Coquina Salon G
Session Chair: Rodney Trice

8:30 AM

(ICACC-S2-009-2015) Prediction of the Cyclic Durability as a Function of Cycle Duration and Temperature of Air Plasma Sprayed Coating Using Inelastic Strain (Invited)

E. H. Jordan*[1]; S. Ahmadian[1]; 1. University of Connecticut, USA

A detailed study of the failure mechanisms in an APS TBC was carried out involving over 1000 micrographs. As a result the kinetics of oxidation and rumpling were characterized. In addition it was found that the failure was always within the ceramic caused by progressive cracking. At approximately half the spallation life, crack linking became the dominant growth mode for cracks. This pattern of damage remained constants over the temperature range of 1066 °C to 1149 °C and for dwell time of 0.5 hours to 10 hours. Through the use of a finite element analysis (FEA) that used an experimentally validated viscoplastic model driven by imposed shape changes derived from measured oxidation and rumpling behavior as well as thermal expansion mismatch, the hot and cold inelastic strains were predicted and used to predict failure. It was possible to predict the entire data set using data from only two cyclic life tests at two different test conditions. This suggests that the hold time dependence and temperature dependence are closely tied to the factors controlling inelastic strain. It was also found that the finite element results can be captured without running the FEA using simple expressions that are calibrated using a large set of FEA runs.

9:00 AM

(ICACC-S2-010-2015) Microstructure characteristics and temperature dependent local elastic response of EB-PVD thermal barrier coatings examined by in-situ synchrotron X-ray diffraction

M. Bartsch*[1]; K. Knipe[2]; A. Manero[2]; S. Sofronsky[2]; C. Meid[1]; J. Wischek[1]; M. Smith[3]; C. Lacdao[3]; J. Okasinski[4]; J. Almer[4]; A. M. Karlsson[3]; S. Raghavan[2]; 1. German Aerospace Center, Germany; 2. University of Central Florida, USA; 3. Cleveland State University, USA; 4. Argonne National Laboratory, USA

Elastic properties of the constituents of a coating system are basic input data for stress analyses. In the case of EB-PVD thermal barrier coatings elastic properties of the ceramic topcoat depend on temperature and stress state, with the latter controlled by (1) the assembly of the different layers, (2) the mismatch of their elastic properties and thermal expansion coefficients, (3) their thermal conductivities, (4) the residual stresses and (5) the temperature field. Furthermore, elastic topcoat properties are non-uniform across the coating thickness due to gradients in microstructure parameters such as porosity and column spacing. For determining comprehensive temperature- and stress-dependent elastic topcoat properties local strains were measured by means of high energy X-ray diffraction. Tubular coated specimens were loaded with systematically varying thermal and mechanical loads while recording the strains in situ. Test parameters were surface temperature, applied mechanical load, and heat flux through the specimens' wall, latter controlled by internal cooling of the tubular specimen. The topcoat surface was heated by infrared radiation up to 1000°C. For capturing ageing effects associated to microstructural evolution due to sintering a pre-aged specimen was investigated besides such in as-coated condition.

9:20 AM

(ICACC-S2-011-2015) Synchrotron x-ray measurements capturing thermally grown oxide behavior in thermal barrier coatings

A. Manero[1]; S. Sofronsky[1]; K. Knipe[1]; C. Meid[2]; J. Wischek[2]; C. Lacdao[4]; M. Smith[4]; J. Okasinski[3]; J. Almer[3]; A. Karlsson[4]; M. Bartsch[2]; S. Raghavan*[1]; 1. University of Central Florida, USA; 2. German Aerospace Center, Germany; 3. Argonne National Laboratory, USA; 4. Cleveland State University, USA

In-situ synchrotron x-ray diffraction was used to identify the mechanical behavior of thermal barrier coatings under extreme environments. Experiments were conducted on ceramic coatings deposited via electron-beam physical vapor deposition on a tubular Inconel 100 substrate. The ceramic top coat consisted of a 7-8% yttria stabilized zirconia (YSZ), which was adhered to the substrate via a NiCoCrAlY bond coat. The specimens were pre-aged at 1000 °C, developing the thermally grown oxide (TGO) layers to thicknesses representative of different stages of a coating lifespan. High-energy x-rays were used to measure lattice strains in these multi-layer coatings with through transmission diffraction. Experiments were conducted under various combinations of applied thermal gradients and mechanical loads to determine the effects of these conditions on stresses within TGO and YSZ layers. Larger applied tensile loads have shown the ability to cause tensile stresses in the TGO at high temperature. The experimental results capturing time and temperature dependent behavior has shown positive contributions that will support the creation of life prediction models.

9:40 AM

(ICACC-S2-012-2015) Imaging and quantification of microstructure evoluations in EB-PVD TBC using 3D X-ray micro-tomography

X. Zhang*[1]; Y. Zhao[1]; P. Xiao[1]; P. Withers[1]; 1. Univ. of Manchester, United Kingdom

Microstructure degradation in an EB-PVD TBC was investigated in 3D non-destructively using X-ray micro-tomography. TGO growth, void formation and growth, local TGO undulations, interface roughness and $\beta \rightarrow \gamma'$ transformation were identified in a series of time-lapse tomography scans. Features observed in tomography were traced and their origins deduced. Local TGO undulation was found to exist in as-deposit state. These features were compared with those from SEM. Quantitative analysis on X-ray tomography data revealed that TGO growth followed a sub-parabolic law. X-ray tomography enabled TGO/bond coat interface roughness to be quantified in 3D. It was found that local TGO undulation enlarged as a result of ratcheting while global interface roughness kept stable throughout thermal cycling. The effect of interface roughness is determined by TGO undulation density and its distribution.

10:00 AM

(ICACC-S2-013-2015) X-ray Tomographic Imaging of APS TBC Damage Progression

N. Asadizanjani*[1]; S. Shahbazmohammadi[1]; E. H. Jordan[1]; 1. university of connecticut, USA

APS TBC typically fails by cracking just above the bond coat to ceramic interface. Sectioning studies have shown a progressive cracking that includes a later stage dominated by linking. In sectioning experiments the crack shape cannot be easily determined and because sectioning is destructive, the progressive growth of a give flaw cannot be recorded nor can the conditions leading to crack linking be studied. X-ray tomography in principal has the capability of providing the missing information. In this presentation the practical steps needed to record APS TBC images capable of recording the progression of damage especially crack linking and crack shapes will be presented. Experiments we done in which samples subjected to cyclic furnace testing were imaged repeatedly in order to track the progression of cracking of specific cracks and to record

the cracks geometries that just preceded crack linking. Data of this type provides a validation data set for any attempts to model crack behavior. In addition because the TGO to ceramic shape change is recorded, it is possible to relate the initiation and growth of cracks to initial and changing TGO to ceramic interface which impose strains related to this shape change on the coating.

CMAS-related Degradation and Mitigation Strategies I

Room: Coquina Salon G
Session Chair: Uwe Schulz, German Aerospace Center

10:40 AM

(ICACC-S2-014-2015) Field Experience in Heavy Duty Gas Turbines Operating in CMAS Type Conditions (Invited)

H. Bossmann[1]; G. Witz*[1]; B. Bordenet[1]; K. Stefansson[1]; 1. Alstom (Switzerland) ltd, Switzerland

Depending on the media specifications, heavy duty gas turbines can operate in conditions which can produce CMAS like deposits. These deposits can come from various sources like: air, fuel or water impurities, but also from fuel additives, or cleaning media. Depending on the type of impurities and the part under consideration, various types of deposits or reactions can occur. This can be the formation of molten deposits, filling of pores with anhydrite, hot corrosion of the bondcoat and TBC, solid state reaction of YSZ with impurities like Ca leading to the formation of fully stabilized zirconia or leading to an increased sintering of the TBC. Such mechanisms will be discussed based on the analysis of parts after service in various operating conditions. This will allow discussing the various reaction mechanisms occurring in the TBC. How in one engine different reaction mechanisms can occur on different parts depending on their loading condition. Finally we will propose some mitigation solutions and provide examples showing how TBC coated parts can operate safely in engines operating in challenging areas and operating conditions.

11:10 AM

(ICACC-S2-015-2015) Erosion and High Temperature Corrosion Performance of PS-PVD TBCs

S. Rezanka*[1]; G. Mauer[1]; D. E. Mack[1]; R. Vassen[1]; 1. Forschungszentrum Jülich GmbH, Germany

Nowadays TBCs are manufactured by APS or EB-PVD. The plasma spray–physical vapor deposition (PS-PVD)-process combines features of both routes and is a promising technology for manufacturing TBCs on highly thermo-mechanically loaded parts. The durability of columnar grown PS-PVD TBCs was investigated in burner rig tests and isothermal furnace tests. Additionally, the influence of the columnar microstructure with high open porosity on further application-relevant properties is part of this study. The resistance of PS-PVD TBCs against high temperature corrosion was analyzed in a modified burner rig test injecting liquid CMAS compounds. Furthermore, PS-PVD TBCs were investigated under erosive attack according to ASTM G76-13. High thermal cycling lifetimes, more than two times longer than those of conventional TBCs, were achieved by pre-oxidation of the BC surface. TGO formation, preventing the occurrence of inter-diffusion at high deposition temperature and allowing improved bonding was found to be crucial for the durability of PS-PVD TBCs. Furthermore results on the CMAS testing indicate that the durability of PS-PVD TBCs is comparable to that of EB-PVD coatings. By varying plasma gas composition, the density of the microstructures could be increased leading to improved erosion resistance. Hence, the resistance of these coatings against high temperature corrosion and erosion attack is comparable to established TBCs.

11:30 AM

(ICACC-S2-016-2015) Understanding a novel failure mode in testing thermal barrier coatings with CMAS attack

A. Harris*[1]; E. H. Jordan[2]; 1. University of Connecticut, USA; 2. 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 simultaneous CMAS application. A novel failure mode was observed, whereby spallation occurred during heating, counter to prevailing models of TBC delamination that assume the coating spalls on cooling. Material characterization techniques were used on these samples to understand failure mechanisms and morphology. To assess the engine relevance of this failure mode, test parameters were varied to determine the conditions under which different failure modes were activated.

S3: 12th International Symposium on Solid Oxide Fuel Cells (SOFC): Materials, Science and Technology

Surface and Interfacial Reactions

Room: Crystal
Session Chairs: Enrico Traversa, King Abdullah University of Science and Technology; Nguyen Minh

8:00 AM

(ICACC-S3-024-2015) Surface Reaction of Doped Lanthanum Cobaltite System (Invited)

K. Yashiro*[1]; H. Sato[1]; M. Sasaki[1]; R. A. Budiman[1]; S. Hashimoto[2]; T. Nakamura[3]; K. Amezawa[3]; T. Kawada[1]; 1. Tohoku University, Japan; 2. Tohoku University, Japan; 3. Tohoku University, Japan

Low operation temperature is preferable for cost reduction and durability of solid oxide fuel cells (SOFC). Improvement of cathode performance is indispensable for low temperature SOFC. A series of (La, Sr)CoO3 (LSC) has attracted attention as a SOFC cathode, which shows both high ionic- and electronic conductivities. It has been reported that surface reaction of LSC is the rate determining step of the cathode reaction. We reported that implementation of hetero-interface is one of possible solutions to improve the surface reaction kinetics. However, the mechanism of improvement is still not clear. In this paper, several evaluation techniques are applied to obtain the comprehensive understandings of surface reaction kinetics of LSC.

8:30 AM

(ICACC-S3-025-2015) Ba deficient NdBaCo2O5+δ oxides for Intermediate Temperature Solid Oxide Fuel Cell Cathodes

R. Pelosato*[1]; A. Donazzi[2]; G. Cordaro[1]; D. Stucchi[1]; I. Natali Sora[3]; C. Cristiani[1]; G. Dotelli[1]; 1. Politecnico di Milano, Italy; 2. Politecnico di Milano, Italy; 3. Università di Bergamo, Italy

The purpose of this study is the evaluation of Ba deficient NdBaCo2O5+δ layered perovskite oxides as cathodes for Intermediate Temperature SOFCs. NdBa1-xCo2O5+δ with x = 0, 0.05, 0.10, 0.20 (NBC0, NBC5, NBC10, NBC20) have been prepared via solid state reactive firing; the crystal structure cell parameters were evaluated via Rietveld refinement of the XRD data, and the chemical compatibility was checked with LSGM and CGO electrolytes. Oxygen content of the compounds vs temperature was evaluated by combined cerimetric titrations and TG-DTA measurements. Electrochemical activity was evaluated via impedance spectroscopy on symmetric cells with CGO electrolyte. NBC0, NBC5 were obtained as single phase, NBC10 sample showed trace impurity, witnessing the reached stability limit of the Ba deficient structure. The crystal structure was refined in a tetragonal cell for all the prepared compounds. TG analysis showed an increasing oxygen loss at increasing Ba deficiency, and the mean oxidation state of Co increases from 3.14 to 3.20 to compensate Ba deficiency. The compounds slightly reacted with LSGM electrolyte at 900°C 12 h with formation of new phases, while neither new phases nor apparent peak shifts were observed in mixtures with CGO electrolyte up to 1100 °C. These preliminary results show that Ba deficient NdBaCo2O5+d oxides could be promising cathode materials for CGO based IT-SOFCs.

8:50 AM

(ICACC-S3-026-2015) The Enhancement of Surface Oxygen Exchange Constant in the Composite Electrode

R. A. Budiman*[1]; H. Kudo[1]; T. Miyazaki[2]; S. Hashimoto[3]; K. Yashiro[1]; T. Kawada[1]; 1. Tohoku University, Japan; 2. Tohoku University, Japan; 3. Tohoku University, Japan

Recent study on the composite electrode shows the enhancement of the electrochemical performance compared to mixed conductor electrode. The question has been raised on the reason why interfacial conductivity of the composite electrode enhanced compared to that of mixed conductor single cathode. The effective reaction length is expected as the reason of enhancement of interfacial conductivity. However, it may have another reason of the enhancement such as the enhancement of surface oxygen exchange constant. To prove the enhancement of surface oxygen exchange constant, the isotope exchange experiment by secondary ion mass spectrometry and pulse isotope exchange has been done so far. Both of technique determined the enhancement of catalytic activity and also give slight insight on the oxygen reduction mechanism.

9:10 AM

(ICACC-S3-027-2015) Metallic conductors for cathode in Solid Oxide Fuel Cells and their electrochemical properties

A. Stoeck*[1]; S. Mnich[1]; S. Kuehn[2]; 1. eZelleron GmbH, Germany; 2. eZelleron GmbH, Germany

Andrea Stoeck, Stephan Mnich and Sascha Kuehn A major issue for the use of ceramic cathodes in solid oxide fuel cells (SOFCs) is their limited conductivity and fragility. Therefor silver based current collectors were used to obtain highly conductive cathodes. Incorporation of oxide particles prevents densification and led to stable porous films with excellent electrochemical properties.

9:30 AM

(ICACC-S3-028-2015) Structural and electrochemical performance stability of perovskite - fluorite composite SOFC electrode

S. Gupta*[1]; M. K. Mahapatra[1]; P. Singh[1]; 1. University of Connecticut, USA

Lanthanum chromite- based perovskite and stabilized zirconia composites offer the potential as alternative solid oxide fuel cell (SOFC) anodes. Interaction between the lanthanum chromite and zirconia phases form secondary phases, modifies the thermo-physical properties leading to anode performance degradation. This study provides chemical (secondary phases) and structural changes of the strontium and manganese doped lanthanum chromite ((La0.75Sr0.25)0.95Cr0.7Mn0.3O3 (LSCM)) – zirconia (yttrium stabilized zirconia (8YSZ) and scandium stabilized zirconia (10ScSZ)) composites exposed to reducing atmosphere (Ar-3%H2-3%H2O) using in-situ X-ray diffraction (RT-1200°C). Electrochemical impedance spectroscopy (EIS) on the symmetrical cells shows higher performance for LSCM+10ScSZ/8YSZ/LSCM+10ScSZ when compared to LSCM+8YSZ/8YSZ/LSCM+8YSZ in oxidizing (air) as well as in reducing atmosphere (Ar-3%H2-3%H2O). A qualitative correlation between the electrochemical performance degradation and the interaction between the LSCM and 8YSZ/10ScSZ will be established.

10:10 AM

(ICACC-S3-029-2015) Bio-template Assisted Nano-catalyst Infiltration of Porous SOFC Electrodes

O. Ozmen*[2]; S. Lee[1]; K. Gerdes[1]; J. W. Zondlo[3]; K. Sabolsky[2]; E. M. Sabolsky[2]; 1. U.S. Department of Energy, USA; 2. West Virginia University, USA; 3. West Virginia University, USA

Nano-catalyst infiltration of porous Solid Oxide Fuel Cells (SOFC's) electrodes is a well-known process to increase electrochemical performance. Conventional dripping method to the electrodes has some limitations, such as the multiple infiltration steps (which are labor and time consuming) to achieve a specific loading level. Moreover, the homogenous deposition and retention of nano-particles deep into the electrode microstructure close to the triple phase boundary brings additional challenges. Our objective is to develop a process to efficiently infiltrate nano-catalyst into the NiO/YSZ anode structure of anode-supported SOFC's and improve the long-term stability. In the study, catechol-based bio-templates were adapted as a surfactant within the porous anode microstructure to better control of the kinetics and dispersion of the nano-catalyst. In order to insure efficient impregnation of the 3-D porous anode network, the cell was first immersed into the surfactant solution and then immersed directly into the catalyst precursor solution. This two-step procedure resulted in nano-catalyst deposition levels up to 0.5-8 mg. After calcination, a correlation between ~50-300 hour cell performance and the final nano-catalyst characterization was developed. Voltage-current-power and impedance spectroscopy at various times were used to characterize degradation trend of the infiltrated SOFC button cells.

10:30 AM

(ICACC-S3-030-2015) Development of microtubular solid oxide fuel cells using hydrocarbon fuels (Invited)

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

Solid oxide fuel cells (SOFCs) can, in principle, directly use not only hydrogen but also hydrocarbon fuels such as methane, butane and so on. However, hydrocarbon is decomposed into hydrogen and solid carbon at high temperatures. Carbon deposition causes rapid deterioration of anode performance on SOFCs. We found that oxide species in nickel-based anodes affected the durability under direct hydrocarbon utilization. Ni-scandia stabilized zirconia (ScSZ) anode indicated high durability than Ni-yttria stabilized zirconia (YSZ) anode in methane at 1273 K and a low steam/carbon (S/C) ratio of 0.03. While graphite nanofibers growth on the Ni-ScSZ anode suffered less degradation under direct methane utilization, a large amount of amorphous carbon deposition on the Ni-YSZ anode damaged the Ni catalyst. However, the Ni-ScSZ anode deteriorated rapidly for less than 4 h in butane at 873 K and S/C = 0.04 due to the increase in the carbon deposition rate compared to methane. The cell with Ni-gadolinia doped ceria (GDC) anode was able to generate power continuously for more than 24 h under direct butane utilization, because GDC had high catalytic activities against butane reforming and/or electrochemical carbon oxidation. We were successful to developed microtubular SOFC stacks with the Ni-GDC anode, and to demonstrate a prototype portable SOFC system using a commercially available LPG cartridge.

11:00 AM

(ICACC-S3-031-2015) Interaction between glass-based sealants and MnCo spinel coated interconnects for Solid Oxide Cells

F. Smeacetto*[1]; A. Sabato[1]; A. De Miranda[1]; M. Salvo[1]; M. Bindi[2]; A. Chrysanthou[3]; M. Ferraris[1]; 1. Politecnico di Torino, Italy; 2. Edison S.p.A., Italy; 3. University of Hertfordshire, United Kingdom

The development of sealants for solid oxide cells (SOFCs and SOECs) is a critical issue. Special focus has to be given to the sealant-metallic interconnect interface. The application of MnCo spinel-based coatings on the interconnect has been demonstrated as an effective method to inhibit Cr volatilization and thereby prevent cathode poisoning. The coated interconnect/sealant interface should be pore and crack free; to fulfil this requirement, the glass-ceramic sealant should adhere and strongly bond to the interconnect. This study focuses on the design and characterization of new glass sealant compositions and on their compatibility with MnCo spinel-based coated Crofer22APU. The crystallization and sintering behaviour were studied by thermal analyses and the interaction with MnCo coated Crofer22APU is reviewed and discussed. Dense, homogeneous and crack-free MnCo spinel based coatings (thickness ranging from 1 to 15 micron) were obtained on Crofer22APU by different techniques. Excellent thermo-mechanical compatibility was observed between the MnCo spinel-based coated Crofer22APU and the glass-ceramic sealants after thermal cycling and ageing tests in relevant conditions, as demonstrated by post-mortem examinations, thus showing that the sealants can provide gas-tightness and the MnCo-based spinel protection layer can effectively act as a barrier to outward diffusion of Cr.

11:20 AM

(ICACC-S3-032-2015) Sealants for SOFC/SOEC stacks: challenges of sealing and operating temperature

J. C. Schilm*[1]; A. Rost[1]; M. Kusnezoff[1]; A. Michaelis[1]; 1. Fraunhofer IKTS, Germany

The operation of solid oxide cells in fuel cell and electrolysis modes, require gastight and long term stable sealing materials. Due to the operation temperatures between 700 and 950°C gas leakages will not only cause losses in efficiency but also damage by combustion of fuel gas. Among suitable sealing materials, glass ceramic sealants are these which can be adapted best to the joining conditions in terms of the requirements of the sealing partners, the joining temperature profile and long term stability at operating temperatures. For common used stack interconnect materials Crofer22APU and CFY a number of different sealing materials suitable for application with ESC and ASC cells have been developed and successfully tested. In SOFC mode glass ceramic seals have been proven up to several 10.000 hours. In SOEC mode the high water content of more than 50% in combination with high operating temperature is challenging for all applied materials. In this study the degradation behavior of different glass ceramic sealant materials under different electrolysis conditions is compared. The observed phenomena will be discussed in terms of gas tightness of the seals after different operating time, changes in the microstructure of the sealing materials and in the bonding interfaces of joints. Resulting from these findings the directions for the development of glass ceramic sealants for SOEC are discussed.

11:40 AM

(ICACC-S3-033-2015) Investigation on the carbon deposition behavior of Ni-YSZ Cermet in various types of hydrocarbon gas

N. Ohmura*[1]; T. Nakamura[2]; K. Matsuoka[4]; T. Kudo[4]; T. Kawada[3]; K. Amezawa[2]; 1. Tohoku University, Japan; 2. Tohoku University, Japan; 3. Tohoku University, Japan; 4. JX Nippon Oil & Energy Corporation, Japan

In order to obtain knowledge on the degradation of SOFCs by carbon deposition, quantitative evaluation of the deformation of the Ni-YSZ cermet, which is a typical anode material, was carried out when a hydrocarbon gas was introduced. The deformation of the Ni-YSZ cermet was investigated by using the dilatometer. The deposited carbon was observed after the exposure of hydrocarbon gas by SEM and analyzed by EDX. A moisturized 1%CH_4-N_2, 1%C_2H_6-N_2, 1%C_3H_8-N_2 or 10%CH_4-N_2 was chosen as a hydrocarbon gas. In case of steam/carbon ratio: S/C=0.1, Ni-YSZ cermet drastically expanded during the exposure to hydrocarbon gas, the expansion ratio reached 1% within 5 hours for 1%CH_4-N_2 and 1 hour for the others. Then there was delay time between the introduction of each hydrocarbon gas and the beginning of the expansion. According to SEM observation, the visible amount of carbon was found inside of the specimen after the exposure. Carbon was segregated in the near surface of the specimens for 1%C_2H_6-N_2 and 1%C_3H_8-N_2. In contrast, carbon was dispersed in the whole of the specimens for the case of 1% and 10%CH_4-N_2. The difference in these two types of the carbon deposition might be caused by the decomposition mechanism of the hydrocarbon gas. And it was indicated that carbon distribution in the specimen determined the expansion behavior including the delay time for expansion.

12:00 PM

(ICACC-S3-034-2015) Performance and Stability of LSM-based Cathode Infiltrated with Electrocatalyst

G. Tao*[1]; 1. Materials & Systems Research Inc., USA

A Solid Oxide Fuel Cell (SOFC) is capable of converting chemical energy of hydrocarbon fuels directly into electricity at a high efficiency. Large costs attributed to cathode low performance and long-term stability issues are the current limitation of SOFCs that must be addressed before commercializing the technology. Because of its adequate catalytic activity for O2 reduction and excellent chemical stability with YSZ electrolyte, LSM was used as a cathode material widely. One of the most efficient solutions to SOFC performance enhancement and thus cost reduction is to lower the cathode overpotential losses via infiltrating an active electrocatalyst. Considerable R&D efforts were reported in literature. However, neither long-term degradation issue nor repeatability was stressed extensively. MSRI has been developing a cost-effective, single-step infiltration technique that was implemented successfully on LSM-based SOFCs. Mitigation strategies were developed for suppressing the growth/coarsening of the infiltrated nano-size electrocatalyst. Validation tests of button cells (2 cm2) and single cells (100 cm2) showed significant performance improvement. Periodical VI sweeps and EIS tests suggested that the mitigation solution retained the catalyst activity effectively over thousands of hours degradation tests. Details of the development efforts and results will be presented and discussed in this talk.

S4: Armor Ceramics: Challenges and New Developments

Modeling / Testing and Evaluation / Quasi-Static and Dynamic Behavior I

Room: Coquina Salon E

Session Chair: Costas Fountzoulas, ARL; Matthew Bratch, ARL

8:30 AM

(ICACC-S4-030-2015) Protection – New Ideas, Advanced Materials, New Penetration Models

I. V. Kartuzov*[1]; J. Campbell[2]; V. Kartuzov[1]; 1. IPMS NASU, Ukraine; 2. ARL, USA

A key idea of personal protection is to protect from different ballistic threats (projectiles, ceramic (or metallic) fragments, pressure impulse on the interface armor – body. From physics point of view to reduce projectile's energy and impulse to safe level is required. To resolve this problem requires, the application of varios ballistic materials in different combinations (steel, Ti, Al, Al2O3, B4C, etc). Armor design and the ways of its improvement – mass and cost reduction are well known. Thus a solution needs new ideas and new armor materials. New penetration models are an integral part of development of both of those. This effort is to present the results obtained at IPMS NAS of Ukraine. They concern a new class of composite AlB12 based ceramic materials with matrix nanostructure, application of granular technology and foam materials to form «Taylor» structures, formation of required structure of reflected wave to mitigate projectile's impulse. The main idea of the suggested approach is to develop the required structure in different parts of armor design, which makes possible to obtain a definite level of ballistic properties, required to effectively resist against various threats, the level of those properties in armor design at impact loading is preliminary calculated. Optimization of properties shall account for mass and cost characteristics of armor design components.

8:50 AM

(ICACC-S4-031-2015) Use of microstructural control to alter ballistic performance in silicon carbide-boron carbide composites

T. Williams*[1]; J. Yeomans[1]; A. Heaton[2]; C. Hampson[3]; 1. University of Surrey, United Kingdom; 2. Dstl, United Kingdom; 3. Morgan Advanced Materials, United Kingdom

A range of silicon carbide – boron carbide ceramic composites have been produced by pressureless sintering and used for ballistic testing. Within the range of materials, four different microstructural parameters have been varied; the volume ratio of the two phases, the porosity level, the second phase distribution and the matrix phase grain size. The materials have been produced such that only a single parameter is varied in materials selected to test that parameter. For example porosity has been varied without significant change in grain size and second phase distribution without significant change in density or porosity. These materials have been tested using the V50 method with 7.62 mm armour piercing rounds. Microstructural information, physical property data and standardised ballistic performance data for the different materials are presented. The ballistic performance of the materials is compared with that of a standard sintered silicon carbide produced by the same processing route.

9:10 AM

(ICACC-S4-032-2015) Properties and performance of cubic-boron nitride

J. Swab*[1]; L. Vargas[1]; E. Wilson[1]; E. Warner[1]; 1. Weapons & Materials Research Directorate, USA

Cubic-Boron Nitride (c-BN) is a lightweight (ρ = 3.45 g/cm^3) ceramic material that is harder than all materials except diamond. Since harder ceramics tend to perform better as armor this material is of interest to the military community to protect soldiers. C-BN is synthetically produced and is primarily used as an abrasive and in cutting tool applications. It is difficult to make in large sizes needed for armor applications or even sizes sufficient to determine basic mechanical properties. However, disks of c-BN nominally 97 mm in diameter with thicknesses between 2.3 and 6.4 mm have recently been obtained. The properties (elastic modulus, strength, toughness, hardness, etc) of this material were determined and compared to a commercially-available boron carbide (B_4C) and silicon carbide (SiC).

9:30 AM

(ICACC-S4-033-2015) TNO's research on ceramic based armor; experiments and modelling (Invited)

E. Carton*[1]; G. Roebroeks[1]; J. Weerheijm[1]; A. Diederen[1]; M. Kwint[1]; 1. TNO, Netherlands

Several specially designed experimental techniques and an alternative test method have been developed for ceramic armor. Armor grade ceramics and a range of combined materials have been tested using 7.62 AP rounds. Using the Energy method (see Armor Symposium 2014) the dwell-time and total energy absorbed from the AP core were determined. In additional tests time-resolved fracturing and out-of-plane movement of the ceramic tile (fragments) were recorded using high-speed video at one million frames per second. Also the thermal energy and particle size distribution of the fragments were measured in order to determine the total created heat and fracture surface area. The information provided by the results of all tests has in addition resulted in an energy-based engineering model calculating the dwell-time, forces, erosion of the projectile and the residual velocity of an AP-core. The model predicts the mass and velocity of residual AP cores rather well assuming a failure wave that transfers the intact ceramic material into a massively broken medium. The model does not require mechanical properties of the ceramic materials. This reflects the difficulty within the ceramic armor research community to find a relation between ceramic mechanical properties and its ballistic efficiency. This model creates a renewed understanding of the relevant phenomena that could explain the ballistic efficiency of ceramic armor.

10:20 AM

(ICACC-S4-034-2015) Adhesion Between Alumina Ceramic and Glass Fibre-Reinforced Polyester Composite in a Hybrid Armour System

B. B. Johnsen*[1]; K. B. Lausund[2]; D. B. Rahbek[1]; F. Hansen[3]; 1. Norwegian Defence Research Establishment (FFI), Norway; 2. University of Oslo, Norway; 3. University of Oslo, Norway

In this work, the adhesive strength between an alumina ceramic and a glass fibre-reinforced polyester composite for use in hybrid body armour has been investigated. The effect of various alumina surface treatments, including degreasing, etching, plasma, grit-blasting and silanisation, was evaluated. The physical and chemical surface properties were investigated by microscopy, profilometry, contact angle measurements and X-ray photoelectron spectroscopy. This analysis showed that the treatments removed organic contaminants from the alumina, resulting in higher surface energies. Alumina/composite hybrid plates were prepared by a vacuum moulding technique, and the adhesion was evaluated quasi-statically on rectangular test specimens employing the fixed arm peel test. In this test, the flexible composite arm was peeled off the rigid alumina substrate at a fixed angle, and the peel strength was determined. All surface treatments had a pronounced effect on the peel strength, and the adhesion was improved compared to the as-received alumina. The silanisation produced a thin film on the surface and had the greatest effect on the strength. This could be explained by better wetting of the more planar silanised surface by the thermoplastic polyester, the silane acting as a coupling agent between the alumina and the composite, and a more defect-free alumina/polyester interface.

10:40 AM

(ICACC-S4-035-2015) Experimental and computational study on fracture patterns of alumina ceramic tiles upon ballistic impact

D. B. Rahbek*[1]; B. B. Johnsen[1]; T. Thorvaldsen[1]; J. Simons[2]; T. Kobayashi[2]; D. Shockey[2]; 1. Norwegian Defence Research Establishment, Norway; 2. SRI International, USA

In this work, the fracture patterns of alumina ceramic tiles that were subjected to ballistic impact by armour piercing projectiles have been investigated. The projectile velocities were in the range from 175 m/s to 325 m/s. Fracture of the tiles occurred at all velocities, and the resulting crack patterns in the ceramic were studied and quantified using microscopy. The extent of damage was found to increase with increasing projectile velocity. One mode of damage was radial cracks. The number of radial cracks increased with velocity. This could be due to an effect similar to that seen in expanding rings, where development of cracks relieves stress and prevents other cracks. At lower velocities there is more time for stress relief and thus fewer cracks. Besides a higher number of radial cracks, the higher velocities also resulted in the formation of conical cracks. In addition to the experimental work, finite element analysis was performed to analyse the results.

11:00 AM

(ICACC-S4-036-2015) Crack and Damage Velocities in Ballistic Experiments

C. E. Anderson*[1]; R. P. Bigger[1]; C. E. Weiss[1]; 1. Southwest Research Institute, USA

A series of ballistic impact experiments were conducted against a borosilicate glass (Borofloat®33) bonded to a polycarbonate substrate. Two of the objectives of the experiments were to measure crack velocities in the glass and to measure the damage velocity in the glass. The speed of distinct propagating cracks was found to be 1.92 +/- 0.03 km/s, independent of impact velocity. The maximum rate of damage propagation was found to be a function of impact velocity, but the damage velocity plateaued at 2.07 +/- 0.04 km/s. The results are compared to reverse ballistic experiments and edge-on-impact experiments.

11:20 AM

(ICACC-S4-037-2015) Dynamic fracture toughness of pressureless-sintered and reaction-bonded SiC and B_4C composites

J. J. Pittari*[1]; G. Subhash[1]; 1. University of Florida, USA

The fracture toughness (K_{Ic}) of several pressureless-sintered and reaction-bonded ceramics was investigated via four-point bend chevron-notch testing method. Static tests were conducted using a conventional universal testing machine, while the dynamic experiments were performed using a modified-Hopkinson Pressure Bar apparatus. Thirteen silicon carbide (SiC) and/or boron carbide (B_4C) ceramic composites with varying compositions and microstructures manufactured through pressureless sintering (PS) and reaction bonding (RB) processes were tested. Two optical measurement techniques (digital image correlation (DIC) and interferometry) were used to record crack mouth opening displacement (CMOD) and verify stable crack nucleation and growth for tests within both strain rate regimes. The fracture surfaces were investigated through scanning electron microscopy (SEM) and optical profilometry to determine the presence of various toughening mechanisms and the influence of strain rate on the mode of fracture due to differing microstructures. All the reaction-bonded composites displayed higher fracture toughness values than the pressureless-sintered ceramics. Strain rate sensitivity was noted in the fracture toughness values of all materials as an increased toughness response at higher deformation rates.

11:40 AM

(ICACC-S4-038-2015) Laser-shock spall testing of glass and glass-ceramics

M. J. Davis*[1]; C. Weinhold[1]; P. Vullo[1]; 1. SCHOTT North America, Inc., USA

The identification of a useful screening test for armor materials remains a subject of considerable interest, particularly for protection against chemical energy threats like shaped charges. Here, we report on high strain-rate experiments (> 10^6 sec^{-1}) using laser-shock techniques in which the energy of a 10-nsec laser pulse is converted at the sample surface into a sharp pressure wave which then propagates into the sample. Well-defined spall threshold conditions were quantified for soda-lime, SCHOTT Borofloat, and fused silica glasses, as well as the SCHOTT glass-ceramic Robax and four other developmental glass-ceramics. In general, the glasses all exhibited higher spall thresholds than the glass-ceramics, although some of the glass-ceramics exhibited low levels of subsequent fracturing even when tested above threshold conditions. Under long-pulse conditions (200 nsec), only two materials—-one transparent and one opaque glass-ceramic—-did not spall, whereas all of the other materials exhibited intense spall. These results will need to be compared to other testing protocols to determine the extent to which, if any, they correlate to physically-meaningful aspects of importance to real impact events.

S6: Advanced Materials and Technologies for Energy Generation, Conversion, and Rechargeable Energy Storage

Solid Electrolytes and Characterization

Room: Tomoka A

Session Chairs: Dany Carlier, ICMCB-CNRS; Robert Dominko, National Institute of Chemistry

8:30 AM

(ICACC-S6-025-2015) Lithium Metal Phosphate Solid Electrolytes via Reactive Sintering (Invited)

M. Badding*[1]; 1. Corning Incorporated, USA

Solid electrolytes offer new design options for high energy density cell constructions, particularly as solids achieve conductivities approaching or on par with liquid electrolytes. Lithium metal phosphate compositions with the NASICON structure have shown excellent conductivity, but proven difficult to sinter to full density via traditional ceramic processing. Here we report reactive sintering of lithium aluminophosphate glasses and metal oxide powders can achieve >95% relative density and, consequently, high total Li+ ion conductivity in tape cast lithium alumino-metal phosphate electrolytes Li1+xAlxM2-x(PO4)3 (M=Ti, Sn, Ge). Application to Li-water cell chemistries will be discussed.

9:00 AM

(ICACC-S6-026-2015) Design of Solid-state Electrolytes using High-throughput First Principles Computations (Invited)

S. Ong*[1]; Y. Mo[2]; W. D. Richards[3]; L. Miara[4]; H. Lee[4]; G. Ceder[3]; 1. University of California San Diego, USA; 2. University of Maryland College Park, USA; 3. Massachusetts Institute of Technology, USA; 4. Samsung Advanced Institute of Technology, USA

Solid-state electrolytes exhibit good safety and stability, and are promising to replace current organic liquid electrolytes in rechargeable battery applications. In this talk, we will present our efforts at developing scalable first principles techniques to design novel solid-state electrolytes. Using the recently discovered Li10GeP2S12 lithium super ionic conductor as an example, we will discuss how various properties of interest in a solid-state electrolyte can be predicted using first principles calculations. We will show how the application of these first principles techniques has suggested two chemical modifications, Li10SiP2S12 and Li10SnP2S12, that retains the excellent Li+ conductivity of Li10GeP2S12 at a significantly reduced cost. These modifications have recently been synthesized, and the measured Li+ conductivities are in excellent agreement with our first principles predictions. We will conclude with a demonstration of how relatively expensive first principles calculations can be intelligently scaled and combined with topological analysis to be a useful screening tool for novel solid-state electrolytes.

9:30 AM

(ICACC-S6-027-2015) In-Situ TEM study of energy storage materials (Invited)

C. Wang*[1]; 1. Pacific Northwest National Laboratory, USA

Over the last decades, we have witnessed tremendous progress on the development of aberration corrected transmission electron microscopy and scanning transmission electron microscopy. As a result of this development, imaging of materials at atomic scale and spectroscopying at sub-nanometer scale become a routine practice. The questions now come to how we extend the microscopy and spectroscopy methodologies to analyze materials at or near realistic/operating condition, typically such as real time observation of catalytic process, oxidation and reduction, bio-tissue in a liquid cell, defects generation and interaction under deformation conditions, mass transport and microstructural evolution, charge and

ion transport process in electrochemical cells. In this presentation, I will focus on in-situ TEM techniques that developed for probing into the structural and chemical information of energy storage materials. In-situ high resolution imaging enables direct observation of structural evolution, phase transformation and their correlation with mass, charge and electron transport, which provide insights as how active materials failure with cyclic charging and discharging of a battery. In perspective, challenges and possible direction for further development of the in-situ TEM imaging and spectroscopic methods for energy storage materials and other field will also be discussed.

10:20 AM

(ICACC-S6-028-2015) In-situ characterization of deformation creep response Li-ion electrode materials (Invited)

S. J. Dillon*[1]; 1. University of Illinois Urbana-Champaign, USA

Deformation creep can significantly affect the stress-state and fracture of electrode particles undergoing volumetric expansion and contraction. Despite the large interest in chemo-mechanical coupling during electrochemical cycling, the creep response of electrode materials has received limited attention. Here, we demonstrate its importance in affecting the evolution and fracture of electrode particles during lithaition and delithiation through a combination of in-situ X-ray, SEM, and TEM experiments. Specifically, Sn is shown to be sensitive to power-law creep and surface diffusion mediated creep during cycling, which affects particle fracture and porosity evolution.

10:50 AM

(ICACC-S6-029-2015) Local impedance spectroscopic and microstructural analyses of Al-in-diffused Li7La3Zr2O12

J. Ahn*[1]; S. Park[1]; J. Lee[1]; 1. Korea university, Korea (the Republic of)

The effect of Al diffusion on the microstructure, phase composition, and Li-ion conductivity of Li7La3Zr2O12 (LLZ) was investigated using a cylindrical LLZ specimen that was sintered in contact with an Al2O3 crucible. The spatially resolved local-impedance spectroscopy and compositional analysis revealed that the Li-ion conductivity and Al concentration decrease with increasing distance from the contact area with the Al2O3 crucible. Abnormally large LLZ gains (size > 0.7 mm) within a matrix of fine grains (size: ~10 μm) with a high Li-ion conductivity (8.5 x 10-5 S/cm) were found in the region close to the Al2O3 crucible. In stark contrast, uniform fine grains (size: ~10 μm) with low Li-ion conductivity (1.1 x 10-6 S/cm) were found in the region far from the Al2O3 crucible. The high Li ionic conductivity of LLZ specimen near Al2O3 crucible was attributed to the incorporation of Al into the LLZ lattice and consequent increase of Li-ion vacancies. The origins of the abnormal grain growth induced by the diffusion of Al were explained in relation to the atomic surface structures of LLZ and the presence of intergranular liquid phase.

11:10 AM

(ICACC-S6-030-2015) MXene 'Clay': High capacitance from Ti3C2 electrodes produced by rolling

M. Ghidiu*[1]; M. Lukatskaya[1]; M. Zhao[1]; Y. Gogotsi[1]; M. W. Barsoum[1]; 1. Drexel University, USA

MXenes, a relatively new family of 2D materials produced from MAX phases (nanolayered transition metal carbides and nitrides) by hydrofluoric acid (HF) etching, have been demonstrated as active materials in Li-ion batteries and electrochemical capacitors. However, since HF is relatively dangerous and is potentially damaging to the MXenes themselves, an alternative etching route was sought. We have devised a new method for producing MXenes from a mixture of hydrochloric acid and various metal salts. MAX phases were reacted in heated etchant for 16-48 h, followed by washing with distilled water. This procedure yielded a clay-like sediment, which was moldable into shapes that could be dried into conductive solids. Upon hydration, the material swells, and upon drying, it shrinks. When wet, this 'clay' could be simply rolled into freestanding, flexible films without binders or additives. When the latter were used as electrodes in supercapacitors, capacitances of the order of 900 F/cm3 (almost 250 F/g) were measured, with good rate performance. Even films 75 μm thick (of lower density) exhibited capacitances on the order of 300 F/cm3. Such high volumetric capacitance has promising applications where volume is at a premium, such as mobile electronics or automobiles, and the new process is safer, more economical, and faster compared to previous methods.

S7: 9th International Symposium on Nanostructured Materials: Innovative Synthesis and Processing of Nanostructured, Nanocomposite and Hybrid Functional Materials for Energy, Health and Sustainability

Nanomaterials for Water-splitting I

Room: Coquina Salon B

Session Chairs: Ziqi Sun, University of Wollongong, Australia; Shaohua Shen, Xi'an Jiaotong University

8:30 AM

(ICACC-S7-017-2015) Serendipity or design of catalysts and photo-catalysts? (Invited)

P. Fornasiero*[1]; 1. University of Trieste, Italy

Heterogeneous transition metal catalysts are generally based on nanoparticles, that nowadays can be synthesize with uniform size and shape. The extraordinary advances in material science support a new vision for nanoscale-inspired design and synthesis of industrially important catalysts. This precise structural and morphological control, coupled with the possibility to modulate the metal-support interactions, allowed us to have a step change increase in the activity, selectivity and stability of many industrially and environmentally important catalysts. In this context, renewable energy conversion, pollution prevention and control are the real challenge of the 21st century and the focus of the present talk.

9:00 AM

(ICACC-S7-018-2015) Enhanced Water Splitting at Thin Film WO_3 Photoanodes Bearing Plasmonic Nanoparticles (Invited)

R. Solarska*[1]; K. Bienkowski[1]; J. Augustynski[1]; 1. University of Warsaw, Poland

An effective solar light-driven water splitting in photo-electrochemical devices requires use of materials which combine high photo-conversion efficiency and long term stability. For the latter reason the choice of the suitable systems is restricted to the semiconducting oxides that, in most cases, do not undergo photo-corrosion in aqueous solutions and are able to absorb efficiently the visible light. However, the low optical absorption coefficients near the fundamental band edge for a number of semiconductors characterized by an indirect optical transition determine the extent of solar light absorption by many photo-anode materials. Therefore, incoupling of light into semiconductor films by scattering from plasmonic nanostructures and/or resonant coupling of the plasmonic near field to the semiconductor, have a potential to improve the effectiveness of the photocurrent spectral response of the employed photoanode. Ongoing efforts devoted to minimize the bias voltage required to perform visible light-driven photo-oxidation of water at NP WO_3 photoanodes will be discussed. These include the use of dopants and incorporation of plasmonic metal nanostructures allowing to enhance the light capture by the WO_3 films.

9:20 AM

(ICACC-S7-019-2015) One-Step Fabrication of Functionalized Graphene Materials via Submerged Liquid Plasma (SLP) in Solvent under Ambient Conditions (Invited)

M. Yoshimura*[1]; J. Senthilnathan[1]; K. SanjeevaRao[1]; 1. National Cheng Kung Univ., Taiwan

We propose herewith "Submerged Liquid Plasma (SLP)" technique for direct formation of nanostructured carbon material (1,2) and nitrogen polymers (3) at ambient conditions. The SLP process provides number of advantages which includes (a) simple reaction set up (b) reaction can be carried out at ambient conditions (c) periodic collection of samples gives clear information about the product (d) simple procedure and less operating cost. In the present study, we utilized SLP technique for the direct synthesis of Nitrogen functionalized Graphene Nano sheets by these SLP in acetonitrile liquids. We could confirm the functionalized Graphenes are electrochemically active. Then we are challenging to prepare the Nano-particle/Graphene hybrids by this SLP methods. Low temperature and/or Soft Processing of nanostructured carbon and NPs by SLP process will open up new possibilities for the development of functionalized/hybrid nanostructured carbon materials for various applications including Photovoltaic and Solar Cell areas.

9:50 AM

(ICACC-S7-020-2015) Cu-doped ZnO with the addition of graphene for use as photocatalyst

S. Hsieh*[1]; J. Ting[1]; 1. National Cheng Kung University, Taiwan

We report a novel Cu-doped ZnO/graphene nanocomposite photocatalyst that exists enhanced efficiency. Nanostructured Cu-doped ZnO was first synthesized using a hydrothermal method. The hydrothermal bath consisted of zinc acetylacetonate, distilled water, ethanol, citric acid, CuSO4-5H2O and with or without the addition of graphene. In selected samples, the graphene was doped with nitrogen. The material characteristics of the obtained nanocomposite samples were characterized using X-ray diffracometry, scanning-electron microscopy, Brunauer–Emmett–Teller, X-ray photoelectron spectroscopy, UV-visible spectroscopy, Raman spectroscopy. The photocatalytic efficiency was evaluated through the degradation of methyl blue under UV and visible light. Effect of materials characteristics on the photocatalyst behavior is addressed and discussed.

Nanomaterials for Water-splitting II

Room: Coquina Salon B

Session Chairs: Renata Solarska, University of Warsaw; Paolo Fornasiero, University of Trieste

10:30 AM

(ICACC-S7-021-2015) Nanostructure engineering of metal oxides for solar energy harvesting (Invited)

Z. Sun*[1]; J. Kim[1]; S. Dou[1]; 1. University of Wollongong, Australia, Australia

Metal oxides are known to possess unique functionalities that are absent or inferior in other solid materials. Their nanostructures have emerged as an important class of materials with a rich collection of properties and general potential for device applications. In this presentation, we will show our recent results on the rational design of the diverse morphologies of the typical metal oxides, like TiO2, ZnO, WO3, etc, with 1D, 2D, and 3D architectures, based on the precise controlling of the starting solutions, to meet the materials requirements for high-performance solar energy harvesting devices. Particularly, a generalized and fundamental approach to molecular self-assembly synthesis of ultrathin 2D nanosheets of transition metal oxides is developed by rationally employing lamellar reverse micelles. These metal oxide nanostructured materials offer huge surface to volume ratios, favourable transport properties, altered physical properties, and confined quantum size effects, and thus boost the performance of the solar energy harvesting.

11:00 AM

(ICACC-S7-022-2015) Structural effect of TiO2-Hematite multilayer anode on water splitting efficiency fabricated by PECVD

M. Pyeon*[1]; T. Hwang[2]; K. Moon[3]; S. Mathur[1]; 1. University of Cologne, Germany; 2. Korea Institute of Industrial Technology, Korea (the Republic of); 3. Korea Institute of Industrial Technology, Korea (the Republic of)

PEC (Photoelectrochemical) solar water splitting is one of the most interested research topics. As a candidate material, hematite (α-Fe2O3) has been considered intensively due to its chemical stability, abundance and appropriate band structure. However, to prevent recombination of photo-excited electron-hole pair which can reduce photon-to-hydrogen conversion efficiency, fabricating heterogeneous multilayer is studied. Here we present an effect on water splitting efficiency of TiO2-hematite multilayer. The multilayers were fabricated by plasma enhanced chemical vapor deposition with patterned mask. To see the difference between multilayers with- and without- pattern, we designed several kinds of masks. Moreover, the sequence of fabricating multilayer and the thickness of films are also controlled and examined.

11:20 AM

(ICACC-S7-023-2015) Atomic/Molecular Layer Deposited Inorganic-Organic Hybrid Thin Films for Enhanced Thermoelectrics (Invited)

M. Karppinen*[1]; 1. Aalto University, Finland

Nanostructuring is an important approach to e.g. enhance the performance of thermoelectric materials; it potentially works as a means to suppress thermal conductivity without significantly reducing electrical conductivity of the material. In our nanoengineering approach we employ a combined ALD (atomic layer deposition) and MLD (molecular layer deposition) technique to fabricate hybrid inorganic-organic thin films such as (Zn,Al)O:HQ and (Ti,Nb)O2:HQ (HQ stands for hydroquinone) in which periodically introduced thinner organic layers between thicker thermoelectric oxide layers hinder the phonon transport thereby enhancing the thermoelectric figure-of-merit of the material. Here in this presentation I discuss the future potential of the hybrid inorganic-organic superlattice and nanolaminate thin-film structures in thermoelectrics and other energy-related applications. The ALD/MLD technique provides us an elegant and versatile tool to realize such new materials in a highly controlled and industrially feasible way.

11:50 AM

(ICACC-S7-024-2015) Surface engineered doping of hematite nanorod arrays for efficient solar water splitting (Invited)

S. Shen*[1]; 1. Xi'an Jiaotong University, China

Hematite (α-Fe2O3), commonly known as "rust", has emerged as a promising candidate for photoelectrochemical (PEC) water splitting due to its favorable physicochemical properties of narrow band gap (2.1–2.2 eV), chemical stability, nontoxicity, abundance, and low cost. Given the narrow band gap enabling excellent optical absorption, increased charge carrier density and accelerated surface oxidation reaction kinetics become the key points for improved photoelectrochemical performances for α-Fe2O3 photoanodes. In this study, a facile and inexpensive method was demonstrated to develop core/shell structured α-Fe2O3 nanorod arrays. The obtained α-Fe2O3/AgxFe2-xO3 core/shell nanorod films demonstrated much higher photoelectrochemical performances as photoanodes than the pristine α-Fe2O3 nanorod film, especially in the visible light region; the incident photon to charge carrier efficiency (IPCE) at 400 nm was increased from 2.2% to 8.4% at 1.23 V vs. RHE. Mott-Schottky analysis and X-ray absorption spectra revealed that the Ag-doped overlayer not only increased the carrier density in the near-surface region but also accelerated the surface oxidative reaction kinetics, synergistically contributing to the improved photoelectrochemical performances.

S8: 9th International Symposium on Advanced Processing and Manufacturing Technologies for Structural and Multifunctional Materials and Systems (APMT9)

Novel Ceramic Processing IV

Room: Coquina Salon A
Session Chairs: Rajendra Bordia, Clemson University; Satoshi Tanaka, Nagaoka University of Technology

8:30 AM

(ICACC-S8-029-2015) Analysis and Simulation Guided Processing of Hierarchical Porous Ceramics (Invited)

R. K. Bordia*[1]; A. Lichtner[2]; H. Shang[2]; D. Roussel[3]; D. Jauffres[3]; C. Martin[3]; 1. Clemson University, USA; 2. University of Washington, USA; 3. Université de Grenoble - Alpes, France

Our current research is focused on developing processing strategies to control the microstructure of ceramics at different length scales. One of the focal areas is porous ceramics. Many of the applications of porous ceramics demand optimization of a multitude of properties some of which have conflicting requirements on the microstructure. Materials with designed anisotropic and/or hierarchical microstructures have the potential to optimally address the requirements. We will present results from a collaborative project focused on microstructural control in hierarchical and/or anisotropic porous ceramics. Porous ceramics are used in a broad range of technologies including electrochemical applications like electrodes for solid oxide fuel cells. In this case, the properties of interest are mechanical, thermal, electrical and ionic conductivity, gas diffusion and chemical reactivity. In this presentation, results will be presented on the processing approaches to make these designed microstructures, the quantification of the 3D microstructure at different length scales and meso-scale simulations to simulate the mechanical and transport properties and their comparison with experimental results. The coupling between 3D images obtained by X-ray tomography and meso-scale simulations will also be highlighted.

9:00 AM

(ICACC-S8-030-2015) Design and Fabrication of high-temperature heat exchangers and microreactors

C. Lewinsohn*[1]; J. Fellows[1]; H. Anderson[1]; M. Wilson[1]; 1. Ceramatec, Inc., USA

Recovery of energy from combustion gas or processes is usually a critical feature of affordable high-temperature power generation or chemical processing. Currently, the maximum temperatures that heat exchangers can withstand are limited by oxidation or creep of the materials of construction. Ceramatec has designed, fabricated, and tested microchannel heat exchangers capable of reliable operation at high temperature using a variety of ceramic materials. The benefits of the tube-fin designs will be discussed. The efficiency and potential costs savings obtained by increasing allowable temperatures will be presented. Basic features of the design methodology will be discussed, illustrating additional benefits of the designs due to their compact size. The reliability of the designs will be compared with conventional shell-and-tube designs. Assembly and environmental degradation considerations will be discussed.

9:20 AM

(ICACC-S8-031-2015) Slip-Casting by Water-Absorbing Resin Mold Enables Crack-Free and Even-Packing Ceramic Molding System

A. Matsumoto*[1]; 1. TOTO LTD, Japan

Only plaster mold has been used for non-pressurized slip casting of ceramics in these 200 years. But CaSO42H2O is slightly water-soluble, so even adhesion to green body is not expected. So plaster mold with short mold life causes crack occurrence by drying shrinkage in mold and uneven-packing by casting pressure loss at mold surface. In this study, new water-absorbing resin mold with semi-permanent mold life is proposed, which enables crack-free (no drying shrinkage in mold) and even-packing ceramic molding system for large or complicated-shaped product. And water-absorption speed of this new resin mold can be controlled within a wide range, which also enables a product having partially different thicknesses.

9:40 AM

(ICACC-S8-032-2015) Additive Manufacturing - Strategies for the Selective Volume Sintering of Ceramics

T. Mühler*[1]; J. G. Heinrich[1]; J. Günster[2]; 1. Clausthal University of Technology, Germany; 2. Federal Institute for Materials Research and Testing, Germany

By dealing with the basic physics a novel way can be realized to generate a free formed ceramic body, not like common layer by layer, but directly by Selective Volume Sintering (SVS) in a compact block of ceramic powder. To penetrate with laser light into the volume of a ceramic powder compact it is necessary to investigate the light scattering properties of ceramic powders. Compared to polymers and metals, ceramic materials are unique as they offer a wide optical window of transparency. The optical window typically ranges from below 0.3 μm up to 5μm wavelength. In the present study thin layers of quartz glass (SiO_2) particles have been prepared. As a function of layer thickness and the particle size, transmission and reflection spectra in a wavelength range between 0.5 and 2.5 μm have been recorded. Depending on the respective particle size and by choosing a proper relation between particle size and wavelength of the incident laser radiation, it is found that light can penetrate a powder compact up to a depth of a few millimeters. With an adjustment of the light absorption properties of the compact the initiation of sintering in the volume of the compact is possible. First samples will be shown and evaluated.

10:20 AM

(ICACC-S8-033-2015) Manufacturing Complex-Shaped Ceramic Components with Aligned Microstructural Features through Room-Temperature Injection Molding and 3D Printing of Ceramic Suspension Gels (CeraSGels)

L. Rueschhoff*[1]; J. P. Youngblood[1]; R. W. Trice[1]; 1. Purdue University, USA

A novel processing technique of injection molding ceramic suspension gels (CeraSGels) at room temperature is proposed to overcome the forming difficulties associated with various ceramic systems. CeraSGels are a combination of a ceramic powder, dispersant, water-soluble polymer and water. CeraSGels have recently been shown to be optimal 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 ceramics since near-net complex shapes can be easily formed. These CeraSGels can also be tailored for a novel forming processes using a modified syringe type 3D printer to form complex-shaped geometries with high sintered densities (>99%). Additionally, the shear and flow stresses generated during mold filling and syringe 3D printing can be used to align high aspect ratio microstructural features. Advanced analysis software has been used to visualize flow and shear stresses for various mold designs. This alignment of features has been

quantified using optical analysis and mechanical properties have been measured.

10:40 AM

(ICACC-S8-034-2015) Development of 3-dimensional orientation in $MgTi_2O_5$ by tape casting in a strong magnetic field

T. S. Suzuki*[1]; Y. SUZUKI[2]; T. UCHIKOSHI[1]; Y. SAKKA[1]; 1. National Institute for Materials Science, Japan; 2. University of Tsukuba, Japan

The physical properties of a crystal depend on the direction of the crystal axis. Tri- or bi-axially orientation is expected to obtain the single crystal-like ceramics with superior properties compared with the random orientation ceramics. The colloidal processing in a strong magnetic field was able to control the crystallographic orientation even in diamagnetic ceramics. In this process, a strong magnetic field is applied to the particles in a stable suspension. The particles become rotated to an angle that minimizes the system energy and one-dimensional orientation can be achieved. We have already reported that two dimensional orientation could be control by using both anisometric particles and a strong magnetic field, but it is difficult to distinguish the a and b axis in bismuth titanate. In this study, we attempt to control three dimensional orientation of $MgTi_2O_5$ (MT2) by using the rod-like particles and a strong magnetic field. MT2 has orthorhombic psuedobrookite-type structure and shows anisotropic thermal expansion. Aqueous slurries were prepared from the MT2 granular powder and 50 wt% rod-like MT2 particles. The tape casting was performed in a strong 12T magnetic field. The b-axis of MT2 was aligned parallel to the magnetic field and the a-axis is aligned by the geometric effect during tape casting. We achieved to control three dimensional orientation by a magnetic field.

11:00 AM

(ICACC-S8-035-2015) Transparent textured ceramics fabricated by colloidal processing in strong magnetic field

S. Tanaka*[1]; T. Takahashi[1]; T. Tanaka[1]; K. Uematsu[1]; 1. Nagaoka University of Technology, Japan

Transparent polycrystalline ceramics with anisotropic crystal system was prepared by crystal orientation technique using a colloidal processing in magnetic field and subsequent sintering. Scattering of incident light at grain boundary and pores could be prevented by crystal orientation and subsequent densification. In this study, we focused on strontium barium niobate (SrxBa1-xNb2O6, SBN), which is a one of candidate materials of lead-free electro-optic materials. In experimental, SBN powder was synthesized by solid state reaction. In order to obtain transparency, aggregates in synthesized powder were carefully removed by the sedimentation treatment. A mold with slurry was set in a strong magnetic field 10T until drying. After drying, a particle-oriented powder compact is sintered in vacuum, then it was sintered by hot isostatic pressing. The Lotgering factor of SBN ceramics, which is degree of orientation, is achieved to 1.0. The relative density is 99.9%. The transmittance of the crystal-oriented SBN was 50% at 1500 nm. This material showed electro-optic effect by applying electrical field. Fabrication using strong magnetic field and subsequent densification process is very effective for crystal-oriented ceramics with transparency.

11:20 AM

(ICACC-S8-036-2015) Estimation of State Transition Probability Matrix of Coordination Number Distribution of Particles in Ceramic Powder Compact

K. Yasuda*[1]; 1. Tokyo Institute of Technology, Japan

The author has already reported an experimental data of the coordination number distribution of particles in ceramic powder compact, and discussed the change in the distribution with increasing the number of cycles of cold isostatic pressing. In this presentation, the author analyzes the data with stationary Markov process and estimates the state transition probability matrix to express the change. The resultant matrix shows that even coordination numbers are more stable than odd ones.

S9: Porous Ceramics: Novel Developments and Applications

Membranes and High SSA Ceramics II

Room: Coquina Salon H

Session Chair: Ingolf Voigt, Fraunhofer Institute for Ceramic Technology and Systems IKTS

8:30 AM

(ICACC-S9-009-2015) Polymer-Derived Ceramic (PDC) Aerogels (Invited)

G. Soraru*[1]; 1. University of Trento, Italy

Since the first discovery of silica aerogels by Kistler in 1932 many other oxide, organic (natural and synthetic), hybrid O/I, and C aerogels have been reported. One common feature of these materials is their poor high temperature stability and, in this case, carbide or nitride aerogels would be preferred. This paper shows how novel Si-C, Si-O-C and Si-O-C-N aerogels can be synthesized from preceramic polymers (PDC route). The process allows tailoring the porosity, pore size and particle size by the proper choice of few synthesis parameters. These aerogels maintain high porosity and surface are up to ultra-high temperatures, 2000°C. PDC aerogels also show functional properties and possible application as gas sensors or anodes for Li-ion batteries will be shown. Finally, preliminary results of the synthesis of B-N, Al-N and Si-B-C-N aerogels will also be presented.

9:00 AM

(ICACC-S9-010-2015) Hierarchically structured Silicon Carbide derived Carbon monoliths for Catalyst support structures

B. Zierath*[1]; A. Kern[2]; B. Etzold[2]; P. Greil[1]; T. Fey[1]; 1. Friedrich-Alexander-University Erlangen-Nuremberg, Germany; 2. Friedrich-Alexander-University Erlangen-Nuremberg, Germany

The authors present the production of highly porous cellular silicon carbides (SiC) with micrometer porosity which was converted to carbide derived carbon (CDC) with additional nanometer porosity to provide a catalyst support structure. The SiC was produced by uniaxial pressing of silicon powder, paper derived carbon fibers and phenolic resin followed by gas- or liquid-phase sintering between 1300°C and 1550°C. The conversion to CDC is carried out by a chlorination step where the silicon is extracted from the SiC. This near net shape process leads to a hierarchically structured material with high porosity with up to 60% and 90% for SiC respectively CDC. The four-point-bending test determined a mechanical strength of 45 MPa for SiC and 2,5 MPa CDC. The microstructure and the high porosity lead to a high specific surface area of 25 m^2/g for SiC and up to 700 m^2/g for SiC-CDC. The heat conductivity measured by the laser-flash method shows up 5 W/(m*K) for SiC and 0,5 W/(m*K) for CDC. The high specific surface area, the high mechanical strength and the good heat conductivity provide excellent qualifications for a catalyst support structure.

9:20 AM

(ICACC-S9-011-2015) Shaping of porous CaO-based sorbents for CO_2 capture

B. Michielsen*[1]; J. Deckx[1]; J. Sysmans[1]; S. Mullens[1]; 1. Flemish Institute for Technological Research, Belgium

Calcium looping is a CO_2 capture technology which uses solid CaO-based sorbents to remove CO_2 from flue gases and results in a concentrated CO_2 stream. It takes advantage of the reversible gas–solid reaction between CO_2 and CaO to form $CaCO_3$. We have used the vibrational droplet coagulation technology to shape different calcium cabonates into porous microspheres. This technology results in microspheres between 100 and 3000 μm with a highly uniform size distribution and high sphericity. A laminary flow of a water based suspension containing the $CaCO_3$ powder and a coagulating agent is broken up into droplets by introducing a vibration on the liquid. These droplets solidify upon entering a hardening solution. Afterwards they are dried and thermally treated to obtain the final prous sorbent. We have studied the process parameters affecting the microsphere formation, starting from both a commercial $CaCO_3$ powder and $CaCO_3$ from a food company's waste stream . The size of the microspheres was changed by controlling process parameters such as the nozzle size, frequency, powder loading and feed flow. The porosity of the sorbents was optimized by tuning the bindersystem and introducing additives. The CO_2 sorption capacity of the microspheres was determined in a modified TGA-instrument. The long-term stability and sorption capacity of the sorbent over several cycles was determined as well.

9:40 AM

(ICACC-S9-012-2015) Structuring of AlPOs and Zeolite Powders into Hierarchically Porous CO2 Adsorbents

F. Akhtar*[1]; 1. Luleå University of Technology, Sweden

Hierarchically porous structured monoliths and laminates have been reported with high performance for CO2 separation from N2. Such structured monoliths and laminates with tailored porosity at various length scales combined high volumetric efficiency, good mass and heat transfer, rapid adsorption/desorption kinetics and structural integrity. Here, we demonstrate a binder-less approach to consolidate 8-ring window zeolite and aluminophosphate (AlPO4's) powders into mechanically strong monoliths with high CO2 uptake capacity and CO2-over-N2 selectivity, and a rapid adsorption and release kinetics. Adsorption isotherms of CO2 and N2 were used to predict the co-adsorption of CO2 and N2 using ideal adsorbed solution theory (IAST). The IAST predictions showed that monolithic zeolite adsorbents of partially K exchanged NaA could reach an extraordinarily high CO2-over-N2 selectivity in a binary mixture with a composition similar to flue gas. Furthermore, zeolite monoliths showed high tensile strength of 2.2 MPa. AlPO-17 and AlPO-53 monoliths were consolidated by the binder-less process with a tensile strength over 1 MPa. AlPO-17 monoliths showed high CO2 adsorption capacity while AlPO-53 exhibited high CO2-over-N2 selectivity. Cyclic CO2 adsorption tests showed that AlPO4 monoliths required less energy for regeneration compared to zeolite and could be regenerated to their full capacity at low pressures.

Innovations in Processing Methods and Synthesis of Porous Ceramics II

Room: Coquina Salon H

Session Chair: Tobias Fey, Lehrstuhl Glas und Keramik

10:20 AM

(ICACC-S9-013-2015) Processing, Structure and Thermal Properties of Solid-state Sintered SiC Foams by Aqueous Gelcasting (Invited)

G. Sundararajan*[1]; D. Jana[2]; K. Chattopadhyay[3]; 1. ARCI, India; 2. ARCI, India; 3. IISc, India

Closed cell silicon carbide (SiC) foams are processed through direct foaming followed by gelcasting. Monomer weight percentage in gelcasting batches are tailored not only to improve the strength of the porous bodies in the green state but also to obtain carbon additive for solid-state sintering of SiC through decomposition of the gel. Closed cell foams with porosity ranges between 56 and 88 vol. % are made by control of gelcasting parameters including surfactant concentration, slurry viscosity and foaming time. The investigation of foam structure by X-ray tomography shows that the proportions of large size cell get increased with increase in overall porosity of the foam. Microstructural observation by SEM also reveals that closely packed sharp interfaced grains gradually changes to smooth interfaced grains as the porosity of the foams is increased from 55 to 80 vol. %. The effect of porosity on thermal properties of SiC foams is also investigated. Our study shows that effective thermal conductivity of SiC foams varies approximately linearly with relative density of foams in the density range of 0.12 to 0.34. The linear dependence of thermal conductivity with relative density at different temperature is observed to be in agreement with the Ashby's model.

10:50 AM

(ICACC-S9-014-2015) Three-dimensional printing of preceramic polymers and fillers

A. Zocca*[1]; G. Franchin[1]; E. Hamada[1]; C. M. Gomes[2]; E. Bernardo[2]; M. A. Lopez Heredia[3]; C. Knabe[3]; J. Günster[2]; P. Colombo[1]; 1. University of Padova, Italy; 2. BAM Bundesanstalt für Materialforschung und –prüfung, Germany; 3. Philipps University Marburg, Germany

The polymer-derived route has been used as an approach for the production of ceramic materials. A novel approach for the production of porous polymer-derived ceramics by additive manufacturing will be discussed, which is the application of the three-dimensional printing processes to preceramic polymers followed by pyrolysis and thus ceramization. The implementation of two technologies to the printing of preceramic polymers and fillers will be presented: a powder-based and an extrusion-based processes will be discussed and compared. Firstly, the powder-based three-dimensional printing of a filler-free preceramic polymer, giving a SiOC amorphous phase upon pyrolysis in inert atmosphere, will be described. Furthermore, 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 in air. Different phase assemblages can be achieved by incorporation of calcium oxide and zinc oxide precursors, resulting in different bio-related properties, such as solubility and ions release. A proprietary apatite-wollastonite glass-ceramic was also mixed as inert filler to some of the compositions.The latest developments on the extrusion-based three-dimensional printing of pastes based on a preceramic polymer and fillers will be presented, together with the results for the powder-based process based on similar compositions.

11:10 AM

(ICACC-S9-015-2015) Controlling the Pore Structure of Freeze-Cast Preceramic Polymers

M. Naviroj*[1]; P. Colombo[1]; K. Faber[2]; 1. Northwestern University, USA; 2. Universita di Padova, Italy

Freeze casting has been shown to be a reliable method for fabricating porous ceramics with unique pore structures. In addition to the use of ceramic powders and slurries, preceramic polymers can also be used as precursors. Preceramic polymers allow for a broad selection of phase compositions that are unavailable with traditional powders. Additionally, varying solvents and processing conditions will allow for various pore structures to be generated, including dendritic morphologies and prismatic channels. In this study, polysiloxane is used as a precursor to fabricate SiOC while tert-butyl alcohol, cyclohexane, and camphene are used as solvents. Different processing conditions, such as polymer concentrations and temperature gradients, are used in order to study their effects on the pore structure. Mercury intrusion porosimetry and various imaging techniques are employed to gain a detailed understanding of the pores generated.

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: Ponce DeLeon
Session Chair: Anne Joulain, Pprime Institute - POITIERS

8:30 AM

(ICACC-S12-029-2015) A Genomic Approach to MAX Phases: An Overview (Invited)

W. Ching*[1]; 1. University of Missouri-Kansas City, USA

A comprehensive data base on 665 screened MAX (Mn+1AXn) phases with n = 1 – 4 has been established recently. The data contains accurate results on equilibrium crystals structures, elastic coefficients, bulk mechanical properties, electronic structure and bonding properties. All the experimentally reported phases are shown to be stable and many other equally stable phases with unusual properties can be explored in laboratories. In this talk, I focus on detailed analysis of correlations between the electronic structure (charge transfer, bond order, bond order density, density of states at Fermi level, etc.) and the mechanical properties (elastic coefficients Cij, bulk modulus K, shear modulus G, Young's modulus E, Poisson's ratio η and Pugh ratio G/K, etc.). This highly accurate database on MAX phases is used to validate the efficacy of data mining algorithms and machine learning tools with calculated properties as descriptors. It is shown that the total bond order density for the crystal and its components between various type of bonding (M-M, M-A, M-X, A-A) play a dominant role in the prediction. Further extension of the genomic approach will be discussed.

9:00 AM

(ICACC-S12-030-2015) Modeling of Fusion Zone Temperatures in ZrB_2-ZrC Ceramic Weld Pools

D. King*[1]; G. Hilmas[1]; W. G. Fahrenholtz[1]; 1. Missouri S&T, USA

Plasma arc welding has been used to join ZrB_2 containing 20 vol.% ZrC (ZrB_2-20ZrC). The resulting fusion zones exhibit exaggerated growth of ZrB_2, which can limit the mechanical properties of the welded ceramic. Therefore, there is a need to understand the grain growth and nucleation kinetics of the ceramic crystals that are forming in the fusion zone. Taking the power input from welding into consideration, the thermal gradients and temperatures within the fusion zone can be modeled. An IR camera was used to monitor the welding process where pixel brightness was correlated to the temperatures produced during welding. The measured temperatures were then compared with the predicted temperatures from the model. An accurate model for predicting temperature can then be applied for a better understanding of grain growth and nucleation kinetics. The presentation will discuss development of the model and implementation such that during welding the weld pool temperature allows for high nucleation rates while limiting growth of ZrB_2.

9:20 AM

(ICACC-S12-031-2015) Crack Healing Mechanism of Cr_2AlC Studied by X-ray Tomography

R. Pei*[1]; L. Shen[2]; W. Sloof[2]; S. van der Zwaag[3]; P. Mummery[4]; P. Withers[1]; 1. University of Manchester, United Kingdom; 2. Delft University of Technology, Netherlands; 3. Delft University of Technology, Netherlands; 4. University of Manchester, United Kingdom

The aim of this study is to reveal crack healing mechanism of Cr_2AlC through the non-destructive 3D characterization method, x-ray tomography. A pre-cracked Cr_2AlC cylindrical sample was annealed in a furnace at 1200°C for 30mins, 1h, 2h, 4h, 8h and 16h. The sample was scanned in-between each step in order to monitor the changes in terms of crack repair. The microstructure of oxide layer was characterized by scanning electron microscopy (SEM), with SEM images correlated to x-ray tomographic slices. The grain orientation relationship between oxide layer and matrix was further studied by electron backscattered diffraction (EBSD). The crack healing process of Cr_2AlC at 1200°C was recorded in 3D by x-ray tomography with a spatial resolution of $0.65\mu m^3$/voxel. The availability of oxygen plays a critical role in the overall healing process, whereas local healing behavior is related to crack surface morphology.

Novel Processing Methods (Bulk, Coatings and Thin Film)

Room: Ponce DeLeon
Session Chairs: Yanchun Zhou, Institute of Metal Research; Gregory Thompson, University of Alabama

10:20 AM

(ICACC-S12-032-2015) Synthesis and Characterization of Pulsed Cathodic Arc Deposited $Zr_2Al_3C_4$ Thin Films

C. Lai*[1]; M. Tucker[1]; J. Lu[1]; P. Eklund[1]; J. Rosen[1]; 1. Linköping University, Sweden

Transition metal carbides have long served as materials for protective coatings since they are in general hard, refractory, resistive to wear, chemically inert, and electrically and thermally conductive. Ternary carbides with inherently nanolaminated structures exhibit additional improvements such as better damage tolerance and good machinability. $Zr_2Al_3C_4$ is one of the nanolaminated carbides that has been synthesized and characterized in bulk previously, and that has been proposed as a potential candidate for protective coatings, see the recent review of Zhou *et al.* Here we have synthesized $Zr_2Al_3C_4$ thin films from pulsed cathodic arc deposition with multiple cathodes. The films presented were deposited with varied composition, at different substrate temperatures and on different substrate materials. From x-ray diffraction (XRD) analysis, peaks assigned to $Zr_2Al_3C_4$ phase appear when the flux ratio of (Al/C) > 0.75, and (Zr/C) ~ 0.50. XRD also shows suppression of competitive phases at higher growth temperature. Improved epitaxial growth is obtained on 4H-SiC(001) compared to α-Al_2O_3(001), with an orientation relation of $Zr_2Al_3C_4$[11-20] ‖ 4H-SiC[11-20] (in-plane) and $Zr_2Al_3C_4$[0001] ‖ 4H-SiC[0001] (out-of-plane). High resolution transmission electron microscopy images also validate the epitaxial growth from XRD with a c lattice parameter of ~22.2 Å.

10:40 AM

(ICACC-S12-033-2015) Ultra High Temperature Coatings for environmental protection of C_f/SiC composites

F. Uhlmann*[1]; C. Wilhelmi[1]; F. Wigger[2]; S. Schmidt-Wimmer[2]; S. Beyer[2]; 1. Airbus Group Innovations, Germany; 2. Airbus Defence and Space, Germany

During operation, combustion chambers (e.g. of orbital thrusters) have to withstand very high thermo-chemical and thermo-mechanical loads. Because of its low weight and high temperature stability, Ceramic Matrix Composites (e.g. C_f/SiC material fabricated via Polymer Infiltration and Pyrolysis process, PIP) are promising materials for this application. To protect carbon fibers as well as the SiC matrix against oxidation and ablation especially above 1650 °C, the application of an Environmental Barrier Coating (EBC) on the C_f/SiC composite material is mandatory. In this work a suitable Ultra High Temperature Coating (UHTC) based on ZrB_2 is developed. Microstructure, composition and adhesion behavior of the developed coatings were studied on flat samples. It was possible to create a dense and adherent ZrB_2 coating, where the thickness could be increased from ~300nm up to 20μm. Furthermore the oxidation and thermal shock behavior as well as the ablation resistance at elevated temperatures were investigated by long-term material testing in the Airbus Group Environmental Relevant Burner Rig (ERBURIG[K]) test facility using kerosene and oxygen as fuel to generate a combustion chamber-like environment. Pre-tests have shown that the coating shows well adhesion during testing and is therefore very promising for further investigations. The latest results of the study will be discussed in this presentation.

11:00 AM

(ICACC-S12-034-2015) ZrB2-SiC-ZrC ternary composites: co-effects of ZrC and SiC phases on microstructures and mechanical properties

G. Zhang*[1]; H. Liu[1]; J. Liu[1]; H. Ma[1]; H. Wu[2]; 1. Shanghai Institute of Ceramics, China; 2. Loughborough University, United Kingdom

ZrB2-SiC-ZrC ternary composites with different contents of SiC and ZrC are investigated in this work. Compared with ZrC, SiC grains grow slower, which is more effective to hinder the grain growth of ZrB2. The ternary ceramics ZrB2-20SiC-20ZrC (in vol.%) exhibits the finest and most stable microstructure due to the co-effects of SiC and ZrC. On the other hand, ZrC and SiC play different roles on mechanical properties. ZrC phase reduces the temperature at which the thermal stresses start to build up during cooling process from the sintering temperature for the ceramics (for example, ~650 °C for ZrB2-SiC-ZrC) according to a theory analysis and Raman spectroscopy measurement. Toughening effects are ~1 MPa m1/2 from the crack deflection induced by ZrC grains, which is the major toughening mechanism in ZrB2-ZrC-based ceramics. The strengths of ZrB2-SiC-ZrC ceramics are improved due to the small SiC cluster sizes and low residual stresses.

11:20 AM

(ICACC-S12-035-2015) Novel Synthesis, Mechanical Properties and Oxidation Behavior of Ultra-High-Temperature Ceramic (UHTC) Nanocomposites

L. Zhang*[1]; W. Wu[1]; A. L. Ortiz[2]; N. P. Padture[1]; 1. Brown University, USA; 2. University of Extremadura, Spain

Ultra-high-temperature ceramics (UHTCs) with microns-scale grains have been studied extensively in the literature. However, the influence of further reduction of the grain size to submicron or nano-scale on the mechanical properties and the oxidation resistance of UHTCs is still unclear. In this work, the effects of grain-refinement and oxygen content on the oxidation resistance and the room- and high-temperature mechanical properties of UHTC nanocomposites have been studied systematically. Composite nanopowders of ZrB2 with various additions of carbides (SiC, B4C, WC) have been prepared using high-energy ball-milling in ambient and inert atmospheres. Near-full density ZrB2-based UHTC nanocomposites of varying oxygen contents are obtained via spark-plasma sintering of the composite nanopowders, and are fully characterized using a battery of analytical techniques. Oxidation mechanisms in these nanocomposites are elucidated and related to their “microstructures”. Room-temperature mechanical properties (hardness, toughness, strength) and high-temperature strength of these nanocomposites have also been evaluated as a function of their “microstructures”. These results will be presented, together with a discussion of the effects of grain refinement and oxygen content on the oxidation-resistance mechanisms and mechanical properties of ZrB2-based UHTC nanocomposites.

11:40 AM

(ICACC-S12-036-2015) In situ synthesis of ZrB2/SiC hybrid composite for leading edges of hypersonic vehicles

N. Patra*[1]; D. Jayaseelan[1]; W. Lee[1]; 1. Imperial College London, South Kensington Campus, United Kingdom

Hybrid composite of zirconium diboride and silicon carbide (ZrB2/SiC) was synthesized via solution based process. ZrB2 was prepared by using polyethylene glycol, boric acid and a zirconium alkoxide while SiC was prepared using tetraethoxy orthosilicate (TEOS) and polyethylene glycol. The two different solutions finally mixed together for preparing the binary system. The synthesized hybrid composites were subjected to drying and crushed to powder. The as synthesized powders pyrolized and heat treated from 1000 to 1500 oC in argon. The pyrolized hybrid composites powder was characterized by FTIR, XRD, TG/DTA, SEM and TEM analysis. XRD revealed the hybrid composite consisted of ZrB2/SiC phases. SEM images show uniform distribution of SiC in the ZrB2 matrix. Fabrication, properties and performance of C/ZrB2/SiC composites will be investigated in further research.

S13: International Symposium on Advanced Ceramics and Composites for Sustainable Nuclear Energy and Fusion Energy

Thermo-structural Ceramics for Nuclear Systems

Room: Tomoka B

Session Chairs: Chad Parish, Oak Ridge National Lab; Ji-Jung Kai, National Tsing-Hua University

8:30 AM

(ICACC-S13-028-2015) Ultra-High Temperature Ceramics and their Potential in Nuclear Applications (Invited)

G. Hilmas*[1]; W. G. Fahrenholtz[1]; 1. Missouri University of Science and Technology, USA

Nuclear power currently comprises ~16% of the world’s electrical power generation while providing a low carbon footprint. As the world transitions toward the next generation of nuclear energy, ranging from accident-tolerant light water reactors to fusion energy, new advanced ceramics that can withstand extreme conditions including high temperatures, intense radiation, and chemically harsh environments will be needed. Ultra-high temperature ceramics (UHTCs) are family of transition metal borides, carbides, and nitrides with melting temperatures above 3000°C, and an inherent resistance to loss of properties in extreme environments. As an example, zirconium diboride (ZrB_2) based UHTCs possess a unique combination of properties including high strength (1000 MPa at RT and 300 MPa at 2300°C), high thermal conductivity (>120 W/m-K at RT and >70W/m-K at 2000°C), and resistance to oxidation and corrosion to temperatures beyond where metal alloys, currently used in reactor designs, are expected to fail. Further, ZrB_2 can be reactively processed from purified Zr (low Hf content) and isotopically pure B to produce either strongly neutron absorbing ($Zr10B_2$) or neutron transparent ($Zr11B_2$) ceramics. The presentation will focus on the processing and high temperature properties of ZrB_2-based ceramics while considering the potential for these unique ceramics in the future of nuclear power.

9:00 AM

(ICACC-S13-029-2015) The response of ZrB_2 to simulated plasma-facing material conditions of He irradiation at high temperatures

L. Garrison*[1]; G. L. Kulcinski[2]; 1. Oak Ridge National Laboratory, USA; 2. University of Wisconsin-Madison, USA

Ultra-high temperature ceramics (UHTC) are promising for nuclear applications because of their >3000 K melting temperatures, chemical resistance, and high hardness. Silicon carbide is an UHTC that is being extensively researched for uses in fission and fusion reactors. Zirconium diboride (ZrB_2) is another UHTC, but almost no data exists on the response of ZrB_2 to irradiation. In this work, samples of ZrB_2 were irradiated with 30 keV He^+ to fluences of 8.4×10^{17} and 5.0×10^{18} He/cm^2 at temperatures of 650, 750, and 850 °C in the Materials Irradiation Experiment at the University of Wisconsin Inertial Electrostatic Confinement (UW-IEC) Laboratory to simulate conditions of a plasma-facing component. The samples irradiated to the higher fluence developed severe morphology changes in the ion irradiated zone including rough, porous, and ripple structures, while some smoothing was observed on the same samples outside of the irradiated zone due being held at elevated temperatures for ~80 minutes. The ZrB_2 samples performed better than SiC samples previously irradiated to similar conditions in the HELIOS device at the UW-IEC Laboratory. This first look at ZrB_2 behavior under irradiation is promising and justifies further testing of this novel material.

9:20 AM

(ICACC-S13-030-2015) The microstructure and thermal oxidation effect of nuclear-grade graphite under 700-1600°C

C. Yang*[1]; W. Huang[1]; Z. Wang[1]; J. Kai[1]; 1. National Tsing-Hua University,Taiwan, Taiwan

In previous studies, the oxidation reaction could be divided into three regimes and the increasing trend of oxidation rate would saturate in Regime III (about 1000-1200°C).However; our study found that the oxidation rate would increase again above 1200°C.Therefore, we focused on the oxidation behaviour of nuclear graphite oxidized at very high temperature range (700-1600°C). Petroleum-based coke IG-110 and pitch-based coke NBG-18 were the materials selected in this study. The sample size was 10 mm diameter x 15 mm height. The 3-zone furnace and mass flow controller were used to oxidize these samples under 700 to 1600°C and 2L/min dry air. The specimens were characterized by SEM, Alpha-Step Profilometer, and the weight loss were also measured. Nuclear graphite was composed of filler and binder. Due to higher activation energy and greater crystallinity, filler oxidized lower than binder. Both SEM cross section images and step height results showed that the surface roughness increased with temperature. The increasing roughness implied more exposed area which led the oxidation rate to increase again. In conclusion, the oxidation rate would increase again above 1200°C because of different oxidation behaviour of filler and binder on the surface. In other words, the oxidation mechanism above 1200°C was different from the oxidation reaction under 1000°C to 1200°C.

9:40 AM

(ICACC-S13-031-2015) Multi-Scale Characterization of Irradiation-Induced Microstructural Changes of Fine-Grained Graphite

A. A. Campbell*[1]; Y. Katoh[1]; K. Takizawa[2]; 1. Oak Ridge National Laboratory, USA; 2. Currently at Oak Ridge National Laboratory, USA

Graphite is an important high-temperature structural material for use in fission and fusion nuclear reactors. Graphite has a complex microstructure due to the presence of features of various length scales (i.e. atomic spacing, nanometer-sized Mrozowski cracks, micrometer-sized pores). The exposure of graphite to irradiation results in significant microstructural changes, which lead to dimensional changes, but these changes are not consistent between various graphite grades due to the differences of the pre-irradiation microstructure. The difficulty in determining the microstructure dependence of irradiation-induced dimensional changes is that there is no single analysis technique that can investigate all the relevant features at all their characteristic sizes. Work is currently being conducted to determine a suite of analysis techniques that, when the results are combined, will give a more comprehensive understanding of the many microstructural features present in graphite. This presentation will first discuss the analysis techniques that are being used to investigate these various features. Then the results of the microstructural changes of two graphites (G347A and G458A from Tokai Carbon Co., LTD.), irradiated in the High Flux Isotope Reactor at Oak Ridge National Laboratory at temperatures from 250°C-800°C and fluences of $4.4\text{-}41\times10^{25}$ n/m^2 [E>0.1MeV], will be presented.

10:20 AM

(ICACC-S13-032-2015) Potential and Opportunities for MAX Phase in Nuclear Applications (Invited)

D. J. Tallman[1]; E. N. Hoffman[2]; E. N. Caspi[1]; B. Garcia-Diaz[2]; G. Kohse[3]; R. L. Sindelar[2]; M. W. Barsoum*[1]; 1. Drexel University, USA; 2. Savannah River Site, USA; 3. Massachusetts's Institute of Technology, USA

Advanced materials are required to meet growing demands posed by next generation nuclear reactor designs, including long term operation in extreme environments of elevated temperatures, corrosive media, and fast neutron fluences with up to 100 displacements per atom. Aging fleets of current reactors also call for redesigned fuel cladding materials to provide improved protection during loss of coolant accidents and improve fuel assembly longevity. The Mn+1AXn phases have shown potential for use in such extreme environments because of their unique combination of high fracture toughness values, high thermal conductivities, machinability, oxidation resistance, and ion irradiation damage tolerance. Herein we report for the first time on the effect of neutron irradiation of up to 0.5 dpa at 300, 500, 700 and 1000 °C on polycrystalline Ti3AlC2, Ti2AlC, and Ti3SiC2. Evidence for irradiation induced dislocation loops and their effect on electrical resistivity is presented. X-ray diffraction refinement of the resultant microstructures is provided. Irradiation induced dissociation into TiC is observed to a great extent in Ti3AlC2. Based on the totality of our results, it is reasonable to assume that the MAX phases, especially Ti2AlC and Ti3SiC2, are promising materials for high temperature nuclear applications. Oxidation, creep and reactions between select MAX phases and zircaloy were also quantified and will be discussed.

10:50 AM

(ICACC-S13-033-2015) Corrosion-resistant nano-laminated ternary carbides for use in heavy liquid metal coolants (Invited)

K. Lambrinou*[1]; T. Lapauw[2]; A. Jianu[3]; A. Weisenburger[3]; J. Ejenstam[4]; P. Szakalos[4]; J. Wallenius[4]; E. Strom[5]; K. Vanmeensel[2]; J. Vleugels[2]; 1. SCK-CEN, Belgium; 2. KU Leuven, Belgium; 3. KIT, Germany; 4. KTH Royal Institute of Technology, Sweden; 5. Sandvik Materials Technology, Sweden

A primary concern in the development of accelerator-driven systems and Gen-IV lead-cooled fast reactors (LFRs) is the compatibility of the candidate structural steels with the heavy liquid metal (HLM) coolant and/or spallation target. For the MYRRHA system, the HLM coolant is the liquid lead–bismuth eutectic (LBE), a potentially corrosive medium for various nuclear grade steels. The inherent LBE corrosiveness is the driving force behind diverse research efforts aiming at the development of corrosion-resistant materials for certain applications. Since MAX phases show a superb corrosion resistance in contact with LBE, they are being assessed as candidate materials for the construction of LFR pump impellers. In the case of MYRRHA, the pump impeller should operate at ~270°C in contact with moderately-oxygenated ([O] > 7×10-7 mass%) fast-flowing LBE (v > 10 m/s locally on the impeller surface). Selected MAX phases are currently being screened with respect to their capability of meeting the targeted material property requirements, especially the high erosion resistance requested by the impeller application. This work gives a state-of-the-art overview of the processing and characterisation of selected MAX phases for the MYRRHA pump impeller. The MAX phases are produced via a powder metallurgical route and their performance is assessed by various mechanical and corrosion/erosion tests in LBE.

11:20 AM

(ICACC-S13-034-2015) The Effect of Neutron Irradiation on Ti2AlC, Ti3AlC2, and Ti3SiC2

D. J. Tallman*[1]; E. N. Hoffman[2]; E. N. Caspi[1]; B. Garcia-Diaz[2]; G. Kohse[3]; R. L. Sindelar[2]; M. W. Barsoum[1]; 1. Drexel University, USA; 2. Savannah River Site, USA; 3. Massachusetts's Institute of Technology, USA

Gen IV nuclear reactor designs require materials that can withstand long term operation in extreme environments of elevated temperatures, corrosive media, and fast neutron fluences (E>1MeV) with up to 100 displacements per atom (dpa). Full understanding of irradiation response is paramount to long-term, reliable service. The Mn+1AXn phases have shown potential for use in such extreme environments because of their unique combination of high fracture toughness values and thermal conductivities, machinability, oxidation resistance, and ion irradiation damage tolerance. Herein we report on the effect of neutron irradiation of up to 0.5 dpa at 300°C, 500 °C, 700 °C, and 1000 °C on Ti3AlC2, Ti2AlC, and Ti3SiC2. Evidence for irradiation induced dislocation loops and their effect on electrical resistivity is presented. Irradiation at 1000 °C results in the formation of large dislocation networks in Ti3SiC2. Lattice distortions are detected by X-ray diffraction refinement in the low temperature irradiations. Irradiation induced dissociation into TiC is seen with a great extent in Ti3AlC2. Based on the totality of our results, it is reasonable to assume that the MAX phases, especially Ti2AlC, are promising materials for high temperature nuclear applications.

11:40 AM

(ICACC-S13-035-2015) Neutron and ion irradiation response of $T_xAl_yC_z$ and Ti_3SiC_2 MAX phases

C. M. Parish*[1]; S. J. Zinkle[2]; C. Shih[1]; A. A. Campbell[1]; L. L. Snead[1]; D. N. Leonard[1]; G. Samolyuk[1]; Y. Osetskiy[1]; T. R. Watkins[1]; J. M. LeBeau[3]; X. Sang[3]; Y. Katoh[1]; 1. ORNL, USA; 2. University of Tennessee, USA; 3. North Carlina State University, USA

MAX phases, such as Ti3SiC2 and Ti2AlC, have properties that are intriguing for nuclear applications. However, both atomistic and phenomenological understandings of their response to high-dose, high-temperature irradiation is lacking. In this research, High-Flux Isotope Reactor (HFIR) neutron irradiations at 400°C to ~2 dpa (calculated as SiC) of commercial Ti2AlC (nominally) and Ti3SiC2 MAX phases and heavy-ion irradiations (4e15 cm-2, 10 MeV Au, 400°C) of the same materials are compared. Neutron irradiated materials suffered reductions in strength, thermal conductivity, and electrical conductivity. X-ray diffraction analyses indicated significant changes in the phases present in the Al-based material. Ion irradiations at 400°C to ~10 dpa followed by sub-angstrom-resolution aberration-corrected analytical scanning-transmission electron microscopy indicated formation of <2 nm sized defected zones in Ti3SiC2, and the formation of defect loops in Ti5Al2C3 and Ti2AlC. Density functional theory (DFT) approaches help to justify the energetics of these defects. The examined materials, in conclusion, suffer significant degradation at 2-10 dpa at 400°C. The observed neutron-induced degradation in thermophysical properties appears consistent with the as-irradiated micro structural change: specifically a transformation of these MAX-phase structures into a defective or TiC-like structure.

FS1: Geopolymers, Chemically Bonded Ceramics, Eco-friendly and Sustainable Materials

Conversion to Ceramics II

Room: Oceanview
Session Chair: Sylvie Rossignol, SPCTS

8:30 AM

(ICACC-FS1-014-2015) Microstructural investigation of carbothermally reacted geopolymer composites, made under specific alkaline conditions (Invited)

C. Bagci*[1]; G. P. Kutyla[2]; W. M. Kriven[2]; 1. Hitit University, Turkey; 2. University of Illinois, USA

A series of geopolymers were prepared using both KOH, CsOH alkaline solution by mixing metakaolin (Al2O3.2SiO2) and then a carbon source was added these geopolymers. Geopolymer test samples were hand fabricated to determine the best composition for carbothermal reduction, with and without carbon. The viscous and homogenous slurries was poured into a mold to obtain bar samples at ambient temperature and cured in a constant 50 °C temperature/humidity oven for 24 h. After determining the best composition for K and Cs-based geopolymer, these geopolymer compositions were carbothermally reacted under argon and nitrogen gas flow. The carbothermal reduction processes of the samples were carried out in an atmosphere controlled, tube furnace under argon and nitrogen flow of 5 cm3.min-1at temperatures varying between 1400-1550 °C for 2h. XRD and SEM analyses were used to determine transformation and morphology of all the products after carbothermal reduction. The results were briefly discussed with respect to the possibility of conversion of specific geopolymer composition into their carbide and nitride analogues.

9:00 AM

(ICACC-FS1-015-2015) HT Mechanical Properties of Alumina or Mullite Fiber/Weave Reinforced Geopolymer Composites (Invited)

S. S. Musil[1]; A. A. Kolchin[2]; S. T. Mileiko[2]; W. M. Kriven*[1]; 1. University of Illinois at Urbana-Champaign, USA; 2. Russian Academy of Sciences, Russian Federation

This body of research investigated several different reinforcement possibilities and characterized their mechanical performance in tension, flexure and flexural creep. Reinforcements can then be chosen based on the resulting properties to tailor the geopolymer matrix composites to a specific application condition. This study incorporated particulate, unidirectional fiber and woven fiber reinforcements. Sodium, potassium, and cesium-based geopolymer matrices were evaluated with cesium-based geopolymer showing great promise as a high temperature matrix material. It showed the best strength retention at elevated temperature, as well as a very low coefficient of thermal expansion when crystallized into pollucite. These qualities made cesium geopolymer the best choice for creep resistant applications. Cesium geopolymer binders were combined with unidirectional continuous polycrystalline mullite fibers (Nextel™ 720) and single crystal mullite fibers, then the matrix was crystallized to form cubic pollucite. Single crystal mullite fibers were obtained by the internal crystallization method and showed excellent creep resistance up to 1400 °C. High temperature flexural strength and flexural creep resistance of pollucite and polycrystalline/single-crystal fibers was evaluated at 1000-1400 °C.

9:30 AM

(ICACC-FS1-016-2015) Effect of Curing Conditions on Crystalline Phase Development of Heat-treated K/Cs Geopolymer (Invited)

A. Steveson*[1]; W. M. Kriven[2]; 1. University of Illinois at Urbana-Champaign, USA; 2. University of Illinois at Urbana-Champaign, USA

In high temperature environments, geopolymers crystallize into their thermodynamically preferred zeolite phases. In the case of the potassium-based geopolymer, leucite ($K_2O{\bullet}Al_2O_3{\bullet}4SiO_2$) forms and undergoes a deleterious phase transformation (between 450 and 650°C) in the process of cooling from crystallization temperatures (~1100°C). Cesium has previously been shown to be an effective dopant for stabilization of the high temperature cubic phase, which prevents the transformation. In this work, we correlate the environmental conditions during the intial solidification of the geopolymer gel to the development of the stabilized leucite phase from subsequent annealing heat treatment. Compositions of $(K_2O)_{1-x}{\bullet}(Cs_2O)_x{\bullet}Al_2O_3{\bullet}4SiO_2$; where x=0, 0.2, 0.4, 0.6, 0.8, 1; were cured at 50, 70, and 90°C for 24, 48, and 72 hours in sealed containers. Subsequent heat treatments were carried out at 1200°C for 3 hours. Powder X-ray diffractograms were collected and analyzed to identify present phases and determine structural parameters.

Novel Applications and Construction Materials I
Room: Oceanview
Session Chair: Hubert Rahier, Vrije Universiteit Brussel

10:20 AM

(ICACC-FS1-017-2015) Ammonia-borane geopolymer (AB-G) composite (Invited)

L. Schomborg[1]; Z. Assi[1]; J. Buhl[1]; C. H. Rüscher*[1]; M. Wark[2]; 1. University of Hannover, Germany; 2. University of Oldenburg, Germany

Boronhydrides have received some attention due to their remarkable gravimetric and volumetric hydrogen contents. However, there are technical problems for application as hydrogen storage, e.g. unfavourable hydrogen releasing temperature, slow releasing rates, formation of borazine and other volatile gases harmful to PEMFC applications, instabilities to moisture leading to uncontrollable hydrogen depletion, lack of reversibility. This has enforced the development of scarffold scenarios for a better handling like the enclosure of such materials in nanoporous materials: for example infusion of ammonia borane (NH3BH3, AB) in nanoporous silica, confined in silica hollow nanospheres, or the protection of the BH4-anion in the sodalite cage. In this sense it is a new approach to enclose such materials in geopolymer-type matices. It has recently been reported that NaBH4 (NB) could be easily recrystallized in geopolymer type matrices, which could be optimized for an easy hydrogen release of up to 80% of the amount obtained for pure NB. Here we are going to show that AB could be handled similarly.

10:50 AM

(ICACC-FS1-018-2015) Geopolymer binder for building systems effect of silica on geopolymer reactivity

S. Rossignol*[1]; F. Gouny[1]; 1. SPCTS, France

Currently, awareness of environmental aspects has grown in the building construction area particularly in the development of new environmentally friendly material. The association of construction materials such as wood and earth brick for the developpement of new building systems seems to be relevant. The problem of such structures (wood and earth) is cracks which can occur along the year at the interface between earth bricks and wood frame due to their hygroscopic properties. A binder that provides proper adhesion between earth and wood must be developed and geopolymer binder appears as a good candidate. This study is focused on the geopolymer binder understanding and particularly on the influence of nature and amount of silica in the binder. Several formulations have been synthesized with different kinds and amount of silica. The silica influence on the geopolymer formation kinetic has been investigated by infrared spectroscopy and NMR measurements. Results show that the available siliceous species at the early stage of the reaction governs the reaction kinetic and the nature of formed networked. Finally one of synthesized sample, which presents porosity, has been used for the manufacturing of a full scale wall. The ability of this formulation to stick on the both natural material was successfully evidenced by NMR results and the assembly present good mechanical properties.

11:10 AM

(ICACC-FS1-019-2015) Synthesis and Characterization of Geopolymer Nanoaggregates and Their Ion-exchange Properties (Invited)

D. Medpelli*[1]; D. Seo[1]; 1. Arizona State University, USA

Geopolymers are synthetic amorphous alkali-aluminosilicate materials whose 3D network structure is formed by corner-sharing AlO4/SiO4 tetrahedra, with charge-balancing Na and K ions loosely bound to the network structure. Recently it has been shown that these alkali cations can be exchanged with others, demonstrating the potential of geopolymers in catalysis and ion-exchange applications. The ion-exchange rate can depend upon the surface area of an ion-exchange material in contact with external ionic solutions. Herein we report the synthesis and microstructural properties of geopolymer nanoaggregates, their ion-exchange capacity for Ag+ ion and the kinetics of Ag+ ion release in comparison to bulk. PXRD, SEM, TEM, N2 sorption and DLS studies revealed that the nanoaggregates are amorphous, have the morphology similar to that of precipitated silica or fumed silica with a high surface area and porosity (BET surface area of 129 m2/g and BJH pore volume of 0.35 cm3g) and aggregate size typically between 200 to 800 nm. The kinetic studies were carried out by monitoring Ag+ and Na+ ion concentrations continuously in solution at various temperatures using ion-selective electrodes, eliminating the cumbersome elemental analysis. According to the results, it is speculated that the Ag-exchanged geopolymer aggregates can be used as an antimicrobial nanofillers incorporated in polymers or coatings.

FS5: Single Crystalline Materials for Electrical, Optical and Medical Applications

Ferro/piezo-electric II
Room: Tomoka C
Session Chair: Hiroaki Takeda, Tokyo Institute of Technology

8:30 AM

(ICACC-FS5-021-2015) Ferroelectric and relaxor BCTZ piezoelectric single crystals (Invited)

M. Maglione*[1]; F. Benabdallah[1]; P. Veber[1]; M. Prakasam[1]; O. Viraphong[1]; K. Shimamura[2]; 1. ICMCB-CNRS, France; 2. National Institute for Materials Science, Japan

The BaTiO3-BaZrO3-CaTiO3 (BCTZ) ternary system was recently shown to display very large piezoelectric parameters, promoting it as a possible alternative to lead-containing PZT. A full understanding of the origin of this strong piezoelectric activity requires large and high quality single crystals. We thus have grown centimeter-sized single crystals using top seeded solution growth. Accurate control of the chemistry was achieved using Electron probe Micro-Analysis (EPMA). Dielectric, ferroelectric and piezoelectric experiments evidenced a cross-over from ferroelectric state at high Ti content to relaxor one on increasing the Zr content. Such a cross-over is a strong support for models including structural fluctuations as the source of the electromechanical flexibility. This is a first step towards the improved understanding of the very large piezoelectric coefficients of such materials already reported in the literature, in particular their relation with the actual crystalline state.

9:00 AM

(ICACC-FS5-022-2015) Relaxor-based single crystals grown by continuous feeding (Invited)

K. Echizenya*[1]; M. Matsushita[1]; K. Nakamura[1]; Y. Tachi[2]; 1. JFE MINERAL COMPANY,LTD., Japan; 2. JFE MINERAL COMPANY,LTD., Japan

Relaxor-based single crystals such as Pb(Mg1/3Nb2/3)-PbTiO3 (PMN-PT) and Pb(In1/2Nb1/2)O3-Pb(Mg1/3Nb2/3)O3-PbTiO3 (PIN-PMN-PT) have attracted attention since they offer high electromechanical coupling factors (k_{33}>0.9). PMN-PT single crystals have been used for ultrasonic medical transducers to provide better image quality. PIN-PMN-PT single crystals exhibit stability suitable for high power applications. The single crystals can be grown by the conventional Bridgman technique. However, the compositional variation along the growth direction due to the segregation phenomena results in large fluctuations of the dielectric /piezoelectric properties. We have therefore developed a new continuous feed growth technique to eliminate the problem of compositional segregation. The main feature of this new technique is to continuously feed raw material into the melt during crystal growth. The melt composition can be controlled by optimizing the feed conditions such as the raw material composition and the feed rate to compensate for the compositional segregation. As a result, property uniformity has been dramatically improved along the length of the single crystal ingot compared to the conventional Bridgman technique. PMN-PT and PIN-PMN-PT single crystals of 80 mm in diameter and 200 mm in length have been successfully grown by this new continuous feed technique.

9:30 AM

(ICACC-FS5-023-2015) Hydrothermal Crystal Growth and applications (Invited)

A. Largeteau*[1]; 1. ICMCB-CNRS, France

Earlier high pressure was mainly used in synthesis of minerals from extraction of metals from ores and for crystal growth of α-quartz called as hydrothermal crystal growth. Hydrothermal crystal growth offers a complementary alternative to many of the classical techniques of crystal growth used to synthesize new materials and grow bulk crystals for specific applications. This specialized technique is often capable of growing crystals at temperatures well below their melting points and thus potentially offers routes to new phases or the growth of bulk crystals with less thermal strain. The hydrothermal process is utilized for growing a wide variety of crystals which are impossible to be grown by conventional technique because pressure helps to amplify the dissolution in solution in additive of temperature. α- Quartz type materials are one among the best known for piezoelectric applications. In the present talk, hydrothermal growth of Ge doped SiO2 crystals for piezoelectric applications and the general principle of high hydrostatic pressure with their diverse applications in various fields will be discussed.

Optical Materials I

Room: Tomoka C
Session Chair: Gisele Maxwell, Shasta Crystals Inc

10:20 AM

(ICACC-FS5-024-2015) Crystalline Phosphor Ceramic Plate for Next Generation Automobile Head Lamp (Invited)

D. Yoon*[1]; Y. Song[1]; 1. SungKyunKwan Univeristy, Korea (the Republic of)

White light-emitting diodes (LEDs) as next-generation light source have significant interest in global market owing to their outstanding characteristic such as environmental-friendly device, low energy-consumption, long life time and high brightness, compared to conventional light source. However, there are still several challenges to overcome in order to replace the conventional light applications. The inefficiency caused by operating of the device and the inability of encapsulants like silicone resin and epoxy resin lead to significant reduction due to thermal quenching. In this communication, we present the feasibility of using crystalline phosphor ceramic plate with nanostructured materials as a remote phosphor. By carefully designing the phosphor composition as well as controlling the sintering temperature, time, and thickness of plate is achieved. Impressively, the crystalline phosphor ceramic plate based LED is believed to lead to highly efficient luminescence properties as well as automobile head lamp.

10:50 AM

(ICACC-FS5-025-2015) Growth of Oxide and Nitride Phosphor Single Crystal using Gas Phase Method (Invited)

K. Toda*[1]; 1. Niigata university, Japan

Eu2+ and Ce3+ -activated many LED phosphors have been used in white LEDs as commercial phosphors. However, there are limited references on precise crystal structure data of LED phosphors using single crystal structure analysis and the doping site of activators in the lattices also has not yet been established definitely. In this study, LED phosphor single crystals are prepared by a novel vapor phase technique, which is gas and solid phase hybridized, and the detail crystal data of these phosphors are obtained by single-crystal structure analysis.

11:20 AM

(ICACC-FS5-026-2015) Garnet single crystals for efficient phosphor and optical isolator applications (Invited)

K. Shimamura*[1]; E. Víllora[1]; 1. National Institute for Materials Science, Japan

Optical technology progress in a wide range of applications, and still demands the further development. Here, novel single crystals with advantageous characteristics will be introduced. A new concept of high-brightness white LEDs based on Ce-doped $Y_3Al_5O_{12}$ (Ce:YAG) 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. Authors would like to thank to Koha Co., Ltd., and Fujikura Ltd., for the collaboration.

2nd European Union - USA Engineering Ceramics Summit

Advanced Ceramic Technologies: Current Status and Future Prospects IV

Room: Coquina Salon F
Session Chairs: Sanjay Mathur, University of Cologne; Jerzy Lis, AGH University of Science and Technology

8:30 AM

(ICACC-PRECS-021-2015) The UK Ceramic Community's Interaction with the EU and the USA: Learning from Both (Invited)

W. E. Lee*[1]; E. Saiz[1]; J. Binner[2]; 1. Imperial College London, United Kingdom; 2. Birmingham University, United Kingdom

The UK's ceramics academic community is thriving and playing key roles in several large European programmes funded through recent Framework VII and pending Horizon 2020 schemes. The large scale and success of such programmes including the support for exchange of personnel between countries and institutions is leading to improved research collaborations and training opportunities. The success of the Journal of the European Ceramic Society (JECS) and the funding available through the JECS Trust is also contributing to pan European ceramics projects. Funding for UK-USA projects in the ceramics field is less extensive so that collaborations between UK and USA partners are largely based on internal funding and as a result are on a smaller scale than those with the EU involving fewer partners. Some support from the military is available (e.g. from the Office of Naval Research Global and the US Army Engineering Research and Development Centre) and National Science Foundation/Engineering and Physical Sciences Research Council (EPSRC) and Department of Energy/EPSRC calls have been made in the materials and nuclear areas but opportunities more specific to ceramics should exist.

9:00 AM

(ICACC-PRECS-022-2015) The experiences in research and transfer of innovative high tech ceramic technologies in Poland (Invited)

J. Lis*[1]; 1. AGh University of Science and Technology, Poland

The paper presents an actual status and nearest development perspectives of ceramic industry in Poland with the examples of cooperation between companies and research university centers in commercialization of new High Tech Ceramics solutions. The author shows: (i) applications of new high tech materials in traditional ceramic industry like production of tiles, sanitary ceramics, refractories or electro-ceramics and (ii) developing of new innovated companies selling high-tech ceramic products. The discussion is based on experience of the Faculty of Materials Science and Ceramics, AGH University of Science and Technology (AGH UST). AGH UST is an important center for the development and transfer of innovative technologies in Poland, also associated with the ceramic industry. In order to create of mechanisms facilitating and intensifying the transfer of innovative technologies from AGH UST to entrepreneurs and other external institutions, some of the institutional tools like the Centre for Transfer of Technologies or the company called the Kraków Centre of Innovative Technologies INNOAGH have been established. In a developing of the transfer technology system, AGH UST draws from experiences of the fruitful cooperation with many of US partners universities.

9:30 AM

(ICACC-PRECS-023-2015) New trends of electronic materials for future needs (Invited)

D. Suvorov*[1]; 1. Jozef Stefan Institute, Slovenia

Ferroelectric-based electronic materials for future applications should possess a novel combination of properties and better energy efficiency with further miniaturization of the components and relevant devices. Ceramics of interest for such development consist of well characterized materials having well controlled chemical composition and phase distribution architecture in the desired heterostructures with optimized electronic properties. In this respect several new synthesis techniques will be required which enable downsizing towards the formation of thinner films based on nano-sized particles and heterostructures on nearly atomic scale. The aim of this presentation is to critically evaluate synthesis and properties of the different nano-sized based structures (thin films, heterostructures, etc) for the application of newer electronic components.

10:20 AM

(ICACC-PRECS-024-2015) On the Evolution of Nanomechanical Characterization for Brittle Solids (Invited)

T. Wyrobek*[1]; 1. Hysitron, Inc., USA

Ceramics have undergone great evolution in the last several decades which has been augmented with the onset of nanomechanical testing of material properties. The research was primarily consumed with the challenges of repeatable testing and quantitative values were the result. The dawn of in-situ technologies such as the scanning nanoindenter, SEM and TEM nanoindenters, and environmental control expanded the research capabilities to allow testing of a greater variety of new materials, coatings and composites at the scale where the material is intended to be employed. As this drew the attention of the modelers and researchers from collaborative disciplines, the research community developed a need for multiple dimensional testing combined with in-situ capabilities to spawn a line of hybrid technologies that provided the ability to test the material in the environment it will be used. The evolution from material property testing to in-situ testing to in-operando testing opening the exploration of structure-property relationships will be discussed.

10:50 AM

(ICACC-PRECS-025-2015) The Rare Earth Elements among the Critical Elements (Invited)

G. Meyer*[1]; 1. Iowa State University, USA

Modern technologies often afford rather small amounts of highly specialized materials. Among these, some of the rare-earth elements are of paramount importance, especially for catalysis, magnets and lighting devices. This also holds for other elements like gallium and indium, but the criticality of the supply of rare-earth elements is intensified by the balance problem, i.e., the most important elements are among the rarest and they are always found together in minerals, albeit in different concentrations. Thus, recycling of functional materials and substitution of rare-earth elements by less critical elements have become important issues.

11:20 AM

(ICACC-PRECS-026-2015) Niobium carbide for a reliable value chain

M. Woydt*[1]; H. Mohrbacher[2]; 1. BAM Federal Institute for Materials Research and Testing, Germany; 2. Niobelcon bv/ba, Belgium

Hard metals are a synonym for wear resistance and are dominated by tungsten carbide. ~80% of the global tungsten production is mined in China from a total of 75.000 tons. Niobium is a refractoty metal, like tungsten, and represents a possibility in substitution and in supply to tungsten. ~85% of the global supply is mined in Brazil and ~10% in Canada of a total between 70.000-85.000 MTPa. ~90% of the niobium is today used as a micro-alloying and property-determining constituent element in steels for petrochemical industries, structural steels and high strength car body steels to control the micro-structure. This presentation will illuminate the global availability and reserves, the historical pricing and also the tribological properties of NbC-bearing materials.

11:40 AM

(ICACC-PRECS-027-2015) Cerium Oxide Nanoparticles in Nanomedicine: Panacea or Trojan Horses?

L. Ghibelli*[1]; 1. Universita' di Roma Tor Vergata, Italy

Metal oxides nanoparticles promise to revolutionize clinical medicine providing novel diagnostic and therapeutic strategies. Their particulate (as opposed to molecular) nature allows solving intrinsic problems of molecular drugs, but poses unprecedented hazards that toxicologists must approach for safe delivery of particulate pharmaceuticals [1]. Cerium oxide nanoparticles, due to the double valence (3+/4+) of cerium, possess unique redox features conferring auto-regenerating antioxidant activities while scavenging the most noxious reactive oxygen species [2]. Accordingly, nanoceria exert potent antioxidant effects at the cellular and organism level, protecting cell viability and organ functionality from a variety of oxidative injuries, including UV light and X-rays [2]. The double valence of nanoceria is compensated by oxygen vacancies on particles surface; the mechanism responsible for the redox-protective effects is due to the redox switch, as demonstrated by studies where the substitution of the Ce3+ redox-active atom with the redox-inactive Sm3+ caused loss of antioxidant activity [3]. However, biological activity of the oxygen vacancies is theoretically possible. Interestingly, nanoceria seem to exert a smart anticancer activity, killing tumor cells while protecting healthy cells.

4th Global Young Investigator Forum

New Materials for Energy Applictions

Room: Coquina Salon C

Session Chairs: Craig Smith, Ohio Aerospace Institute; Chinghuan Lee, National Cheng Kung University

8:30 AM

(ICACC-GYIF-032-2015) Development of PtCeO2 electrocatalysts via sol-gel and chemical reduction for Direct Ethanol Fuel Cells

M. J. Paulo*[1]; E. Pereira[2]; A. C. Tavares[1]; 1. INRS, Canada; 2. Federal University of Sao Carlos, Brazil

Efficient catalysts for the electrooxidation of small organic molecules such as ethanol are needed to prompt the use of direct ethanol fuel cells. Low cost metal oxides as CeO_2, have been used to improve the electrocatalytic properties of platinum nanoparticles with a positive effect on the tolerance of this metal toward poisoning by intermediate products of ethanol oxidation. In this work we focus on the effect of CeO2 on the structure and electronic properties of Pt nanoparticles. The nanoparticles are prepared by two methods: polymeric precursor method (Pechini) and reduction method. While the first allows a good control of phase segregation the second allows a smaller particle size. The catalysts are characterized by X-ray diffraction, X-Ray Photoelectron Spectroscopy and its electroactivity is evaluated by cyclic voltammetry and chronoamperometry. The effect of CeO2 on the rate of ethanol oxidation is discussed.

8:50 AM

(ICACC-GYIF-033-2015) Fabrication and chemical heat storage property of Mg layered hydroxide salts

S. Yamashita*[1]; Y. Sugie[1]; H. Kita[1]; 1. Nagoya University, Japan

A chemical heat storage method is advantageous in terms long periods of time storage and the high storage density are possible as compared to the direct storage methods. Normally, a reversible single reaction is utilized, then the heat storage temperature is limited. On the other hand, in order to store industrial waste ranging widely in the temperatures, it's necessary to develop a new material which allows heat storage in a stepwise manner in response to temperature changes.In this study, we have investigated the effect of several experimental conditions on the synthesis of Mg based layered hydroxide by simple aqueous solution derived methods. In addition, the potentials of the multistep chemical heat storage property have been investigated.

9:10 AM

(ICACC-GYIF-034-2015) Fatigue mechanisms in blended cathode materials for lithium ion batteries

M. Lang*[1]; M. Darma[1]; H. Ehrenberg[1]; 1. Karlsruhe Institute of Technology, Germany

A new approach in upgrading the performance of cathode materials for lithium ion batteries is blending well known cathode phases to combine the unique properties of each phase in a single cathode blend system. The desired properties of such blends are better thermal stability, better specific capacity and higher cycle life stability. Different blends of two layered oxide materials of the LiCoO2 type and a spinel phase of the LiMn2O4 type were studied. Multiple cells built with graphite as the anode material were cycled at different temperatures and charged and discharged at different C-rates for more than thousand cycles. The pristine and the fatigued blend materials were investigated with different surface analysis techniques such as XPS, ToF-SIMS and SEM/EDX to see changes in the chemical composition as well as morphological changes. Half cell measurements with Lithium metal as anode were performed to study the changes in electrochemical behavior. Knowing the electrochemical behavior of each of the single phases, phase specific changes could be detected and linked to the results of the surface analysis giving insight in the fatigue mechanisms of the blended cathode as a function of the different ageing conditions such as temperature and power.

9:30 AM

(ICACC-GYIF-035-2015) $Ba(Ti_{1-x}Rh_x)O_{3\pm\delta}$ perovskite-type oxides for hydrogen reformer catalyst

Y. Gönüllü*[1]; B. Saruhan-Brings[2]; G. Mondragon Rodriguez[2]; 1. University of Cologne, Germany; 2. German Aerospace Centre, Germany

Perovskite-type oxides with the composition of $Ba(Ti_{1-x}Rha_x)O_{3\pm\delta}$ were prepared applying a new chemical route that assures the formation of a clear sol and homogeneous distribution of Rh in the final mixed metal oxide. The high dispersion of Rh and the formation of a solid solution between Rh and the $BaTiO_3$ perovskite is confirmed by means of standard X-ray diffraction (XRD) and extended X-ray absorption fine structure spectroscopy (EXAFS). The presence of Rh stabilized the hexagonal perovskite $Ba(Ti_{1-x}Rh_x)O_{3\pm\delta}$ which decomposes into Barium Orthotitanate $BaTi_2O_4$ and metallic Rh° in reducing environments. This face transformation starts already at 700° and it is only partially completed at 900°C suggesting that part of the Rh present in the perovskite might not be reached by hydrogen. These aspects and further open questions are discussed in this study.

9:50 AM

(ICACC-GYIF-036-2015) Nano-structured Metal Oxide Gas Sensors

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

Selectivity, Sensitivity, Stability and Speed (4S) have been the main criteria for gas sensor development in the last years. Especially metal oxides, which allow a simple resistive readout on the one hand, show highly unspecific sensor signals, when gas mixtures and/or humidity are present. Using nanostructured materials and surface modifications for tuning the gas/solid interface reactions, selective and sensitive sensor platforms can be fabricated starting from molecular precursors applied in gas phase deposition systems. In addition to the 4S criteria the Scaleability of the manufacturing process as well as the Systemability are crucial aspects for commercial applications of nanostructurd devices. The presentation will focus on the targeted growth of nanostructured metal oxide films and nanowires via a modified chemical vapor deposition (CVD) technique on multifunctional sensor substrates. A detailed insight on the growth and functional properties of the resulting films regarding their gas sensing performance will be given.

Mechanical Properties of Ceramics and Composites

Room: Coquina Salon C

Session Chairs: Thomas Fischer, University of Cologne; Yakup Gönüllü, University of Cologne

10:30 AM

(ICACC-GYIF-037-2015) Monitoring Crack Extension in Ceramic Matrix Composite during Interlaminar Fracture Testing Using Electrical Resistivity

R. Mansour*[1]; E. Maillet[1]; G. N. Morscher[1]; 1. The University of Akron, USA

Interlaminar fracture properties in fiber-reinforced ceramic matrix composites have been addressed as a limiting feature in certain applications, especially at elevated temperatures. Few if any fibers bridge cracks in the interlaminar direction, resulting in a weaker toughness and a higher probability to failure in this direction. The main challenge in evaluating interlaminar fracture toughness is the difficulty to detect the crack initiation and to measure crack length directly at high temperature, primarily because of the limited visual accessibility of the area of interest. Therefore, in this work, a method has been introduced to monitor crack growth using electrical resistivity for melt-infiltrated woven SiC/SiC composite at room temperature using a DCB wedge test. In-situ optical measurements, in addition to microCT post-inspection, were used to validate this method before utilizing it for high temperatures testing. Acoustic emission was also used to discern relevant experimental features such as crack initiation and propagation as well as interaction of the wedge with the specimen arms (e.g., frictional events).

10:50 AM

(ICACC-GYIF-038-2015) Microstructural development and intrinsic fracture toughness of monolithic Si_3N_4 ceramics prepared by spark plasma sintering

C. A. Lee*[1]; H. Lu[2]; C. Wang[3]; H. Lin[4]; D. Lii[5]; J. Huang[1]; 1. National Cheng Kung University, Taiwan; 2. National Chin-Yi University of Technology, Taiwan; 3. Tsinghua University, China; 4. Oak Ridge National Laboratory, USA; 5. Cheng Shiu University, Taiwan

Monolithic Si_3N_4 ceramics doped with 6wt% Y_2O_3 and 8wt% Al_2O_3 were fabricated by spark plasma sintering. Their microstructures were controlled by applying different heating rates and sintering temperatures. The nanostructured ceramic can be obtained at a relatively low sintering temperature of 1400ºC, while anisotropic grain growth is accelerated above 1500ºC, due to concurrence of both dynamic Ostwald ripening and grain coalescence as observed by TEM. The intrinsic and bridge toughness for nanostructured and self-reinforced Si_3N_4 were identified by crack opening displacement. The values of intrinsic toughness are 1.3, 2.7, and 1.7 MPa*m$^{1/2}$ for samples sintered at 1400ºC, 1500ºC, and 1600ºC with a heating rate of 200ºC/min, respectively. A set of additional specimens containing seeding was prepared at 1900ºC, and their intrinsic toughness is about 3.0 MPa*m$^{1/2}$. These results indicate that intrinsic toughness is directly related to sintering temperatures rather than microstructures. On the other hand, with regard to bridging toughness, it is associated with microstructural characteristics. The bridging stress factors increase with increasing grain width and aspect ratio of Si_3N_4. The frequency of distribution for deflecting angles of the radial cracks was measured to show the degree of energy dissipation by large grains in the present work.

11:10 AM

(ICACC-GYIF-039-2015) Correlating tensile creep of SiC/SiC composites with changes in electrical resistance

C. Smith*[1]; G. N. Morscher[2]; 1. NASA Glenn Research Center, USA; 2. University of Akron, USA

SiC/SiC ceramic matrix composites are becoming popular alternatives to metals in the hot sections of turbine engines. The development of these composites for structural applications brings about the need for simple techniques to detect mechanical degradation. Electrical resistance monitoring is one relatively simple method that shows good sensitivity to matrix crack formation as well as creep. Melt infiltrated SiC/SiC with a Si-rich matrix demonstrates particularly good self-sensing capability, due to the high conductivity of silicon. Data from tensile creep tests in air at 1315°C with in-situ electrical resistance monitoring will be presented for SiC/SiC with a melt infiltrated matrix and 2D woven Sylrami-iBN fibers.

11:30 AM

(ICACC-GYIF-040-2015) Acoustic Emission and Electrical Resistivity During Tensile Testing of SiC/SiC Composites with different fiber types and Interphases

A. Almansour*[1]; E. Maillet[1]; G. N. Morscher[1]; 1. The University of Akron, USA

Ceramic Matrix Composites (CMCs) are candidates for high-temperature applications such as the new generations of aircraft engines and hypersonic vehicles. In severe conditions, durability of CMCs is controlled by fiber exposure to environment, which depends on the damage state in the matrix. The ability to model the stress-dependent matrix cracking in CMCs for various fiber types and fiber volume fractions is crucial for lifetime assessment in service conditions. Hi-Nicalon, Hi-Nicalon Type S and Tyranno ZMI reinforced minicomposites with a BN or Carbon interphase and a chemically vapor infiltrated SiC matrix were tested in tension at room temperature and tests were monitored using acoustic emission and electrical resistivity measurement. The effects of fiber type, fiber volume fraction and interphase on matrix cracking onset and growth will be discussed. The influence of constituents and damage progression on electrical resistivity will also be examined with different fiber volume fractions.

11:50 AM

(ICACC-GYIF-041-2015) Evaluation of R-curve of nano-polycrystalline stishovite using micro cantilever specimens

K. Yoshida*[1]; N. Nishiyama[2]; F. Wakai[1]; Y. Shinoda[1]; A. Takashi[1]; M. Sone[1]; 1. Tokyo Institute of Technology, Japan; 2. Deutsches Elektronen-Synchrotron, Germany

Stishovite is the high-pressure phase of silica (SiO2) in which silicon has octahedral coordination, while quartz and cristobalite have tetragonal coordination. Stishovite with a hardness of 31 GPa, is the third hardest material after diamond and cubic boron nitride. Generally, the relationship between hardness and toughness is trade-off. But, recently, Nishiyama et al. synthesized nanocrystalline bulk stishovite with high fracture toughness of 10-13 MPa m1/2 (IF method) [Scripta Mater., 2012]. The nano-polycrystalline stishovite sample synthesized by ultra-high pressure process is very small, therefore we cannot evaluate the fracture toughness by conventional method using notched beam specimens with a few tens millimeters length. Here, we evaluated the fracture toughness and the R-curve of the nano-polycrystalline stishovite using micro-cantilever beam specimens, whose size is 20×20×100 μm, prepared by focused ion beam technique. By bending the specimens using indentation, we obtain the load displacement curve during fracture, and derive the R-curve of nano-polycrystalline stishovite. The R-curve is very steep and saturated at only few μm crack extension. The steep R-curve implies that this material has new toughening mechanism working at very first part of crack extension. The micro-cantilever method make it possible to evaluate the initial stage of R-curve of ceramics materials.

S1: Mechanical Behavior and Performance of Ceramics & Composites

Environmental Effects

Room: Coquina Salon D

Session Chairs: Marina Ruggles-Wrenn, Air Force Institute of Technology; Martha Mecartney, UC Irvine

1:30 PM

(ICACC-S1-040-2015) Quantification and Modeling of Environmental Effects on SiC Fibers (Invited)

R. Hay*[1]; T. Tidball[3]; R. Corns[2]; T. Parthasarathy[2]; 1. Air Force Research Laboratory, USA; 2. UES, Inc., USA; 3. Wright State University, USA

High temperature structural ceramics such as SiC-SiC CMCs will be exposed to a wide range of temperatures and environments, particularly during use in combustion environments. Passive and active oxidation and environmentally assisted subcritical crack growth are known to be important. To map the thermo-chemical regimes of these mechanisms, the effects of high temperature exposure to air, low pO2, and Si(OH)4 saturated and unsaturated steam between 600 and 1300°C on the mechanical properties of Hi-NicalonTM–S fibers were characterized and evaluated. Fiber microstructure, composition, oxide scale thickness, and scale crystallization extent were quantitatively characterized by TEM of fiber cross-sections. Oxidation and scale crystallization kinetics were determined. Thirty single-filament tensile tests per condition were used to characterize fiber tensile strength and Weibull modulus. The residual thermal and growth stresses in oxide scales were calculated for both crystallized and amorphous scales. The relationships between temperature, time, scale thickness, scale crystallization extent, residual stress, and fiber mechanical properties will be discussed. Possible effects of fiber microstructure on mechanical properties, including those from a carbon-rich SiOC glass phase at SiC-SiC triple junctions that contains turbostratic graphite precipitates will also be discussed.

2:00 PM

(ICACC-S1-041-2015) Oxidation of Hi-NicalonTM SiC Fibers

M. Wilson*[1]; E. Opila[1]; 1. University of Virginia, USA

Oxidation of silicon carbide (SiC) to SiO2 is a well-studied process, yet the literature values for kinetic rate constants and activation energies of SiC fibers vary greatly. In this study the oxidation kinetics of Hi-NicalonTM SiC fibers were investigated using thermogravimetric analysis (TGA) with temperatures of 800°-1300°C in flowing oxygen. Weight change vs. time data from the TGA was used to identify the fiber oxidation mechanisms. Linear oxidation results were observed at 800°C, linear-parabolic results at

900°C, and parabolic results from 1000°-1300°C. Scanning Electron Microscopy (SEM) was used to characterize the oxide thicknesses on the fibers. The rate constants and activation energies were calculated in this study and compared to literature values for other SiC fibers. The composition of the SiC fibers studied in the literature varies greatly, resulting in parabolic kinetic rate constants that vary by an order of magnitude. The parabolic rate constants determined in this study are in best agreement with other oxidation studies of Hi-NicalonTM fibers. Finally, the activation energies in the literature were compared with the activation energies for both the linear and parabolic rate constants calculated in this study.

2:20 PM

(ICACC-S1-042-2015) Strength degradation after fatigue at elevated temperatures for SiC Hi-Nicalon and Hi-Nicalon S fibers and tows

J. Lamon*[1]; M. R'Mili[2]; 1. CNRS, France; 2. INSA Lyon/University of Lyon, France

Silicon carbide based fibers have been shown to be sensitive to delayed failure in fatigue at temperatures < 1200°C in air as a result of slow crack growth. The present paper investigates the strength degradation during fatigue of Hi Nicalon and Hi-Nicalon S SiC-based fibers in this temperature range where creep is ineffective. The analysis is based on the tensile residual behaviour of fiber tows after fatigue. The residual behaviour of tows was predicted using closed form equations for filament residual strength after fatigue and for tensile behaviour of tows. Intrinsic parameters of the slow crack growth power law were estimated from experimental statistical distributions of rupture times under constant and identical stresses for Hi-Nicalon single filaments at 500°C and 800°C. Trends were established for residual tensile tow behavior, filament strength degradation and statistical distributions of filament strengths as functions of fatigue duration. The predictions compared fairly well to experimental lifetimes determined on Hi-Nicalon and Hi-Nicalon S fiber tows under constant load at high temperatures. Finally the influence of preponderant factors was discussed.

2:40 PM

(ICACC-S1-043-2015) Creep in Interlaminar Shear of Nextel™720/Aluminosilicate Composite at 1100 °C in Air and in Steam

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

Creep behavior in interlaminar shear of an oxide-oxide ceramic composite was evaluated at 1100°C in laboratory air and in steam environment. The composite (N720/AS) consists of a porous aluminosilicate matrix reinforced with laminated, woven mullite/alumina (Nextel™720) fibers, has no interface between the fiber and matrix, and relies on the porous matrix for flaw tolerance. The interlaminar shear properties were measured. The interlaminar shear strength (ILSS) was determined as 7.65 MPa. The creep behavior was examined for interlaminar shear stresses in the 2-6 MPa range. Primary and secondary creep regimes were observed in all tests conducted in air and in steam. Tertiary creep was noted in the test performed at 6 MPa. Creep run-out defined as 100 h at creep stress was not achieved in any of the tests. Larger creep strains and higher creep strain rates were produced in steam. However, the presence of steam had a beneficial effect on creep lifetimes. Composite microstructure, as well as damage and failure mechanisms were investigated. It appears that matrix strengthening occurred in steam, which resulted in improved creep performance in interlaminar shear.

3:20 PM

(ICACC-S1-044-2015) Fatigue Characterization of Sylramic-iBN/BN/CVI CMC under Combustion Environment

D. J. Bertrand*[1]; V. Sabelkin[2]; S. Mall[2]; L. P. Zawada[1]; 1. Air Force Research Lab, USA; 2. Air Force Institute of Technology, USA

Fatigue behavior of a HyperTherm Sylramic-iBN/BN/CVI SiC CMC was investigated under tension-tension fatigue using a burner rig facility which simulated both the load and combustion conditions of hot-section components of gas turbine engines such as turbine blades and vanes. Fatigue tests were performed using this burner rig at stress ratio = 0.1 and frequency = 1 Hz to establish fatigue life (S-N) data. The combustion environment was created using a High-Velocity Oxygen Fuel Gun, which impinged the flame directly on one side of the specimen as it was subjected to cyclic loading. The flame-impinged surface of the specimen was heated to 1250°C, 1350°C, and 1480°C. The CMC achieved a run-out of 25 hours at 33% of the room temperature ultimate tensile strength (UTS) at 1250°C and at 24% of the room temperature UTS at 1350°C. Run-out was not achieved at 1480°C due to severe degradation of the material. Microscopic analysis showed that the oxidation of material due to the combustion environment occurred near the surface on both the flame side and backside of the specimen, but more on the flame side. The fracture surfaces showed regions with oxides covered matrix and/or fibers, oxides filled of the fiber/matrix interphase, or both leading to embrittlement of CMC.

3:40 PM

(ICACC-S1-045-2015) Oxidation of Ni in Al2O3 after High Temperature Exposure to Dry Air, H2O, or D2O

M. Mecartney*[1]; J. Angle[2]; 1. UC Irvine, USA; 2. UC Irvine, USA

Experiments were conducted exposing dense alumina ceramics with intergranular nickel particles to different atmospheres at high temperatures from 1250C to 1500C for varying times to determine the susceptibility of Ni to oxidation. Upon oxidation of Ni in Al2O3, NiAl2O4 spinel formed. Backscattered SEM of cross-sectioned samples could be used to determine the depth of the oxidation front from the top surface, using the contrast difference between Ni and NiAl2O4. Exposure to water vapor with P(H20) = 0.22 atm generated a significantly deeper oxidation profile than exposure to dry air for the same times and temperatures . When H2O in the atmosphere was replaced by D2O, significantly slower kinetics were observed than for H2O or dry air. The enhanced oxidation depth in the presence of water vapor could be due to faster diffusion of (OH)- compared to (O)2-. The shortest diffusion profiles (slowest diffusion) as marked by oxidation were for D2O. While the mass dependence of (OD)- is expected to give slower diffusion than (OH)-, that these kinetics are even more sluggish than dry air was surprising. A possible explanation is that a significant amount of bound water may be already incorporated into the the alumina grain boundaries during conventional processing. (This project was funded by NSF DMR-1243898.)

4:00 PM

(ICACC-S1-046-2015) Interactions between Na_2SO_4, B_2O_3 and SiO_2 and relevance to hot corrosion of ceramic matrix composites

E. K. Poerschke*[1]; E. Opila[1]; 1. University of Virginia, USA

Reactions between Na_2SO_4, and the oxides B_2O_3 and SiO_2 were studied to characterize hot corrosion reactions relevant for SiC/BN/SiC ceramic matrix composites. Mixtures of Na_2SO_4 and the oxides were heated between 900°C and 1200°C in argon with constant heating rates and stepped heating rates with 50°C isotherms. Thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and x-ray diffraction (XRD) were used to characterize the reactions. Binary mixtures of $Na_2SO_4 + B_2O_3$ and $Na_2SO_4 + SiO_2$ exhibited significant weight loss at temperatures lower than their unary baselines. The $Na_2SO_4 + B_2O_3$ mixture showed large weight loss at high temperatures indicating an increased reactivity with

Na_2SO_4. Results suggest BN-containing SiC composites are more susceptible to hot corrosion than SiC alone.

4:20 PM

(ICACC-S1-047-2015) Influence of Temperature and Humidity on the Strength of Low Temperature Co-fired Ceramics

C. Krautgasser*[1]; R. Danzer[2]; F. Aldrian[3]; P. Supancic[2]; R. Bermejo[2];
1. Materials Center Leoben Forschung GmbH, Austria;
2. Montanuniversitaet Leoben, Austria; 3. TDK-EPC, Austria

Low Temperature Co-fired Ceramics (LTCC) consists of ceramic grains embedded in a glass matrix that can be sintered at low temperatures. The LTCC-technology provides components with improved thermal and geometrical stability compared to the polymer based printed circuit boards. However, subcritical crack growth (SCCG) mechanisms ("stress corrosion") may occur when subjected to tensile stresses, especially in environments with high humidity. Strength degradation may occur, causing by the stable growth of flaws under stresses below the strength of the material. In this work the combined effect of humidity and temperature on the biaxial strength of an LTCC material was investigated using the ball-on-three-balls test (B3B) in air and argon at different stress rates and temperatures (25 °C, 75 °C and 125 °C). Results show that the strength is much higher in argon than in ambient air, decreasing at lower stress rates. Surprisingly – in the investigated temperature range – the strength in air did not depend on the testing temperature despite the significant change in the relative humidity. The influence of temperature on the strength is not pronounced. Fracture toughness has been also measured using the SEVNB technique in different environments and temperatures (25°C and 125°C) showing a significant effect of the environment on the KIc values measured, but almost no effect of the temperature.

4:40 PM

(ICACC-S1-048-2015) Measurement of Physical Properties of Thin Film Ceramic Substrates

C. P. Linseis*[1]; 1. Linseis Inc., USA

Thin film ceramic substrates are widely used in power electronics to provide the interconnections to form electric circuits and to cool the components. The physical transport properties of the thin films are essential to obtain high performance circuit boards. However the measurement of these data used to be very difficult in the nano- and micrometer scale. A new chip based 3-Ω Method is introduced which enables the measurement of the thermal conductivity, electric resistivity and heat capacity on thin films down to 20 nm with high accuracy. On various application examples it can be proved that the transport properties are strongly dependent on the thickness of the material. The thermal conductivity decreases with decreasing sample thickness. The thermal conductivity of the bulk material is much higher by one or two orders of magnitude.

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

CMAS-related Degradation and Mitigation Strategies II

Room: Coquina Salon G
Session Chairs: Peter Mechnich, German Aerospace Center (DLR); Douglas Wolfe, Pennsylvania State University

1:30 PM

(ICACC-S2-017-2015) Lifetime of new single and double layer EB-PVD thermal barrier coatings and their beavior under deposits (Invited)

U. Schulz*[1]; P. Mechnich[1]; R. Naraparaju[1]; 1. DLR, Germany

Thermal barrier coatings (TBCs) are applied to increase lifetime and efficiency of highly loaded turbine components. New topcoat chemistries have been developed for TBCs that offer low thermal conductivity, improved sinter resistance, and higher phase stability. The presentation provides results on several new TBCs deposited on top of NiCoCrAlY coated superalloys. Gadolinium zirconate (GdZ), lanthanum zirconate (LaZ), and dysprosia stabilized zirconia (DySZ) were investigated as single and double layers in comparison to standard 7YSZ coatings. All coatings were deposited by electron-beam physical vapor deposition. The interaction of the coatings with artificial volcanic ash (AVA) and with CMAS was investigated at various temperatures. While the zirconia-based TBCs provide no mitigation potential due to complete infiltration by AVA and CMAS, the pyrochlore TBCs form crystalline phases rapidly which provides a potential for damage mitigation. Both chemistry and TBC microstructure seem to play a decisive role for the interaction between TBC and deposits. Selected TBCs were subjected to cyclic oxidation testing at 1100°C. Both single and double-layered GdZ and DySZ have shown longer lifetimes than the standard YSZ samples. Changes in microstructure, growth of the TGO layer with special emphasis on the reactions between pyrochlore and alumina are discussed.

2:00 PM

(ICACC-S2-018-2015) CMAS Attack and Mitigation Mechanisms in Air Plasma Sprayed Thermal Barrier Coatings

A. R. Krause*[1]; H. Garces[1]; G. Dwivedi[2]; S. Sampath[2]; N. P. Padture[1];
1. Brown University, USA; 2. Stony Brook University, USA

Calcium-magnesium-aluminosilicate (CMAS) deposits, found in aircraft and power-generation engines, infiltrate and degrade thermal barrier coatings (TBCs) used to protect and insulate hot section components. The attack mechanism in conventional 7wt.% yttria stabilized zirconia air plasma sprayed (APS) coatings was studied to design APS TBCs that can mitigate CMAS penetration. CMAS penetrates the coatings via pores and cracks in the APS coating and undergoes a chemical reaction with the TBC. Yttria is depleted from the grains leaving the zirconia susceptible to phase transformation upon cooling. The TBC's microstructure and CMAS composition were identified as important factors in the interaction. A model is proposed to describe failure in 7YSZ TBCs after CMAS penetration. An alternative TBC material, Y_2O_3-$2ZrO_2$, was investigated as a possible candidate for mitigating CMAS penetration.

2:20 PM

(ICACC-S2-019-2015) Durable, Low Thermal Conductivity Thermal Barrier Coatings Modified for Harsh Environments

C. Jiang*[1]; E. H. Jordan[2]; M. Gell[1]; J. Roth[2]; 1. University of Connecticut, USA; 2. University of Connecticut, USA

Thermal barrier coatings (TBCs) are generally applied in gas turbines to insulate hot section components from high temperature gases. But as TBC operation environments become harsher, new corrosion issues arise which have drawn a considerate amount of research focus. The University of Connecticut has demonstrated that, by using the solution precursor plasma spray (SPPS) process, a 50-percent reduction in the thermal conductivity of YSZ TBCs can be achieved with the introduction of planar arrays of porosity, called inter-pass boundaries (IPBs). Subsequent tests showed that such geometric modification comes with no deterioration in thermal cyclic durability and erosion resistance. For applications in IGCC environments, further modifications were made to the low-thermal-conductivity coatings, including doping with alumina/titania and applying a gadolinium zirconate top-layer, to enhance coatings' corrosion resistance to CMAS (calcium-magnesium aluminosilicate). A high temperature moisture rig was also built to evaluate the TBCs' performance in humid environments. These environmental test results will be presented as well.

2:40 PM

(ICACC-S2-020-2015) Protective Mg-Al spinel coatings for oxide CMCs

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

Oxide CMCs are promising materials for hot section components of future gas turbine engines. The application of high temperature stable oxide CMCs allows a reduction in cooling air or a higher combustion temperature so that the efficiency of the gas turbine engines could be enhanced. No protection against oxidation is required, but water vapor in the highly corrosive atmosphere as well as molten CMAS (Calcium-magnesium-alumina-silicate) deposits could affect the oxide CMC. Therefore the development of suitable environmental barrier coatings (EBC) is necessary. Spinel ($MgAl_2O_4$) coatings were deposited by plasma spraying on WHIPOX® (wound highly porous oxide CMC) substrates. Water vapor and hot gas corrosion tests were carried out. The interaction of a model CMAS powder with plasma sprayed spinel coatings was investigated. The corrosion behavior of the coatings is compared to that of the substrate material. X-ray diffraction was used for phase identification; imaging as well as elemental analyses were carried out by means of scanning electron microscopy (SEM) combined with energy-dispersive X-ray spectroscopy (EDS).

3:20 PM

(ICACC-S2-021-2015) Phase Equilibria in Thermal Barrier Coating/Silicate Melt Interactions

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

The leading strategy to prevent the infiltration of molten silicate deposits (CMAS) into the open features of thermal barrier coatings relies on deposit/coating interaction to rapidly crystallize the melt. The crystallization reactions involving cations from a rare earth (RE) zirconate TBC can form one or more of the following products: apatite, fluorite cuspidine, garnet, zircon or RE-disilicate. Evolution of the melt chemistry may then promote the crystallization of phases in the melilite, pyroxene, or spinel families. The ability of the reactions to mitigate CMAS degradation is related to the crystallization kinetics, determined in part by reaction product constitution. Evidence suggests that systems forming a large fraction of apatite offer better performance. Understanding the relationships between the deposit composition and likely reaction product(s) is necessary to assess the expected performance of a given thermal barrier oxide. The present study addresses this need by elucidating relevant CMAS-Y_2O_3-ZrO_2 phase relationships. The Al-Ca-Si-Y-O subsystem was first examined to assess the equilibrium apatite and cuspidine homogeneity ranges. Efforts then focused on understanding the effect of melt chemistry on the reaction product identity and composition. The results offer insight into the factors controlling the crystallization reactions and provide guidance for the design of improved coating systems.

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(ICACC-S2-022-2015) Properties and Crystallization Kinetics of Calcium-Magnesium Aluminosilicate (CMAS) Glass

V. L. Wiesner*[1]; N. Bansal[1]; 1. NASA Glenn Research Center, USA

When an aircraft engine operating at temperatures above 1200°C ingests sand, volcanic ash or other similar debris, the particulates become glassy deposits of calcium-magnesium aluminosilicate (CMAS). CMAS can chemically interact with and degrade thermal and environmental barrier coatings (TBCs and EBCs) used to protect silicon-based ceramic matrix composite turbine engine components from the high-temperature combustion environment. In this study, a CMAS glass was prepared from synthetic sand with composition relevant for aerospace applications. Crystallization kinetics of the CMAS glass were investigated using differential thermal analysis (DTA). X-ray diffraction (XRD) was used to identify the crystalline phases that developed after heating bulk glass specimens at 690°C to 960°C for various durations. Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were used to study the microstructure and chemical compositions of the crystalline phases. Mechanical properties of the CMAS glass that were determined included the elastic moduli, Vickers hardness and indentation fracture toughness. The temperature-dependence of viscosity of CMAS was estimated from glass reference points using the Vogel-Fulcher-Tammann (VFT) equation.

4:00 PM

(ICACC-S2-023-2015) TBC corrosion by volcanic ash – properties and behavior of natural and artificial test dusts

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. Degradation of ceramic thermal barrier coatings (TBCs) of combustor walls, turbine blades and vanes is associated with chemical interaction between the TBC material and molten VA. Infiltration of molten VA also may affect the strain tolerance of TBCs, making them susceptible to "cold shock" fracture and subsequent spallation. Today there is still a major lack in the definition of standardized VA test dusts suited for ground testing and laboratory experiments. Chemical compositions and morphologies of natural volcanic ashes (NVA) are highly complex and variable. Artificial volcanic ash (AVA) is considered a promising alternative to NVA, providing tailored chemical composition and particle morphology. Key properties such as wetting and infiltration behavior of genuine volcanic ash (Ejafjalla, Iceland) and similar AVA test dusts are compared on the example of standard EB-PVD 7-YSZ TBC. Furthermore, a variety of properties of VA relevant to aero-engine operation are investigated.

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(ICACC-S2-024-2015) Durability and CMAS Resistance of Advanced Environmental Barrier Coating Systems

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

Environmental barrier coatings (EBCs) and SiC/SiC ceramic matrix composites (CMCs) systems will play a crucial role in next generation turbine engines for hot-section component applications because of their ability to significantly increase engine operating temperatures with improved efficiency, reduce engine weight and cooling requirements. This paper will emphasize advanced environmental barrier coating developments for SiC/SiC turbine airfoil components, by using advanced coating compositions and processing, in conjunction with mechanical and environment testing and durability validations. The coating-CMC degradations and durability in the laboratory simulated engine fatigue-creep and complex operating environments are being addressed. The effects of Calcium-Magnesium-Alumino-Silicate (CMAS) from road sand or volcano-ash deposits on the degradation mechanisms of the environmental barrier coating systems will be discussed. The results help understand the advanced EBC-CMC system performance, aiming at the durability improvements of more robust, prime-reliant environmental barrier coatings for successful applications of the component technologies and lifing methodologies.

4:40 PM

(ICACC-S2-025-2015) Calcium–magnesium–aluminosilicate corrosion behaviors of rare-earth disilicates at 1400°C

J. Liu*[1]; 1. Guangdong university of technology, China

Environmental barrier coatings (EBCs) are used to prevent oxidation of underlying ceramic matrix composite (CMC) structural components in gas turbines. When the siliceous minerals deposit on the surface of EBCs, a glassy melt of calcium–magnesium–aluminosilicate (CMAS) will be formed, leading to the EBCs degradation. In this study, seven rare-earth disilicates (RE2Si2O7, RE = Yb, Lu, La, Gd, Eu, Sc, and Y) were fabricated to analyze their CMAS corrosion behaviors. The results indicated that the RE2Si2O7 could react with the CMAS in the temperature range of 1250–1350°C. Reaction zones formed at the interfaces. For the Yb2Si2O7, Lu2Si2O7, La2Si2O7, Eu2Si2O7 and Gd2Si2O7, the reaction zones dissolved into the molten CMAS and separated from the RE2Si2O7. As for the Sc2Si2O7 and Y2Si2O7, the reaction zones could stay at the interface. They could effectively block the molten CMAS to penetrate into the RE2Si2O7 and protect them from CMAS corrosion.

S3: 12th International Symposium on Solid Oxide Fuel Cells (SOFC): Materials, Science and Technology

Oxygen Ion, Proton and Mixed Conductors

Room: Crystal

Session Chairs: Nicola Perry, Kyushu University; Federico Smeacetto, Politecnico di Torino

1:30 PM

(ICACC-S3-035-2015) Sinterability and Chemical Stability of BaZr0.1Ce0.7Y0.1Yb0.1O3-δ Proton Conducting Electrolyte for SOFCs

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

Sinterability and chemical stability of BaZr0.1Ce0.7Y0.1Yb0.1O3-δ (BZCYYb), a promising proton conducting electrolyte material were systematically investigated in this research. To study sinterability, the impacts of different parameters including powder synthesis method, sintering temperature and time, substrate type, protective powder covering, and sintering aid on changes in sample density, weight, microstructure, and chemical composition in the sintering process were studied. Among the various findings, it is noted that BZCYYb disks and other similar materials have high tendency to react with aluminum oxide, leading to significant barium loss in BZCYYb disks and forming cerium oxide on the side of the disks in contact with alumina crucible and barium aluminum oxide (BaAl2O4) on the crucible surface. Different substrates and protective layers were examined to understand such phenomena and to improve the sintering process. In addition, chemical stability of BZCYYb was studied by exposing BZCYYb powder and sintered disks at different temperatures in atmospheres with different concentrations of H2S, CO2, or water vapor. The samples after exposure were characterized using XRD, SEM, and Raman microspectroscopy. The observations will be compared with literature and explanations for the difference in experimental observations in the literature will be provided.

1:50 PM

(ICACC-S3-036-2015) Electronic Conductivity Measurement in Mixed Ionic and Electronic Conductors (MIEC) and Solid Electrolytes: A Transient Technique

L. Zhang*[1]; L. Zhu[1]; A. V. Virkar[1]; 1. Univeristy of Utah, USA

Measurement of both ionic and electronic partial conductivities in MIECs and solid electrolytes is of interest. A traditional way is the use of the Hebb-Wagner method, which suffers from several limitations: required long time or high temperatures to achieve steady state. A new technique is proposed here to measure electronic conductivity in YSZ as an example. Cylindrical disc samples with embedded Pt probe are made using die-pressing and sintering at 1500°C. Pt paste is applied to both surfaces to form electrodes (surface electrodes), and the rest bare YSZ surface is covered by a sealant glass. During charging, oxygen ions migrate through the YSZ electrolyte, and electrons migrate through the external circuit. Neutral oxygen molecules are effectively transported to the Pt probe. This process is governed by oxygen ion conductivity, and the ionic resistance can be obtained using Ohm's law. During discharging, both oxygen ions and electrons migrate through YSZ electrolyte driven by the Nernst potential generated between the surface electrode and the embedded electrode. This oxygen flux is limited by electron flux. The observed time dependence of Nernst potential can be used to estimate the electronic conductivity of YSZ. This new technique has extended the measurement range down to 500°C.

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(ICACC-S3-037-2015) Electronic Conductivity Measurement in Mixed Ionic and Electronic Conductors (MIEC) and Solid Electrolytes: A Steady-state Technique

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

Hebb-Wagner blocking electrode method has been widely used to measure electronic conductivity in ionic conductors. We present a new steady-state technique to measure electronic conductivity over a range of temperature from 500 to 800°C using 8YSZ as an example. Cylindrical disc samples with embedded Pt probe are made using die-pressing and sintering at 1500°C. Pt paste is applied to both surfaces to form electrodes (surface electrodes), and the rest bare YSZ surface is covered by a sealant glass. Once a potential is applied across the surface electrode and the embedded Pt probe, oxygen ions migrate through the YSZ electrolyte, and electrons migrate through the external circuit. Neutral oxygen molecules are effectively transported to the Pt probe. In steady state, oxygen ions coming to the embedded Pt probe should equal oxygen ions going away from the Pt probe, which is the basis of the new technique. Using the new technique, we were able to measure electronic conductivity of 8YSZ at a temperature as low as 500°C.

2:30 PM

(ICACC-S3-038-2015) A First-Principles Approach to the Attempt Frequency of Oxygen Ion Jumps in Doped Ceria

J. Koettgen*[1]; T. Zacherle[1]; S. Grieshammer[1]; M. Martin[1]; 1. RWTH Aachen University, Germany

The rate of oxygen ion jumps in a solid oxide depends not only on the activation energy but also on the pre-exponential factor of diffusion. In order to allow a fully ab initio prediction of the oxygen ion conductivity in pure and samarium doped ceria we calculated the attempt frequency for an oxygen ion jump from first-principles using DFT+U, NEB, phonon calculations and the transition state theory. The equivalence of the Eyring and the Vineyard method is shown without restriction to the Gamma point. Convergence checks of the phonon mesh show that the common reduction to the Gamma point is not sufficient to calculate the attempt frequency. The pre-exponential factor is unaffected for doping with a single Sm ion at the migration edge while a Sm-Sm edge exhibits a significantly larger attempt frequency. The attempt frequencies for the constant volume and constant pressure case in harmonic and quasi-harmonic approximation are in agreement with literature approximations and experiments.

3:10 PM

(ICACC-S3-039-2015) Mixed ionic and electronic conductivity of terbium and gadolinium doped ceria solid solutions

R. C. Pillai*[1]; S. Chockalingam[1]; S. Misture[2]; D. D. Edwards[2]; S. Basu[3]; E. M. Sabolsky[1]; 1. West Virginia University, USA; 2. Kazuo Inamori School of Engineering, Alfred University, USA; 3. Indian Institute of Technology Delhi, India

Mixed ionic and electronic conducting, terbium and gadolinium doped ceria, TbxCe0.95-xGd0.05O2-δ (TCGO) with 0.15≤x≤0.40 materials have been synthesized through co-precipitation method. X-ray diffraction results indicate that TbxCe0.95-xGd0.05O2-δ samples crystallize in the fluorite structure, and the lattice volume decreases with increasing Tb content, x. The coefficient of thermal expansion decreases with increasing x, and at x = 0.4 shows a value of 10.8 x 10-6 K-1 from 25 to 800 °C. A maximum ionic conductivity of 0.015 Scm-1 and an electronic conductivity of 0.045 Scm-1 is exhibited by the composition, x = 0.40 at 550 °C. The addition of Gd3+ contributes to ionic conduction by creating oxygen vacancies and Tb4+ contributes to electronic conduction by decreasing the band gap of CeO2 as evident in the UV-Visible spectroscopy results. Stability of TCGO powder is evaluated using High temperature X-Ray diffraction from 25 to 1200 °C.

3:30 PM

(ICACC-S3-040-2015) Nonlinear Current-Voltage Characteristics of Individual Boundaries in Doped Ceria Based on Lamellae Studies

G. Baure*[1]; S. S. Sulekar[1]; M. Buck[1]; J. C. Nino[1]; 1. University of Florida, USA

It is well known that grain boundaries can be detrimental to conduction (ionic, electronic). Grain boundary engineering has been shown to enhance the overall ionic conduction in solid oxide fuel cell electrolytes operating at intermediate temperatures (< 650°C). Therefore, to better understand the blocking nature of grain boundaries, single crystal (i.e. single grain) and polycrystalline lamellae were cut from 10 mol% doped ceria pellets with average grain sizes greater than 10 microns using focused ion beam techniques. The lamellae were fashioned into coplanar platinum electrode structures and tested using broadband impedance spectroscopy. In this way, the electrical response and ionic conductivity through a single grain, a perpendicular grain boundary, and a triple point were studied. Here we will discuss our results and describe the behavior of individual grain boundaries based on impedance spectroscopy analysis (e.g. universal dielectric response, etc.) and current-voltage characteristics (e.g. Kim's power law formalism).

3:50 PM

(ICACC-S3-041-2015) Initial development of oxygen transport membrane technology at St Andrews

Z. Dehaney-Steven*[1]; 1. University of St Andrews, United Kingdom

The oxygen transport membrane is essentially a dense ionically-conductive ceramic layer with catalyst-doped high surface area exchange layers on either side to speed reaction kinetics. The concept shows promise as a replacement for cryogenic oxygen separation as an integral part of oxyfuel combustion for CCS, production of synfuels and lab-scale gaseous oxygen production. However, causes and mechanisms of degradation are not well-understood, and significant potential exists to increase oxygen flux. Flat supported cells have been developed by a combination of tape casting and screen printing, a test stand has been designed and built, and testing is underway. The effect on performance of catalyst exsolution from the fuel oxidation layer, and undesirable third phase formation will be discussed.

4:10 PM

(ICACC-S3-042-2015) Strontium and tungusten incorporated La2Mo2O9 solid electrolyte synthesized via polyol-mediated route for IT-SOFC

P. Singh*[1]; R. Pandey[1]; 1. Indian Institute of Technology (BHU) Varanasi, India

The electrolyte with high oxygen ion conductivity is a key requirement of solid oxide fuel cells (SOFC). Among the available electrolytes for SOFC, La2Mo2O9 system has gained much attention owing to its relatively high ionic conductivity at intermediate temperature range (400–800 °C) under a wide oxygen partial pressure. The oxide-ion conductor (La1−xSrx)2Mo1.5W0.5O9-δ (x ≤ 0.10) were first time prepared by polyol synthesis method. This route of preparation produces fine grain, high specific surface area and smaller particle size at relatively low calcination temperatures. The structural stability and ion conductivity of (La1−xSrx)2Mo1.5W0.5O9-δ system was studied using X-ray Rietveld refinements, DTA/TGA, scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), BET and impedance spectroscopy techniques. The XPS analysis reveals that the constituent are exist in their characteristic oxidation states. Ionic conductivity of the system was found to maximum for Sr content x=0.05 and it was higher than that of the YSZ at 700 °C. Thermal expansion coefficient (TEC) was found to be 12.52×10-6/°C for the compositions x=0.05, is compatible to a few reported components of the SOFC. Thus the investigated system may be proposed as an alternative material as electrolyte in SOFC.

S4: Armor Ceramics: Challenges and New Developments

Modeling / Testing and Evaluation / Quasi-Static and Dynamic Behavior II

Room: Coquina Salon E
Session Chair: Nitin Daphalapurkar, Johns Hopkins University; Michael Golt, ARL

1:20 PM

(ICACC-S4-039-2015) The Relationship between Thermal Shock and Ballistic Behaviours of Ceramic Materials

R. Beaumont*[1]; J. Yeomans[1]; B. James[2]; R. Dorey[1]; 1. University of Surrey, United Kingdom; 2. DSTL, Porton Down, United Kingdom

Currently, there are very few ways to identify ceramic materials with the potential to be deployed in armour applications. If it could be established that there was a relationship between thermal shock resistance and ballistic performance then this might lead to a test,or suite of tests, being devised that would enable promising materials to be identified at an early stage as well as identifying routes to improve existing materials. In the current work, a novel thermal shock test, in which a small volume of water is dropped onto the ceramic surface, has been developed alongside the more conventional total immersion quench test. By examining crack patterns and measuring residual strength, in biaxial tests, it has been possible to draw comparisons between the two types of thermal shock testing, and to rank a series of ceramic materials. These will then be compared with the rankings from ballistic tests.

1:40 PM

(ICACC-S4-040-2015) Phenomenological Mechanochemistry of Fracture and Terminal Ballistics

M. Grinfeld*[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.

2:00 PM

(ICACC-S4-041-2015) Characterisation of ceramics for ballistic applications

A. C. Healey*[1]; J. Yeomans[1]; P. Smith[1]; J. Cotton[2]; S. Maclachlan[2];
1. University of Surrey, United Kingdom; 2. Lucideon Ltd, United Kingdom

The established ballistics tests for ceramic armour development are expensive procedures typically involving numerous test specimens and requiring specialist facilities and equipment, so economically viable, non-ballistic methods to preliminarily characterise potential armour materials are highly sought-after. Fragmentation is a significant response to the ballistic event and recent literature has suggested that the characteristics of fragments, such as size, shape and surface roughness, have an influence on the energy dissipation mechanisms that govern ballistic performance. To capture the ejecta from a ballistic test, a novel method has been developed, allowing the fragments of both bullet and ceramic to be analysed in new ways using techniques such as x-ray computational tomography (XCT). This methodology is used to examine the differences in fragmentation behaviour between different ceramic materials, with the aim of identifying key characteristics that can then be assessed in non-ballistic tests, thus shortening the development cycle.

2:20 PM

(ICACC-S4-042-2015) On the Fragmentation of Advanced Ceramics

J. D. Hogan*[1]; N. Daphalapurkar[1]; K. T. Ramesh[1]; 1. Hopkins Extreme Materials Institute, USA

Understanding brittle fragmentation is important in shielding design, where desired fragmentation outcomes may be engineered to increase ballistic performance through, for example, projectile erosion. In this study, we investigate the effects of confinement and the defect population on the fragmentation of advanced ceramics (e.g., silicon carbide and boron carbide) in dynamic Kolsky bar experiments. We will show that the resulting fragmentation size distributions are bi-modal and propose two plausible fragmentation mechanisms: 1. one smaller fragmentation mechanism associated with the activation, growth and coalescence of fractures initiated from defects. The spacing between defects is linked with the fragmentation size distribution. In this sense, this fragmentation is microstructure-dependent and, thus, can be controlled through design of defect spacing. 2. One larger fragmentation mechanism associated with structural failure of the material. This fragmentation mechanism is dependent on the mechanisms that are activated during failure, which are associated with specimen geometry, and, more importantly, on the strain-rate and stress-state. We develop a theoretical framework for predicting average fragment sizes in the structural-controlled fragmentation regions and compare our new theory with existing ones.

2:40 PM

(ICACC-S4-043-2015) Can Drop-Weight Tests Differentiate the Damage Resistance of Alumina Ceramics with Different Grain Structures for Armour Applications?

J. Wade*[1]; S. Robertson[1]; A. Greig[1]; H. Wu[1]; 1. Loughborough University, United Kingdom

Dynamic damage of ceramics is currently studied by means of normalized ballistic testing, split-Hopkinson pressure bar (SHPB) or Taylor indentation. However, whilst these practices can provide a wealth of information, expertise in both the testing and interpretation of the data is required. As a result, it is often difficult to establish relationships between the quasi-statically derived properties of different ceramic microstructures and measurements of damage, despite both drawing on two fundamental mechanical responses, plastic deformation and brittle fracture. In this research, we explore the potential of scaled-down drop-weight testing (SD-DWT) as a possible method to simulate, to some degree, dynamic damage. In this paper, will focus on two alumina materials of varying grain structures that have been subjected to drop-weight tests, performed at dynamic strain-rates with a blunt-indenter head, as well as conventional quasi-static Vickers indentation and Hertzian indentation tests. In the former experiments, a less than expected phenomenon occurred as a cavity was generated on the surface of the alumina during the impact. We therefore explore the possibilities of using measurements of the impact region to differentiate the dynamic damage resistance of alumina ceramics with different grain sizes and other microstructural characteristics.

3:20 PM

(ICACC-S4-044-2015) Rate-Dependent Hardness and Amorphization Behavior of Nano-structure Boron Carbide

M. DeVries*[1]; J. J. Pittari[1]; G. Subhash[1]; 1. University of Florida, USA

The strain-rate-dependent hardness and amorphization behavior of nano-crystalline boron carbide are investigated. While polycrystalline coarse-grained B_4C has been extensively studied, the behavior of nano-structure B_4C has never been investigated. Quasi-static and dynamic Vickers indentation testing techniques are utilized to evaluate the hardness as a function of both load and strain rate. Studies of coarser-grained B_4C have suggested that the intensity of amorphization beneath dynamic indents is greater than that below quasi-static indentations at similar loads, whereas nano-crystalline materials are expected to resist such weakening mechanisms due to their enhanced strength. Using micro-Raman spectroscopy, the propensity for amorphization of nano-crystalline B_4C is examined using a map-scanning technique. The indentation volume is explored by mechanically polishing successive sub-micron layers of material from the indented surface to reveal subsurface material that is probed to detect the phase transformation. From these maps, comparisons between similar load indentations will be made regarding the size and shape of the amorphous zone, the intensity of amorphization, and the load and strain-rate dependence of those characteristics for nano-crystalline and coarser-grained B_4C.

3:40 PM

(ICACC-S4-045-2015) In-Situ SEM Microcompression of Single Crystal Boron Carbide

J. Ligda*[1]; P. Khoma[2]; V. Domnich[3]; J. LaSalvia[4]; B. E. Schuster[4]; 1. Army Research Laboratory, USA; 2. Army Research Laboratory, USA; 3. Rutgers, The State University of New Jersey, USA; 4. Army Research Laboratory, USA

There is an effort to model the behavior of Boron Carbide at the microscale. To do this, there must be confidence in the single crystal mechanical properties. However, current processing techniques do not produce single crystals large enough to perform a statistically sufficient number of conventional compression tests. Therefore, micron scale, site-specific testing techniques like nanoindentation and microcompression must be used. Initial microcompression tests on Boron Carbide show that pillars completely fracture, leaving nothing for post mortem imaging. The inability to observe any post mortem inelastic behavior means that there must be a transition to a technique which allows imaging of the specimens during compression. Previous development of an in-situ scanning electron microscope microtensile stage allows for tension testing of micron size metallic specimens. This technique can also be effectively used for compression of ceramic specimens. Specimens were fabricated following an ASTM standard, but with a gauge width and length in the micrometer regime. A combination of femtosecond laser machining and focused ion beam milling is used to achieve the desired specimen size. The specimens are tested using a custom

designed in-situ stage, inside of a scanning electron microscope so the compression specimens can be imaged while under load.

4:00 PM

(ICACC-S4-046-2015) Shock experiments on confined TiB2 and SiC

S. Satapathy*[1]; C. Williams[1]; D. Dandekar[1]; 1. U.S. Army Research Laboratory, USA

Rosenberg (1994) had proposed that Griffith's failure criteria should be more applicable for brittle materials in their post-elastic behavior as compared to von Mises plasticity behavior. He supported his proposition with plate impact experiment data for various ceramic materials. Grady (1995) observed that most ceramics agree with Griffith's prediction that the compressive strength should be an order of magnitude higher than the tensile strength, even though the ratio is not a constant for all ceramics. The loading conditions in these Rosenberg's experiments are "radial loading" in that the principal stresses increased in constant proportion to each other. Kanel and Zaretsky (2002) carried out a confined plate impact experiment by radially confining the sample, where the stress state doesn't evolve radially, and found mixed results. We extend the above investigation by carrying out radially confined plate impact experiments with at least three different levels of lateral confinement. With three data points, we would be able to identify the source of inelasticity in a more robust manner than either investigating a "radial loading" path where no confinement pressure is applied, or with only two data points as was reported by Kanel and Zaretsky. The experimental result and analysis of such confined plate impact experiments on TiB2 and SiC will be presented in this paper and the primary source of inelasticity in these ceramics will be discussed.

4:20 PM

(ICACC-S4-047-2015) Efficient implementation of a strain-rate dependent constitutive relationship for ceramics

L. Graham-Brady*[1]; F. Huq[1]; J. Liu[1]; 1. Johns Hopkins University, USA

Pre-existing flaws (pores, microcracks, inclusions, etc.) in brittle materials such as ceramics serve as stress concentrators and play a central role in dynamic failure of these materials. Crack propagation from these flaws results in an evolution of anisotropic damage growth, crack coalescence, and ultimately failure. The micromechanics model proposed by Paliwal and Ramesh (2008) and later extended by Hu et al (2014) provides a tool to address the effect of the initial flaw population on the dynamic constitutive relationship. In the context of that model, recent work by the co-authors develops techniques that address the effects of both anisotropy of damage and explicit coalescence of cracks, both of which have a significant effect on the predicted strength. With the micromechanics tool in hand, the next step is to implement this technique in the material point method, using the technique established by Tonge and Ramesh (2014). In order to maximize efficiency of the implementation, the current study applies a transfer method to minimize the required number of explicit micromechanical calculations. Using this technique computational savings of two orders of magnitude are achieved. Within this transfer method, an efficient binning technique is applied, following on work by Brannon et al (2014), that accurately represents the flaw population by a minimal number of discrete bins.

4:40 PM

(ICACC-S4-048-2015) Anisotropic Damage Modeling of Boron Carbide with an Informed Microstructure

D. D. Mallick*[1]; J. D. Hogan[1]; L. Farbaniec[1]; M. Shaeffer[1]; R. Ayyagari[1]; N. Daphalapurkar[1]; K. T. Ramesh[1]; 1. Johns Hopkins University/ Army Research Lab, USA

The integration of detailed microstructural features into numerical models will lead to improvements in the design of the next generation of advanced ceramic materials. In this presentation we implement defect statistics (size, orientation, and number densities of flaws (#/m^2) of a hot-pressed boron carbide material into a three-dimensional modeling framework formulated from first-principles micromechanics theory that features a tensorial anisotropic damage parameter. We use this model to examine the rate- dependent strength, and compare these results against experimental measurements. Confinement effects are also considered. The model is extended into a larger scale finite element framework to explore complex geometries and loading conditions, all while retaining realistic defect statistics explicitly.

S5: Next Generation Bioceramics and Biocomposites

Bioceramics I

Room: Coquina Salon F

Session Chairs: Delbert Day, Missouri University of Science and Technology; Leif Hermansson, Doxa AB

1:30 PM

(ICACC-S5-001-2015) Multifunctional Glass Microspheres for Medical Applications (Invited)

D. E. Day*[1]; 1. Missouri University of Science and Engineering, USA

Examples of how the inherent versatility of glass can be utilized to create multifunctional glass products for treating diseases in humans will be described. One example is the bioinert aluminosilicate glass microspheres which are used to destroy malignant tumors in the liver by the combined action of delivering a lethal dose of localized radiation and by reducing the blood supply to the tumors—embolization. Such glass microspheres can also be modified to heat the tumors, hyperthermia, which makes the tumor more sensitive to radiation. Another example includes biodegradable microspheres which can deliver radiation and/or drugs to a target site, but degrade in such way that no radiation escapes from the target site, radiation synovectomy. Other multifunctional biodegradable glasses will be described such as those that can function as tissue(vessel) guides and which simultaneously release drugs or antimicrobial agents to a chosen site.

2:00 PM

(ICACC-S5-002-2015) Modelling the Reactivity of Bioactive Glasses with Water (Invited)

A. Cormack*[1]; A. Tilocca[2]; 1. Alfred University, USA; 2. University College LondonLondon, United Kingdom

The interaction with water is a critical process for the biodegradation and the performance of bioactive glasses in a biological medium, since this interaction eventually leads to release of key soluble species such as calcium, phosphate and silica, which play a role in both bonding with bone and the activation of osteogenic cells. We discuss atomistic simulations aimed at investigating the interaction of the bioactive glass surface with water: first, monomers, in order to probe the activity of individual surface sites, and, secondly, simulations of the extended interface between the glass and an aqueous contact medium. This information allows us to build and analyse large models of the surface of glasses of different composition, thus revealing links between surface structure and bioactivity. These studies have allowed us to identify the role of specific surface sites in the key steps of the bioactive mechanism, namely ion release and dissolution of the silicate network. The calculations indicate that unsaturated Si atoms represent the strongest surface sites, able to induce spontaneous water dissociation at room temperature, provided that they are combined with a proton acceptor such as an NBO, with additional strong adsorption sites located near to Na or Ca cations, which appear to be directly involved in the glass dissolution mechanism.

2:20 PM

(ICACC-S5-003-2015) Tantalum-based Diffusion Coating for Increasing the Biocompatibility of Conventional Metal Implant Alloys (Invited)

J. Stiglich*[1]; B. Williams[1]; R. Narayan[2]; 1. Ultramet, USA; 2. University of North Carolina-North Carolina State University, 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 also 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.

2:40 PM

(ICACC-S5-004-2015) Chemical Durability of Oxide Bioceramics (Invited)

N. P. Mellott*[1]; 1. Alfred University, USA

Biomaterials have become an important component in the preventative and reconstructive treatment of patients for a variety of health problems. While a number of diverse material systems including polymers, metals, and composites can be utilized in many applications, oxide based bioceramics have become the preferred system in many cases, due in part to their advantageous performance properties. Throughout the processing, storage, and service lifetime of these materials they come into contact with a variety of dynamic chemical environments. Each of these environments can have a marked effect on the in-contact surface of the biomaterial, which in turn can change the overall functionality and performance. In this talk, a number of experimental design approaches to understand and quantify the chemical durability of bioceramics will be discussed and reviewed. Furthermore, state of the art characterization techniques used to quantify the composition, chemistry, and morphology of the bioceramic surface and near surface with corrosion will be reviewed. Spectroscopic techniques used for the determination of composition and chemistry of the surface and near surface will be discussed as will both advanced x-ray scattering and probe microscopy for the quantification of bioceramic surface morphology. Case studies on a variety of oxide based material systems will be discussed in detail.

3:20 PM

(ICACC-S5-005-2015) Nanoscale structure and modification of Biomaterials (Invited)

F. Rosei*[1]; 1. INRS, Canada

Modifying the nanostructure/chemistry of materials allows to optimize their properties [1]. Our strategy rests on creating nanopatterns that act as surface cues [2,3], affecting cell behavior. Chemical oxidation creates unique topographies [4], becoming a general strategy to improve biocompatibility. Our treatment selectively inhibits fibroblast growth while promoting osteogenic cell activity [5] in vitro. Enhancement of mechano-biocompatibility may occur by coating with spider silk [6, 7]. Improvement of antibacterial properties using laser and plasma strategies will also be discussed [8-10].

3:40 PM

(ICACC-S5-006-2015) Influence of Bioactive Glass/Ceramic Ionic Dissolution Products on the Bioactivity of Hard Tissue Biomaterials (Invited)

A. W. Wren*[1]; 1. Alfred University, USA

Glass and ceramic based biomaterials are uniquely suited to hard tissue restoration due to the ability to incorporate ions that can provide a positive therapeutic response in vivo, in addition to being able to control their chemistry to tailor the specific ionic dissolution process. The addition of Titanium (Ti4+) to silicate glasses can be used to reduce the dissolution rate (ion release, pH) which can provide a more amenable surface for cell adhesion and proliferation (MC-3T3 Osteoblasts). Additionally, controlled crystallization can be used to slow the materials solubility by limiting the release of elements (such as Ca2+, Si4+, Na+) which are critical in the precipitation of a calcium phosphate surface layer. Controlled dissolution is also a critical parameter when investigating the solubility and the effect of novel additions, such as neuro-protective species, Yttrium (Y3+) and Cerium (Ce3+), which can be incorporated into Silicate glasses/ceramics for applications in nerve repair. Additionally, bioactive glass/hydrogel composites can be utilized to further control the dissolution rate and locally concentrate ion migration, in particular, for applications to eradicate residual populations of tumor cells in surgical resection sites after tumor removal.

4:00 PM

(ICACC-S5-007-2015) Review of the 2nd Innovations in Bioceramics Conference (Invited)

S. B. Jung*[1]; 1. MO-SCI Corporation, USA

The 2nd Meeting of Innovations in Bioceramics, held in July 2014, covered many new technologies and applications of ceramics in healthcare. Insights into governmental regulations, intellectual property, product testing, and product innovation were discussed. Novel technologies and uses of ceramics in medicine focused around cancer treatment, soft tissue regeneration, dentistry, coating technology, and orthopedics to name a few. Discussions about the need for clinical data and well designed clinical trials were highlighted throughout the meeting.

4:20 PM

(ICACC-S5-008-2015) On the Formation of Apatites in Chemically Bonded Bioceramic Systems (Invited)

L. Hermansson*[1]; J. Lööf[1]; G. Gomez-Ortega[1]; 1. Doxa AB, Sweden

The biomaterials described are composed of the main binder system (calcium aluminate and/or calcium silicate), and phase(s) to secure apatite formation at pH close to neutrality. Phases with the aim of promoting remineralisation, integration and bone repair, are introduced to combine such seemingly contradictory properties as longevity, slow resorbability, bioactivity and bacteriostatic and antibacterial features. Slowly resorbable glasses and fluorides contribute to the formation of biomaterials containing one or more apatite phases. The presentation deals with the formation of apatite phase(s) at pH normally not considered in the CaO-Al2O3-SiO2-H2O system. The general chemical formula of apatite is, [(Me2+)x(di- or trivalent anion)y(monovalent anion)z]. In contact with body liquid including saliva, ions such as mono- and di-hydrogenphosphates in the body liquids, are transformed to pure phosphate ions, and thereafter added as apatite phases in the biomaterial. The formation of apatite can also be achieved by the presence of complementary ions, such as phosphates, carbonates, and earth metal ions, from slowly resorbable sources added to the main chemically bonded system. Such added phases will give extra contribution to the Me2+ (e.g. Sr2+, Mg2+, Ca2+, Ba2+), and to the monovalent anion (F-, Cl-) positions. The presented chemistry contributes to the possibility of forming apatite at pH close to neutrality.

4:40 PM

(ICACC-S5-009-2015) Novel porous bioceramics from the firing of silicone/calcite mixtures (Invited)

E. Bernardo*[1]; L. Fiocco[1]; 1. University of Padova, Italy

Calcite is a well recognized biomaterial, but the manufacturing of calcite-based ceramics is generally complicated, due to the low decomposition temperature. In the present investigation we refer to a novel strategy, involving directly calcite powders and preceramic polymers, in form of silicone resins. Calcite-rich ceramic foams were prepared by simple mixing of the components; the mixtures were easily foamed, at low temperature (300-350°C), by decomposition of organic additives, and fired at only 700°C. As an alternative, calcite/silicone mixtures were infiltrated in sacrifical "inverse" 3D scaffolds, and direcly ceramized at 700°C, with the development of 3D ceramic scaffolds. The particularly low firing temperature did not cause either the decomposition of calcite or the reaction between calcite and ceramic residue of the silicones, consisting of amorphous silica. Several compositions, starting from a minimum CaO/SiO2 molar ratio of 0.8, were tested; besides mineral calcite, also natural calcite, from egg shell waste, was used. Great part of the calcite, for all the developed ceramics, was converted into carbonate apatite, by immersion in a solution of sodium phosphate. In selected cases, a second firing treatment, at 900°C, caused the reaction between residual calcite and silica, with the development of wollastonite/apatite composites.

S7: 9th International Symposium on Nanostructured Materials: Innovative Synthesis and Processing of Nanostructured, Nanocomposite and Hybrid Functional Materials for Energy, Health and Sustainability

Nanomaterials for Water-splitting III

Room: Coquina Salon B

Session Chairs: Andrea Illiberi, TNO; Corisa Kons, University of South Florida

1:30 PM

(ICACC-S7-025-2015) SOLAROGENIX - Visible Light Active Metal Oxide Nano-catalysts for Sustainable Solar Hydrogen Production (Invited)

S. Mathur*[1]; T. Fischer[1]; L. Mayrhofer[2]; M. Niederberger[3]; J. Augustynski[4]; J. Morante[5]; H. Lemmetyinen[6]; D. Barreca[7]; V. Lüthen[8]; B. Proft[9]; 1. University of Cologne, Germany; 2. Fraunhofer Institute of Mechancs of Materials IWM, Germany; 3. ETH Zurich, Switzerland; 4. University of Warsaw, Poland; 5. Catalonia Institute for Energy Research (IREC), Spain; 6. Tampere University of Technology, Finland; 7. Padova University, Italy; 8. Siemens AG, Germany; 9. Sachtleben Pigment GmbH, Germany

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.

2:00 PM

(ICACC-S7-026-2015) Interfacial Electronic Structure of Energy Conversion/Storage Materials Studied with In Situ X-ray Spectroscopy (Invited)

C. Dong*[1]; J. Guo[2]; 1. National Synchrotron Radiation Research Center, Taiwan; 2. Lawrence Berkeley National Laboratory, USA

Owing to the energy crisis and the global extreme climate, much attention is being paid to renewable energy. The search for new sources of clean energy is rapidly becoming one of the most pressing technological challenges. Vast progress has been made in the development of new materials that are tailored by advanced synthetic methods. In the energy systems such as solar energy conversion, the electronic structures and interfacial phenomena crucially determine material performance. Without knowledge of the fundamental electronic and atomic structures of the materials used or of the changes in those structures upon reaction, better engineering of the material for practical use is difficult. Understanding and controlling the interfaces in these materials requires in-situ characterization tools, of which x-ray spectroscopy has many unique features. X-ray absorption is utilized to probe the local unoccupied electronic structure while x-ray emission is used to probe the occupied electronic structure. This presentation reports upon the development of in-situ cells for x-ray spectroscopic examination on the recent studies of photosynthesis, electrochemical and catalytic reactions. A number of experimental studies are presented and suggest that in-situ/operando x-ray spectroscopy becomes a useful tool for investigating renewable energy materials in working conditions.

2:30 PM

(ICACC-S7-027-2015) Multi-junction Metal Oxide Photoanodes for water-splitting applications

Y. Gönüllü*[1]; T. Fischer[1]; A. Mettenbörger[1]; S. Mathur[1]; 1. Inorganic Chemistry, 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 multilayer metal oxides (TiO_2, Fe_2O_3, Al_2O_3) for photoelectrochemical (PEC) hydrogen production. The deposition parameters for thin film creation were optimized with respect to the PEC performance of the resulting materials. Furthermore the Fe_2O_3–TiO_2 film was supported by graphene.. 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.

Nanomaterials for Solar Energy Harvesting

Room: Coquina Salon B
Session Chairs: Chung-Li Dong, National Synchrotron Radiation Research Center; Thomas Fischer, University of Cologne

3:30 PM

(ICACC-S7-028-2015) Atmospheric vapor-phase-deposition of TCOs for PV (Invited)

A. Illiberi*[1]; P. Poodt[1]; F. Grob[1]; P. Bolt[1]; F. Roozeboom[2]; 1. TNO, Netherlands; 2. Eindhoven University of Technology, Netherlands

The industrial need for high-throughput and low-cost ZnO deposition processes has triggered the development of atmospheric vapor-phase deposition techniques which can be easily applied to continuous, in-line manufacturing. While atmospheric CVD is a mature technology, new processes for the growth of transparent conductive oxides on thermally sensitive materials or flexible substrates are being developed, such as atmospheric plasma-enhanced PE-CVD and atmospheric spatial atomic layer deposition (S-ALD). In this paper, the challenges and recent results on the growth of ZnO under atmospheric pressure by CVD, PE-CVD, and spatial ALD will be described and the use of these films as transparent electrodes in thin film solar cells will be presented. Transparent (90 %) and conductive (~10 Ohm/sq) ZnO:Al films have been grown by an in-line PE-CVD process at atmospheric pressure. These films have been used as front electrode in amorphous silicon p-i-n and in CuInxGa(1-x)Se2 solar cells, resulting in an initial efficiency of ~ 8 % and ~ 16 %, respectively.Doped-ZnO films have been grown by S-ALD at deposition rates as high as nm/s. A minimum resistivity of 3 mOhm cm is achieved for Al/Zn = 8 %, corresponding to a transparency of 90 % in the visible range. The environmental stability of doped-ZnO has been enhanced by using thin Al2O3 films as moisture barrier (intrinsic WVTR: 10-5 g/m2/day).

4:00 PM

(ICACC-S7-029-2015) Encapsulation of silver nanowires in transparent conductive oxides for photovoltaic devices

M. Goebelt*[1]; B. Hoffmann[1]; M. Latzel[1]; S. Schmitt[1]; S. Jaeckle[1]; M. Bashouti[1]; S. Christiansen[2]; 1. Max-Planck-Institute for the Science of Light, Germany; 2. Helmholtz Center Berlin for Materials and Energy, Germany

The development of low-cost materials is one of the main challenges in modern photovoltaic (PV) research. Aluminum doped zinc oxide (AZO) is an inexpensive transparent conductive oxide (TCO) for PV applications due to its high abundance and its suitable electrical and optical properties. However, even after precisely tuning the sheet resistance of AZO with the aluminum concentration it is still rather high for a transparent electrode. Silver nanowire (AgNW) networks encapsulated in an AZO layer hold the promise to significantly decrease the resistivity with an only minor decrease in transparency. But the encapsulation of the high aspect ratio nanowire networks is rather difficult to achieve by conventional deposition techniques. Atomic layer deposition (ALD) is a perfect technique to deposit homogenous and uniform layers on all kinds of nanostructures e.g. used in third generation solar cell concepts. This deposition technique is based on a self-limiting reaction mechanism, which guarantees excellent film deposition conformity and atomic-scale thickness control. The encapsulation of AgNWs by ALD is shown and optimization routes for its conductivity and transparency are pointed out. Furthermore, the application of AgNW/AZO-TCOs for different solar cell concepts is discussed.

4:20 PM

(ICACC-S7-030-2015) Hybrid inorganic-organic solar cells: Integration of nanowires and metal oxide encapsulation

S. Jaeckle*[1]; S. Schmitt[1]; M. Goebelt[1]; M. Mattiza[1]; S. Christiansen[2]; 1. Max Planck Institute for the Science of Light, Germany; 2. Helmholtz Center for Materials and Energy, Germany

Combining nanostructured thin film silicon with highly conductive polymers promises efficient and cost-effective photovoltaic devices. A solution processed polymer can serves as the transparent front contact and introduce the charge separating interface, while the light is absorbed in the inorganic silicon with its good charge carrier transport properties. Decreased reflection and increased absorption by large arrays of homogenously regular nanowires should enable the use of a few μm-thick silicon instead of regular wafers. The junction of the wide-gap polymer PEDOT:PSS and n-doped silicon shows remarkable characteristics. Planar hybrid devices based on silicon wafers with open circuit voltages up to 640mV and power conversion efficiencies of 12% are presented. Hybrid solar cells on silicon nanowire arrays are demonstrated and the importance of PEDOT:PSS penetrating the nanostructure is emphasized by electrical measurments and advanced microscopy techniques. The integration of this hybrid nanostructured concept on multicrystalline thin film silicon on glass will be instigated. Degradation mechanisms of the hybrid solar cells under ambient conditions are unrevealed. The effect of encapsulation with insulating and conductive transparent metal oxides by low temperature atomic layer deposition on the performance and stability of the n-Si/PEDOT:PSS solar cells are presented and discussed.

4:40 PM

(ICACC-S7-031-2015) Deposition of lead halide perovskite onto metallic wires

T. Vu*[1]; J. Ting[1]; 1. National Cheng Kung University, Taiwan

Lead halide perovskite CH3NH3PbI3 is a promising material for use as light absorber in photovoltaic devices. Here we report the deposition of such perovskite films on metallic wires. The deposition is performed using either a single-step or two-step dip coating process. The solution composition and concentration are varied. Due to the use of metallic wire as the substrate, the formation temperature is varied for optimization. The dip coating time is also varied to optimize the thickness of the perovskite layer. The resulting samples are examined for using alpha-step, scanning and transmission electron microscopy, x-ray diffractometry, and ultraviolet photoelectron spectroscopy. Optical properties are investigated through ultraviolet-visible spectroscopy. The flexibility of the resulting wire samples is also evaluated.

5:00 PM

(ICACC-S7-032-2015) Role of CeO2 Addition on the Ionic Conductivity of 8 mol. % Y2O3 – ZrO2 Electrolyte for the Application of Solid Oxide fuel cell

A. Gupta*[1]; K. Balani[1]; S. Omar[1]; 1. INDIAN INSTITUTE OF TECHNOLOGY KANPUR INDIA, India

Solid oxide fuel cells (SOFCs) based on 8 mol.% Y2O3 – ZrO2 (8YSZ) electrolyte requires high working temperatures (800-1000°C) to render a reasonable power density. Most of the research and development work on SOFCs worldwide has been devoted on lowering its high operational temperature to intermediate temperature range (500-700°C). In the present work, the novel CeO2-8YSZ nano-composites were synthesized and tested with the aim to develop higher ionic conductive electrolyte materials for SOFCs. Spark plasma sintering (SPS) method was utilized to synthesize nano-composites of 8YSZ with different CeO2 contents (0, 2, 5, 10, and 15 wt. %). The SPS was performed on the powder mixtures of 8YSZ and CeO2 under 30 MPa at 1250°C and with the soaking time of 5 min. Densities of all the sintered samples were estimated to be 96% of theoretical density or above. The XRD profiles collected at room

temperature suggest dissolution of CeO2 in 8YSZ matrix, whereas TEM investigation shows isolated CeO2 rich regions indicating the formation of composite. The ionic conductivity measurement was performed using AC impedance spectroscopy in air from 250°C to 650°C. The effect of CeO2 addition on the structure and ionic conductivity of 8YSZ will be discussed.

S8: 9th International Symposium on Advanced Processing and Manufacturing Technologies for Structural and Multifunctional Materials and Systems (APMT9)

Advanced Sintering Technologies

Room: Coquina Salon A
Session Chairs: Pavol Sajgalik; Tohru Suzuki, National Institute for Materials Science

1:30 PM

(ICACC-S8-037-2015) Additive-free hot-pressed silicon carbide ceramics – a material with exceptional mechanical properties (Invited)

P. Sajgalik*[1]; J. Sedlacek[1]; Z. Lences[1]; J. Dusza[2]; H. Lin[3]; 1. Institute of Inorganoc Chemistry, Slovak Academy of Sciences, Slovakia; 2. Institute of Materials Research, SAS, Slovakia; 3. Oak Ridge National Laboratory, USA

Dense silicon carbide ceramics, with the density of 3.21 g/cm3 which is more than 99.9 % of the theoretical density was prepared by hot pressing and fast hot pressing of the starting silicon carbide commercially available powder. The starting powder was granulated by freeze granulation. The densification temperature was 1850 °C and the body was densified without any sintering additives. This temperature is 200-300 °C lower compared to the densification of the silicon carbide crystalline starting powder with the addition of carbon and/or boron by solid state sintering. This way prpared silicon carbide ceramic material has exceptional room temperature as well as high temperature properties: high hardness of 27 -29 GPa, medium fracture toughness of 5 MPa.m1/2, and high creep resitance ~ 2 x 10-9 s-1 at 1400°C and 100 MPa of load. The possible mechanisms of sintering is dicussed. Local increase of the aluminum concentration during hot pressing seems to be responsible for the liquid state sintering of silicon carbide in present case. Formation of the aluminosilicate liquid is potentially reason of the decreased densification temperature of granulated SiC powder to 1370 °C and thus higher sinterability and final density of the granulated silicon carbide starting powder.

2:00 PM

(ICACC-S8-038-2015) Modeling and Scale-Up of Direct Current Sintering of ZrB2 Ultra-High Temperature Ceramics

D. Pham*[1]; E. L. Corral[1]; 1. University of Arizona, USA

Electric based sintering techniques, such as direct current sintering (DCS), that use joule heating have become the preferred densification method to process advanced ceramics due to the ability to produce high density parts, limit grain growth, reduce densification times, and produce metastable microstructures. However, DCS has been limited by the lack of development in scalability of the technology due to limited power and load delivery of lab-scale furnaces. The University of Arizona uses a large scale DCS furnace to address the challenges of producing industrially relevant sized parts (>10cm). Zirconium diboride (ZrB2) is an ultra-high temperature ceramic (UHTC) of great interest in aerospace applications for its high temperature properties, however, due to its refractory nature, it is difficult to densify. By using computational modeling software (COMSOL), large scale microstructural uniformity can be predicted and mechanical properties of large scale UHTCs investigated.

2:20 PM

(ICACC-S8-039-2015) Direct Current Sintering (DCS) of Complex Geometries: Modeling in COMSOL to predict and reduce temperature gradients

P. K. Neff*[1]; D. Pham[1]; F. Smith[1]; E. L. Corral[1]; 1. University of Arizona, USA

Electric based sintering techniques utilize joule heating to achieve rapid heating rates, resulting in short processing times and microstructures not obtainable with traditional sintering technologies. Direct current sintering of complex geometries, such as rings, slanted rings, cubes, and hemispheres, is of interest for a number of high temperature applications. Obtaining uniform properties from DCS parts requires minimizing temperature gradient sample experiences. Models of complex shapes produced using a large scale DCS furnace at University of Arizona will be used to validate to predicted temperature distributions over a variety of complex shapes which are minimized for high temperature insulator (Si3N4) and conductor (ZrB2).

2:40 PM

(ICACC-S8-040-2015) Processing and Microstructural Evolution of Spark Plasma Sintered Alumina with Graphene Nanoplatelet Reinforcement

A. Nieto*[1]; L. Huang[1]; Y. Han[2]; J. M. Schoenung[1]; 1. University of California Davis, USA; 2. Yeungnam University, Korea (the Republic of)

The densification behavior of spark plasma sintered (SPS'd) Graphene Nanoplatelet (GNP) reinforced alumina nanocomposites is investigated. GNPs consist of 20-30 sheets of graphene and retain many of the excellent mechanical, thermal, and electrical properties of single layer graphene. GNPs have been used to toughen ceramic matrix composites due to the intrinsic energy dissipating mechanisms of GNPs. The effects of GNP on the sintering behavior of these ceramic composites, however, have received limited attention. In this study, the effect of GNPs on sintering behavior is investigated by systematically varying temperatures (1100 -1500 °C), dwell times (3-10 min), pressure (45-90 MPa), and GNP content (5 – 15 vol. %). High volume fractions of GNPs are incorporated through high energy ball milling thereby resulting in excellent dispersion without significant agglomeration. Powders and sintered compacts are characterized using scanning electron microscopy, transmission electron microscopy, x-ray diffraction, and microhardness testing in order to elucidate densification mechanisms.

3:20 PM

(ICACC-S8-041-2015) Influence of Spark-Plasma-Sintering (SPS) Parameters on Optical Transparency of $MgAl_2O_4$ Spinel (Invited)

K. Morita*[1]; B. Kim[1]; H. Yoshida[1]; K. HIRAGA[2]; Y. SAKKA[1]; 1. National Institute for Materials Science, Japan; 2. Kitami Institute of Technology, Japan

Recently, instead of the well-known HP or HIP techniques, spark-plasma-sintering (SPS) technique has widely been utilized to the fabrication of various types of transparent ceramics. This is because the SPS technique can attain heating rates higher than 50°C/min, and hence, can save the total processing time. The final density, however, is highly sensitive to the SPS parameters. For the fabrication of transparent alumina and spinel ceramics, for example, a low heating rate of ≤10°C/min is effective than the widely used high heating rates of ≥50°C/min. By reducing the heating rate, although the SPSed spinel attains a reasonable in-line transmission of $T_{in} \approx$ 50% by effectively reducing residual porosity, the transmission is still much lower than the highest T_{in} (≈87%) obtained by HIPing technique, especially in the visible range. The limited T_{in} of the SPSed spinel is likely to be related to discoloration in addition to the porosity. The discoloration can be explained by the combination of carbon contaminations and lattice defects (color centers), which are introduced in the spinel matrix depending on the SPS conditions. Although the carbon contamination and defects formations become remarkable with increasing the heating rate, those were found to be introduced in the spinel matrix even for the slow heating rate.

3:50 PM

(ICACC-S8-042-2015) Synthesis by spark plasma sintering (SPS) of a composite of barium aluminosilicate (BaAl2Si2O8) reinforced by oxide fibers

R. Billard*[1]; A. Allemand[1]; Y. Lepetitcorps[1]; 1. LCTS, France

The aerospace industry needs refractory and resistant to oxidation materials at high temperatures between 1200 and 1700 °C. The BaAl2Si2O8 (BAS) partially meets its criteria. BAS is usually synthesized by conventional ceramic routes. BaCO3, SiO2 and Al2O3 powders are the starting precursors. The obtained BAS is in the metastable hexagonal phase. The low reactivity of the system leads to the persistence of the initial or intermediate products. Higher durations and / or temperatures may complete the reaction. However, the hexagonal metastable structure could be transformed in the monoclinic stable phase. A new innovative way, combining another aluminous precursor and the SPS synthesis technique enables to get BAS in a single step. This new synthesis will be presented in detail. SPS technique proved to be effective in reducing the processing time, reduce the level of residues and densify the material. After obtaining the BAS, it may be mixed with oxide fibers as reinforcement and compacted again with SPS to obtain a composite. A patent has been filed on this process. Initial tests also suggest that the composite can be formed in the same step as the synthesis of BAS. Tests of rapid rise to very high temperature (2200 °C/min up to 1700 °C) exhibit no craks inside the BAS sample. The crystalline structure is still hexagonal.

4:10 PM

(ICACC-S8-043-2015) Fast thermal cycling of SiC based ceramics by microwave heating

G. Bianchi[1]; P. Vavassori[4]; A. Ortona*[1]; G. Annino[6]; S. Gianella[5]; B. Vila[2]; M. Nagliati[3]; M. Mallah[2]; M. Valle[4]; M. Orlandi[3]; 1. SUPSI, Switzerland; 2. Fricke und Mallah Microwave Technology GmbH, Germany; 3. BREMBO SGL CARBON CERAMIC BRAKES, Italy; 4. Petroceramics, Italy; 5. Erbicol, Switzerland; 6. Consiglio Nazionale delle Ricerche, Italy

Lightweight ceramics and fiber reinforced ceramic composites, such as non-oxide Ceramic Matrix Composites (CMCs) represent very promising solutions for high temperature applications in strategic industrial sectors, such as transport and energy. In fact, these materials are one of topical priorities of the European Technology Platform EuMAT and a strategic issue of the EC Research Roadmap on Materials. Huge market opportunities are expected for CMC provided to overcome the three major identified gaps: high cost, difficulty of processing and materials reliability. New and more efficient manufacturing technologies can pave the way to improve material quality, reduce processing time, converge towards near-net shape fabrication, trim energy spent and abate production costs. The FP7 project HELM is addressing these challenges by employing innovative high-frequency electromagnetic, microwaves (MW), heating technologies for integrating and, in the long term, replacing standard thermal processing routes for several processes among which stands Liquid Silicon Infiltration (LSI). The process is being applied in several SiSIC applications such as brake discs, antiballistic protections, as well as porous ceramics.

4:30 PM

(ICACC-S8-044-2015) Microwave Processing Cage-like Magnesium Silicate Hosted Phosphor with a 660 nm-featured Emission for Bio-illumination

D. Wang*[1]; Q. Lu[1]; Z. Mao[1]; 1. Tianjin University of Technology, China

The energy-saving, environmental friendly light-emitting-diodes (LEDs) in solid-state lighting (SSL) emerge recently as a very effective means to achieve the specific photosynthesis action spectrum (PAS) to cover well to the absorption spectrum of chlorophyll for plant illumination. A very narrowed breadth of emission spectrum from either blue InGaN chip or red AlInGaP chip does not cover well the specific absorption spectrum of bio-species. Employing microwave (MW) processing procedure, we demonstrate a realization of simultaneous 660 nm red/blue broad band emission phosphor and violet-colored bio-LED prototype by carefully tuning a specific solid solution composition and structure in Ba-Sr binary composition of A3MgSi2O8 (A=Ba, Sr, Ca) from Mn2+ luminous center via energy transfer from Eu2+ sensitizer to give desired 660 nm red emission band. The formation of a green emission A2SiO4 host phase can be effeciently supressed with the aid of MW interaction to allow phase-pure host and cage-like (Ba, Sr)3MgSi2O8:Eu, Mn luminous sphere in micrometer size obtainable. The results suggest that MW firing procedure effects assembling cage-like single-phase particle in meso-, nano- and submicro- meters to achieve photoluminescence (PL) enhancement of the simultaneous red/blue emission in the applicatiopn of plant illumination.

S9: Porous Ceramics: Novel Developments and Applications

Innovations in Processing Methods and Synthesis of Porous Ceramics III

Room: Coquina Salon H
Session Chair: Enrico Bernardo, University of Padova

1:30 PM

(ICACC-S9-016-2015) Fabrication of High-flux Ceramic Hollow Fibers for Gas and Liquid Separations (Invited)

Z. Lai*[1]; 1. King Abdullah University of Science and Technology, Saudi Arabia

Ceramic membranes have a much longer history than polymeric membranes in gas and liquid separation applications; although the latter one current dominates the membrane market. One of the main reasons is because of the high cost of ceramic membranes which is mainly associated to their lengthy and complicated membrane fabrication procedure. An important technology that has been widely used in polymeric membrane fabrications is hollow fiber spinning coupled with phase-inversion. The spinning process is fast, easy to scale-up, and able to produce the desired asymmetric porous structure in one-step. Recently this technology has been successfully migrated to ceramic membrane fabrications, which potentially may lead to significant reduction in the cost ceramic membranes. In our lab we have successfully used this technology to fabricate hollow fibers out of many different types of inorganic materials including alumina, yttrium-stabilized zirconia, glass, stainless steel and nickel. The membrane can be made in single-layer and dual layers. In this talk we will discuss the relationship between the fiber microstructure and the spinning conditions. These hollow fibers have been used as high-flux supports in separation of hydrocarbon mixtures and seawater desalination and have achieved excellent separation performances.

2:00 PM

(ICACC-S9-017-2015) Fabrication of porous SiC ceramics using silicon, carbon and polysiloxane

E. Lee*[1]; Y. Kim[1]; D. Kim[1]; 1. SungKyunKwan University, Korea (the Republic of)

Porous SiC ceramics were fabricated from Silicon (Si), carbon (C) powders and polysiloxane mixture. During the heating, the Si powder was reacted with C powder and synthesized to β-SiC. When the formed β-SiC particles transformed to α-SiC at >2373K, rapid grain growth of α-SiC was consumed the β-matrix SiC particles and porous structure with huge elongated plate-like grain was formed. To improve the strength of porous SiC ceramics, polysiloxane was added. The effect of initial composition on the microstructure formation of porous SiC ceramics and their mechanical properties were investigated and discussed.

2:20 PM

(ICACC-S9-018-2015) Innovations and novel techniques used to manufacture low cost environmentally friendly porous ceramics

J. E. Lancien*[1]; S. O. Matthews[1]; E. Branigan[1]; 1. SCF Processing Ltd, Ireland

Polyurethane sacrificial scaffolds based ceramics are mainly used in the manufacturing of the open porous ceramic parts. These porous ceramics are not environmentally friendly, they are expensive to produce, and secondary processing is usually required in order to achieve the desired part geometry. SCF Processing Ltd has undertaken an extensive R&D program to assess and optimize alternative routes to manufacture open porous ceramic foams. This paper presents the final phase of the R&D program that has resulted in low cost and environmentally friendly sacrificial scaffolds. The innovative techniques used, such as natural fiber scaffolds, starch scaffolds, and most recently 3D printing of ceramics will be discussed. These techniques will be compared to the conventional polyurethane route for a variety of ceramics so that cost and property assessments can be made.

2:40 PM

(ICACC-S9-019-2015) Porous 3D ceramic structures formed using a modified weaving technique

S. O. Matthews*[1]; J. E. Lancien[1]; J. Matthews[1]; 1. SCF Processing Ltd, Ireland

Conventional materials and weaving processes have been successfully combined and modified to produce porous ceramic 3D structures. Two key developments; the development of suitable ceramic slurries and the development of the technique for the infusion of the slurry into the wool have contributed to the R&D process moving to the next phase i.e. the technology scale up. This paper will discuss the scaling up challenges encountered and present a selection of porous ceramic products manufactured using the technique.

Innovations in Processing Methods and Synthesis of Porous Ceramics IV

Room: Coquina Salon H
Session Chair: Siobhan Matthews, SCF Processing Ltd

3:20 PM

(ICACC-S9-020-2015) Hierarchical Porous Ceramics Fabricated by Freeze-Casting Method and Their Energy and Environmental Applications (Invited)

D. Kim[1]; S. Yong[1]; W. Jung[1]; D. Kim*[1]; 1. KAIST, Korea (the Republic of)

There have been many attempts to have porous structure in various ways, and one of them is a freeze-casting method. The freeze-casting method, which is an environmentally friendly and cost-effective technique, has attracted considerable interest due to its unique and interesting features. A porous microstructure can be obtained by freezing a suspension and subsequently removing the ice crystals by sublimation, leading to well-defined hierarchical porous structures with homogeneous lamellar pore channels. In the present work, we have fabricated the unique porous structures of various ceramics by using freeze-casting, and evaluated their characteristics for some applications. Porous Si_3N_4 ceramic with hierarchical pore structures was prepared for a filter application. The open pore channels and the hierarchical microstructure are expected to have better permeability and the filterability. In addition, the freeze-casted $LiFePO_4$ and TiO_2 thin films with hierarchically aligned pores were fabricated for the electrode of rechargeable battery and photoelectrode of dye-sensitized solar cells, respectively. It was found that the hierarchical porous electrodes give rise to the efficient charge collection, resulting in the enhancement of device performance. The influence of fabrication conditions on the device performances was discussed in detail.

3:50 PM

(ICACC-S9-021-2015) Imaging of Internal Microstructure of Porous Titania Granules by Epoxy Infiltration

N. Ku*[1]; R. A. Haber[1]; 1. Rutgers University, USA

Porous ceramics offer many unique properties such as low density, low thermal conductivity, high temperature stability, etc. These properties are often directly related to the microstructure of the porous material, with the pore size, shape, and distribution affecting the desired function. For this reason, a method for imaging the microstructure of porous ceramics is important in the characterization. In this study, loosely-packed granules of titania powder are imaged using a scanning electron microscope. These granules are infiltrated with an epoxy resin to preserve the microstructure and allow for polishing of the sample to expose a flat surface. The surface is then imaged to show a two-dimensional cross-section of the granule. The images are then analyzed to show not only the overall porosity of the granule, but also the variation of the porosity across the internal microstructure.

4:10 PM

(ICACC-S9-022-2015) Effect of Pore Former Shape on Cast $Ce_{0.9}Gd_{0.1}O_{1.95-\delta}$ Tapes Properties

C. Grings Schmidt*[1]; A. Kaiser[1]; K. Kammer Hansen[1]; K. Bøhm Andersen[1]; A. Roosen[2]; Z. Fu[2]; 1. Technical University of Denmark, Denmark; 2. University of Erlangen-Nuremberg, Germany

Air pollution from fossil fuels combustion is an increasing problem in today's cities. Electrochemical gas purification is an attractive possibility to contour this problem, where the reduction of NOx and the oxidation of soot and hydrocarbons are activated by the use of a solid state electrochemical cell based on an oxide ion conductor. Such cells must tailor a high gas permeability, conductivity and mechanical strength. In the present work, the electrolyte layer ($Ce_{0.9}Gd_{0.1}O_{1.95-\delta}$) was studied using six different types of pore formers, which were varying in shape and size, and was fabricated via the processes of slurry preparation, tape casting and sintering. Porosity, pore size, pore orientation, microstructure, shrinkage, gas permeability, mechanical strength and conductivity of the sintered reactors were characterized. Using the present ceramic processing route, flat and crack-free tapes were successfully achieved. The gas permeability seems to be influenced by the orientation of the pore formers during tape casting and by the pore size, but not by the total porosity. As expected, the mechanical strength depends on the total porosity, but further studies are being conducted to evaluate whether the pore shape and orientation also have an influence on it. Also the higher the gas permeability the lower the conductivity, therefore a better tailoring of these parameters have still to be met.

4:30 PM

(ICACC-S9-023-2015) Advanced electrodes for Tubular Ceramic Fuel Cells

A. Hanifi*[1]; T. H. Etsell[1]; P. Sarkar[2]; 1. University of Alberta, Edmonton, Canada; 2. Alberta Innovates - Technology Futures, Canada

The development and advancement of tubular ceramic fuel cells in Canada are discussed. Infiltration of both the anode and cathode enables fabrication of advanced electrodes with a suitable microstructure for fuel cell applications. The electrochemical performance and stability as well as redox and thermal cycling tolerance of fully infiltrated tubular cells are discussed in this research. The fuel cells studied contain infiltrated Ni-SDC ($Sm_{0.2}Ce_{0.8}O_{1.9}$) in the anode and infiltrated LSM ($La_{0.80}Sr_{0.20}MnO_{2.9}$) in the cathode. The infiltrated cells deliver a reasonable power density especially at low temperatures (600-700°C). The microstructure of the infiltrated fuel cells shows a suitable distribution of fine LSM and Ni-SDC particles (50-100 nm) both at the electrode/electrolyte interfaces and within the electrodes. Also, the effect of $Nd_2NiO_{4+\delta}$ cathode infiltration on improved performance of tubular fuel cells is shown.

S10: Virtual Materials (Computational) Design and Ceramic Genome

Ceramic Genome and Modeling of Structure and Property I

Room: Coquina Salon C
Session Chairs: Jingyang Wang, Institute of Metal Research; Wai-Yim Ching, University of Missouri-Kansas City

1:30 PM

(ICACC-S10-001-2015) Use of Ab Initio Data in Materials Informatics: Application to MAX Phases (Invited)

W. Ching*[1]; R. Sakidja[1]; 1. University of Missouri-Kansas City, USA

There are many different strategies in which the emerging area of materials informatics are pursued. They all aim at accelerating the discovery of new materials with novel properties, and use data-intensive computational tools on supercomputers. The approach we take is to generate a high quality data base for a specific materials system and explore various correlations amongst them using data mining approach. The layered ternary compound MAX phase (Mn+1AXn) where "M" is an early transition metal. "A" a metalloid element and "X" is either C or N is used as an example for such an approach. A large data base of the elastic properties and electronics structures of 665 MAX compounds has been established. They are used to test and validate the efficacy of several data mining algorithm and machine learning tools with calculated properties as descriptors. In this talk, I will discuss the results of this application and its implications emphasizing the importance of the accuracy and the uniformity of the data. Extension of this highly promising research to several other materials systems will also be presented.

2:00 PM

(ICACC-S10-002-2015) Highly Selective Hybrid Gas Sensors: Insights from DFT (Invited)

L. Mayrhofer*[1]; M. Hoffmann[2]; J. Prades[3]; F. Hernandez-Ramirez[3]; T. Järvi[1]; M. Moseler[1]; A. Waag[2]; H. Shen[2]; 1. Fraunhofer IWM, Germany; 2. Technical University of Braunschweig, Germany; 3. University of Barcelona, Spain

Organic–inorganic hybrid gas sensors can offer outstanding performance in terms of selectivity and sensitivity towards single gas species. The enormous variety of organic functionalities enables novel flexibility of active sensor surfaces compared to commonly used pure inorganic materials. Here, we show that density functional theory (DFT) can be used to simulate such systems and is an appropriate tool to identify the basic mechanisms that determine the effective interaction between sensor and different gas species. DFT simulations were applied to a prototypical ultra-selective NO2 sensor that was realized experimentally on the basis of amine-terminated semiconductive SnO2 nanowires (NWs). Only minor or no response occurred in presence of possible interfering gas species. The selectivity of the sensor including a small reversed sensor signal for NO gas was correctly reproduced by the simulations. The energetic position of the SAM–gas frontier orbitals with respect to the NW Fermi level was identified to be the crucial parameter to ensure or impede an efficient charge transfer between the NW and the gas. As this condition strongly depends on the gas species and the sensor system, these insights into the charge transfer mechanisms can have a substantial impact on the computer aided development of highly selective gas sensors.

2:30 PM

(ICACC-S10-003-2015) Multiplet Energy Diagrams of d^3 Ions Based on First-Principles Calculations for Theoretical Design of Red Phosphors for White LEDs (Invited)

K. Ogasawara*[1]; 1. Kwansei Gakuin University, Japan

In order to improve the production cost and color rendering properties of white LEDs, red phosphors activated with Mn^{4+} are drawing attention. Although the Tanabe-Sugano diagrams are widely used for the analysis of multiplet energies of transition metal ions in crystals, they cannot be used for the quantitative prediction of the multiplet energies since these diagrams include empirical parameters. Therefore, energy diagrams without any empirical parameters are desired for the theoretical search of novel red phosphors. In this work, more practical multiplet energy diagrams of d^3 ions ($Cr^{3+}$and Mn^{4+}) in oxides and fluorides in terms of bond length and absolute multiplet energies were created based on first-principles calculations. The TMO_6 (TM = Cr, Mn) model clusters with O_h symmetry with gradually changed TM-O bond lengths were constructed. The multiplet energy calculations were performed based on the Discrete-Variational Multi-Electron (DVME) method. The effects of electron correlation and covalency were investigated in details. The results indicated that the bond-length dependence of the ^2E_g and $^2T_{1g}$ energies is domianted by electron correlation rather than covalency. In order to investigate the effect of distortion, two-dimensional multiplet energy maps for distorted clusters were also created.

3:20 PM

(ICACC-S10-004-2015) Strategy to achieve lower intrinsic lattice thermal conductivity (Invited)

J. Wang*[1]; 1. Institute of Metal Research, China

Searching for ceramics with extremely low lattice thermal conductivity are the key concern to improve the performances of advanced thermal insulation materials. The well understood qualitative guidelines are described by complex crystal structure, soft and heterogeneous atomic bonding, larger average atomic weight. In addition, minimum lattice thermal conductivity at high temperature limit also frequently serves as a material selection criterion. In this presentation, theoretical lattice thermal conductivities of novel candidates, such as silicate, aluminosilicate, phosphate, and zirconate, are quantitatively predicted based on Debye approximation and Slack model. The results clearly demonstrate that first-principles calculation can conveniently and precisely represent the temperature dependence of intrinsic lattice thermal conductivity of insulating ceramics. We will focus on discussing the mechanisms to decrease lattice thermal conductivity by tailoring chemical composition and crystal structure.

3:50 PM

(ICACC-S10-005-2015) Theoretical Investigations on the Structural, Electronic, Mechanical and Thermal Properties of MP2O7 (M = Ti, Zr, Hf)

H. Xiang*[1]; Y. Zhou[1]; Z. Feng[1]; 1. Aerospace Research Insitute of Materials and Processing Technology, China

In this work, the structural, electronic, mechanical, and thermal properties of MP2O7 (M = Ti, Zr, Hf) are studied by density functional theory. Heterogeneous bonding nature is revealed based on the calculated equilibrium crystal structure. Full set of elastic constants, polycrystalline mechanical properties and elastic anisotropy of MP2O7 are predicted. MP2O7 ceramics are determined to be "quasi-ductile" In addition, the temperature-dependent thermal conductivities of MP2O7 are estimated and the minimum thermal conductivities are determined to be 1.52, 1.15, and 0.99 Wm-1K-1 for TiP2O7, ZrP2O7, and HfP2O7, respectively. Low thermal conductivities are originated from phonon scattering due to the heterogeneous bonding nature. The theoretical results emphasize the importance of weak M-O bonds in the determination of mechanical and thermal properties of MP2O7 and highlight the potential application of MP2O7 as a thermal barrier coating.

4:10 PM

(ICACC-S10-006-2015) Calculation of Lattice Thermal Conductivity of MAX Phases

C. Dhakal*[1]; R. Sakidja[1]; S. Aryal[1]; W. Ching[1]; 1. University of Missouri-Kansas City, USA

The temperature dependent lattice thermal conductivity (κph) of MAX phases Mn+1AXn with n = 1, 2, 3 and X = C and N are calculated using the theory outlined by Slack. At high temperature, the formula derived by Slack is a reasonable approximation to estimate the κph for complex crystals. The calculations used the large data base established recently on the elastic coefficients and electronic structure of all potentially stable MAX phases. It is found that MAX phases with "A" = Al have higher lattice thermal conductivity at 1300k, and MAX carbides have higher phonon thermal conductivity than nitrides. Also calculated are the minimum thermal conductivity based on the empirical formula suggested by Clarke. Our calculated phonon thermal conductivity data for 8 MAX phases at 1300k are in reasonable agreement with the reported experimental data especially in Ti2AlC, Nb4AlC3, Ta4AlC3, Nb2AlC and Nb2SnC phases. The reason behind for such agreement with the rather simplified calculation will be discussed.

4:30 PM

(ICACC-S10-007-2015) Studies of the Cracked MMCs with Lamellar Microstructure

M. Kashtalyan[2]; Y. Sinchuk[1]; R. Piat*[1]; 1. Karlsruhe Institute of Technology, Germany; 2. University of Aberdeen, United Kingdom

Stress fields in a single-domain sample of MMC containing multiple cracks in the ceramic layer are investigated. The MMC cracked microstructure 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 result in work [6]. According to the obtained result, the average axial stress between the two cracks is decreasing with decreasing the distance between the cracks.

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

Methods to Improve the Oxidation Resistance and Damage Tolerance

Room: Ponce DeLeon
Session Chair: Xiaohui Wang, Institute of Metal Research

1:30 PM

(ICACC-S12-037-2015) The Role of Microstructure on Mechanical Behavior of Ti2AlC (Invited)

M. Radovic*[1]; 1. Texas A&M University, USA

From more than 60+ different MAX phases, Ti2AlC is considered to be one of the best candidates for high temperature applications because of its excellent oxidation resistance in air and water vapor due to the formation of spallation-resistant layer of Al2O3 with crack healing capabilities. However, mechanical properties of Ti2AlC still need to be improved substantially to make it attractive for high temperature application. In this paper we review the means of tailoring microstructure to process high strength Ti2AlC and its composites with the mechanical properties that are comparable to those of other high temperature materials currently in use such as Ni-based superallys. The results of comprehensive mechanical testing of Ti2AlC with different microstructure and its composites reinforced with Al2O3 fibers, together with post-mortem microstructural analysis suggests that mechanical properties of Ti2AlC can be significantly improved. The effect of grain size, amount of secondary or reinforcing phases on the strength, mechanical damping, brittle-to-plastic transition temperature and creep resistance of Ti2AlC and it composites is discussed in more detail in this paper, as well as potential ways to further improve their mechanical properties.

2:00 PM

(ICACC-S12-038-2015) Development of MAX phases for nuclear fuel cladding applications

D. Horlait*[1]; D. D. Jayaseelan[1]; W. E. Lee[1]; S. Grasso[2]; 1. Imperial College London, United Kingdom; 2. Queen Mary University, United Kingdom

In 2011, the loss-of-coolant accidents at Fukushima induced temperatures of over 1200°C inside reactors cores. This led to reactions between steam and the zirconium-based alloy fuel cladding, resulting in a build-up pressure of substantial amounts of H2, causing explosions in the reactor buildings. To improve passive safety of nuclear reactors and avoid similar accidents, coating, or replacement of the Zr cladding with a compound protective against hydro-corrosion and oxidation for at least several tens of hours at temperatures over 1200°C is being sought. Among the few possibilities to satisfy this industrial need, MAX phases are promising candidates for mid-term solution. On the basis of numerous criteria (neutron transparency, existing knowledge on high-temperature oxidation and corrosion behavior, stability under irradiation, etc.), several MAX phases (Ti2AlC, Cr2AlC, Ti3SiC2) and also derived ZrxAlyCz ternary layered carbides compositions have been selected and they are at present intensively investigated. Dense (Cr,Ti)2AlC compounds were prepared, characterized and tested at 1500°C in air to determine the optimized composition resulting in improved oxidation resistance. Furthermore, attempts to prepare Zr2AlC, (Ti,Zr)2AlC and (Cr,Zr)2AlC MAX phases will be reported as well as first developments of methods to enhance the properties (density, adherence, composition) of the outer protective oxide scale.

2:20 PM

(ICACC-S12-039-2015) Interaction of selected MAX Phases with pure sodium

G. Bentzel*[1]; M. W. Barsoum[1]; 1. Drexel University, USA

Herein we report on the interaction of the MAX Phases – Ti2AlC, Ti3AlC2, Ti3SiC2, and Cr2AlC – with pure sodium (Na). The selected MAX phases were sealed within 316 stainless steel tubes filled with Na. Samples were heated to 550 °C and 750 °C for 168 hours (one week) in a box furnace. Scanning Electron Microscopy, Energy Dispersive X-ray Spectroscopy, and X-ray Diffraction techniques were used to observe any interaction between the MAX and Na. All results suggest that, even at 750 °C, little or no interaction occurs.

2:40 PM

(ICACC-S12-040-2015) SiC Depletion in ZrB_2-30 vol% SiC During Oxidation at Ultra-High Temperatures

K. Shugart*[1]; E. Opila[2]; 1. UES, Inc., USA; 2. University of Virginia, USA

The porous structure formed during oxidation of ZrB_2-SiC due to SiC depletion could lead to reduced load-bearing capability or reduced thermal conductivity of ZrB_2-SiC for applications at ultra-high temperatures. Therefore understanding conditions necessary for the formation of a depleted layer should help in developing this material for future use. Specimens were oxidized using standard box furnace and resistive heating methods. The oxides were characterized using scanning electron microscopy and energy dispersive spectroscopy. The presence/absence of SiC depletion was determined at a series of temperatures (1300°C-1800°C) and times (5 minutes – 100 hours). At T<1627°C, SiC depletion was not observed. Instead, the formation of a ZrO_2+C/borosilicate oxidation product layer sequence was observed above the ZrB_2-SiC base material. At T≥1627°C, SiC was depleted in the ZrB_2 matrix below the ZrO_2 and borosilicate oxidation products. The SiC depletion was attributed to active oxidation of SiC to form SiO(g). The transition between C formation in ZrO_2 (T<1627°C) and SiC depletion in ZrB_2 (T>1627°C) is attributed to variation in the temperature dependence of thermodynamically favored product assemblage influenced by the local microstructural phase distribution. The growth kinetics of the SiC depletion region is consistent with a gas phase diffusion controlled process.

New Precusors for Powders, Coatings and Matrix or Fibers of Composites

Room: Ponce DeLeon

Session Chair: Guo-Jun Zhang, Shanghai Institute of Ceramics

3:20 PM

(ICACC-S12-041-2015) Preparation and Microstructure Investigation of UHTC Fibers (Invited)

W. Zhang[1]; M. Ge[1]; Y. Tian[2]; X. Lv[2]; S. Yu[1]; X. Wei*[1]; 1. Institute of Process Engineering, Chinese Academy of Sciences, China; 2. University of Chinese Academy of Sciences, China

A novel transition metals substituted polycarbosilane was synthesized via one-pot homogeneous catalytic insertion polymerization of dimethyldichloridsilane at temperatures below 100deg C. Synthesis and polymerization mechanism of the organic polymers, conversation process and microstructure of the derived fiber were investigated in detail. It was found that polycarbosilane synthesized through this novel process exhibits very narrow polymolecularities (Mw/Mn<1.5) and linear chain structure, which was found to be suitable for spinning of composite ceramic fiber. And it was also confirmed that this hybrid pre-ceramic polymer was converted to UHTCs of SiC-ZrC-ZrB2 or SiC-TiC-TiB2 at temperatures above 1200 deg C, which can improve the oxidation resistance of traditional SiC fiber.

3:40 PM

(ICACC-S12-042-2015) Influence of Nitrogen Pressure on SHS Synthesis of Ti_2AlN Powders

L. Chlubny*[1]; J. Lis[1]; M. M. Bucko[1]; D. Zientara[1]; M. Bednarska[1]; 1. AGH-University of Science and Technology, Poland

Among many covalent materials such as carbides or nitrides in the Ti-Al-C-N system exists group of interesting ternary and quaternary materials called MAX-phases. These materials are characterised by heterodesmic layer structure and have a $M_{n+1}AX_n$ stoichiometry, where M is an early transition metal, A is an element of A groups (mostly IIIA or IVA) and X is carbon and/or nitrogen. Their specific structure consisting of covalent and metallic chemical bonds affects their properties locating them on the boundary between metals and ceramics. The SHS synthesis with local ignition system has been applied for obtaining sinterable powders of Ti_2AlN materials. The nitrogen pressure may play an important role during the SHS synthesis of this material. Seven different chemical reactions were tested and various nitrogen pressures, from 0.5 atm. to 10 atm., were applied in order to obtain powders containing high amount of MAX phase ternary material. The XRD method was used to establish phase composition of the final product of the synthesis.

4:00 PM

(ICACC-S12-043-2015) Fiber Interface Coatings via UVCVD for High Temperature Fiber-reinforced Ceramic Matrix Composites

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

Ultraviolet-activated chemical vapor deposition (UVCVD) is a rapid, low cost method developed by Ultramet to apply oxide, nitride, and multilayer interface coatings to carbon and silicon carbide fibers at temperatures as low as 200°C, thus avoiding problems associated with fiber damage during conventional high temperature deposition. A broad selection of interlayer coating materials allows in-service fiber protection to be optimized for specific high temperature combustion environments. The thin, strain tolerant, fully dense, and high-purity coatings applied by UVCVD exhibit few defects and enhance fiber load distribution. UVCVD coatings have been effectively applied to individual fiber tows as well as woven and braided fabric, and continuous coating reactors for each have been demonstrated. Ultramet's use of interface coatings on fibers is mainly directed to the fabrication of fiber-reinforced ceramic matrix composites used in advanced rocket and turbine engines to significantly increase safety, enhance performance, reduce weight, improve durability, and lower total fabrication cost. UVCVD interface coating processing and the results of hot-gas testing of ceramic composites that used the coatings will be presented.

4:20 PM

(ICACC-S12-044-2015) Synthesis of doped hafnium diboride for UHT applications

P. Zheng*[1]; J. Binner[2]; B. Vaidhyanathan[1]; 1. Loughborough University, United Kingdom; 2. University of Birmingham, United Kingdom

HfB_2-based ceramics are considered to be potential materials for ultra-high temperature aerospace applications as they possess extremely high melting points, reasonable thermal and electrical conductivities and moderate oxidation resistance. Nevertheless, the oxidation resistance of HfB_2 is limited by the phase transformation of the HfO_2 oxide scale. The volume change caused by the phase transformation from tetragonal to monoclinic on cooling results in the protective oxide layer becoming cracked/porous allowing further attack by oxygen species. The present work was focused on adding various dopants to HfB_2 with a view to stabilizing the tetragonal form of HfO_2 formed during oxidation. Among different dopants investigated, TaB_2 was found most suitable for this purpose. Doped HfB_2 powders were synthesized via a two-step method; viz. a co-precipitation approach to produce homogeneous precursors and a subsequent carbo/borothermal reduction to yield Ta-doped HfB_2 powder. The lattice parameter investigations showed that $(Hf,Ta)B_2$ solid solution was formed (<15 wt% of TaB_2) and the particle size of the doped powders were in the sub-micron range. Furnace oxidation tests revealed that the oxide scale formed was completely stabilised in the tetragonal form, enhancing the prospect of using these materials for UHT applications.

4:40 PM

(ICACC-S12-045-2015) Synthesis and Sintering of Nanoscale Hafnium Diboride Powders

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

Hafnium diboride (HfB2) has an extremely high melting point, making it suitable for high temperature applications. The processing of conventional micron-sized HfB2 powders requires extremely high temperature and often leads to formation of minor defects, which can result in breakdown under extreme conditions. However, the demanding applications of this material require optimal physical properties to maximize safety and efficiency. To address this problem, nanocrystalline HfB2 particles were synthesized using low cost aqueous-solution based processing method. Hafnium chloride, sucrose as a carbon precursor, and boric acid as a boron source were dissolved in water to form the solution gel, which then went through processing steps including drying, pyrolysis, and carbothermal reduction (CTR) reaction. The solution processing allowed for homogeneous mixing and yielded nano HfB2 after the CTR reaction. The nanocrystalline HfB2 particles will then be sintered into ceramic parts via conventional pressureless sintering as well as spark plasma sintering (SPS). The benefits of using nanocrystalline particles as compared with micron-sized HfB2 will be studied by evaluating the thermal and mechanical properties (such as strength, hardness and toughness). The study is expected pave the way for new manufacturing process of ultra-high temperature ceramics for critical aerospace and civilian applications.

5:00 PM

(ICACC-S12-046-2015) Recent Studies to Understand the Tribology of MAX Phases and Their Composites

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

Recently, first generation MAX Phase based composites shafts were successfully tested against Ni-based superalloy at 50,000 rpm from RT till 550oC during thermal cycling in a foil bearing rig. The author also proposed a novel way of classifying the different tribofilms to understand the complex tribological behavior of these solids over a wide range of different experimental conditions. Briefly, the tribological behavior of MAX Phases and their composites can be divided into four types, namely, I, II, III, and IV. Initially, the author will discuss the characteristics of each type of tribofilms. Therafterr, the author will present recent progress and understanding about the tribological behavior of MAX Phases and their composites during dry sliding.

S13: International Symposium on Advanced Ceramics and Composites for Sustainable Nuclear Energy and Fusion Energy

SiC Composites R&D for Fusion Energy

Room: Tomoka B

Session Chair: Monica Ferraris, Politecnico di Torino

1:30 PM

(ICACC-S13-036-2015) Japanese activities on SiC/SiC composites toward fusion DEMO

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

SiC/SiC composites are attractive candidates for a demonstration power reactor (DEMO) of fusion applications. To meet DEMO requirements, it is essential not only to have a practical database but also to demonstrate composites' functionality under DEMO relevant environments. Under the Broader Approach (BA) project between the EU and Japan, developing the fundamental mechanical, physical and chemical properties database of SiC/SiC composites is addressed. Since composite functionality is closely linked to structural integrity, mechanical properties are evaluated even for assuming functional applications of SiC/SiC composites in near-term. Reliable test methods are also essential in data-basing and being developed coupled with various damage monitoring tools. In contrast, understanding irradiation effects on mechanical and physical properties of SiC/SiC composites is a key issue, because they are readily affected by irradiation. Irradiation creep, transmutation issue, radiation-induced conductivity and radiation-induced electrical deterioration, etc. are addressed. Chemical compatibility with liquid lead lithium alloy as tritium breeding material is another issue and considered. This paper aims to review recent progress in Japanese activities of SiC/SiC composites toward DEMO application. Specifically, lifetime, anisotropy, electrical resistivity, hydrogen permeability and compatibility issues are more emphasized.

1:50 PM

(ICACC-S13-037-2015) Silicon Carbide Composite Research in U.S. Fusion Materials Program

Y. Katoh*[1]; L. L. Snead[1]; C. H. Henager[2]; 1. Oak Ridge National Laboratory, USA; 2. Pacific Northwest National Laboratory, USA

The development and maturation of the SiC/SiC system for fusion applications has seen the evolution from fundamental development and understanding of the material system and its behavior in a hostile irradiation environment to the current program which is essentially a broad based program of technology, directed at moving this material class from a laboratory curiosity to an engineering material. Recent SiC/SiC composite R&D for fusion energy combines several elements, including the identification and definition of design-limiting performance envelopes for application in DEMO and beyond, development of integration technologies to be used in component fabrication, studies directed at establishing and qualifying SiC-based flow channel insert technology for specific liquid metal-breeding blanket concepts, and exploration of alternative materials and manufacturing routes. This paper provides a high level overview of the recent progress, current status, and future directions of SiC/SiC composite R&D in U.S. fusion materials program.

2:10 PM

(ICACC-S13-038-2015) On the Research Activities and Achievements in SiCf/SiC Composites for Fusion Structural Applications (Invited)

S. Novak[1]; A. Ivekovic[1]; M. Ferraris[2]; A. Galatanou[3]; J. I. Pastor[4]; D. Blagoeva[5]; S. Gonzalez da Vicente*[6]; 1. Jozef Stefan Institute, Slovenia; 2. Politecnico di Torino, Italy; 3. National Institute for Materials Physics, Romania; 4. Universidad Politécnica de Madrid, Spain; 5. NRG, Netherlands; 6. EFDA Close Support Unit, Germany

The aim of the paper is to summarise the latest achievements and current research activities oriented to the development of SiCf/SiC composites as candidate materials for application in future fusion reactors. The SiCf/SiC remains on the agenda of research groups worldwide due to the exceptional intrinsic properties of the SiC ceramics, i.e. high temperature- and chemical stability, low neutron activation and afterheat levels as well as due to the fact that it is the only non-magnetic candidate material. However, due to the extremely demanding set of requirements, fabrication of the composites represents a major challenge for material scientists. Thermal conductivity was identified as the most critical characteristic, which is highly temperature dependent, but also depends on the composition and microstructural characteristics. Although the current value of the thermal conductivity of the recently developed SITE-SiCf/SiC meets the requirements set by EFDA, the inevitable decrease of the value after exposure to neutron irradiation dictates the need for further improvement. The approach is based on identification of the key issues of the state-of-art processing techniques to control the critical characteristics such as porosity, amorphous phases, grain size, etc. Further attention is paid to maximise the mechanical properties of the composite parts as well as of joints.

Ceramic and Glass Technology for Nuclear Waste Management

Room: Tomoka B

Session Chair: Josef Matyas, Pacific Northwest National Lab

3:20 PM

(ICACC-S13-039-2015) Stabilization of Concetrated Low Activity Waste in a Cementitious Waste Form (Invited)

A. Cozzi*[1]; K. Fox[1]; E. Hansen[1]; J. Farell[2]; 1. Savannah River National Lab, USA; 2. University of Alabama, USA

In the DOE Complex, the immobilization of low activity waste (LAW) is achieved through vitrification (planned for Hanford) and cementation (current at the Savannah River Site and considered for Hanford). The cementitious waste forms benefit from the use of inexpensive raw materials (and materials that would otherwise be considered wastes themselves) and require a minimal amount of energy for processing. However, the volume of low temperature waste forms can be large relative to the volume of waste immobilized within them. Stabilizing waste in a low temperature waste form intensified by increasing the concentration of the waste will allow for volume reductions of 50% or more, greatly reducing the disposal footprint and reducing the operating lifecycle of the facility. Waste forms were prepared from concentrated simulated waste solutions using cement and pozzolans in different combinations and ratios. The freshly prepared mixes were used to measure processing properties and cast into cylinders, stored, and subsequently tested for cured properties.

3:50 PM

(ICACC-S13-040-2015) Glass Ceramic Waste Form Development for High-Level Waste from Reprocessed Spent Nuclear Fuel (Invited)

J. V. Crum*[1]; V. Maio[2]; J. Marra[3]; J. Vienna[1]; 1. Pacific Northwest National Laboratory, USA; 2. Idaho National Laboratory, USA; 3. Savannah River National Laboratory, USA

Glass Ceramics are being developed to immobilize the high-level waste (HLW) fission products from aqueous reprocessing of spent nuclear fuel. The projected waste stream contains a high fraction of Mo, lanthanides (Ln), noble metals, alkaline, and alkaline earths resulting in phase separation and crystallization in borosilicate glass even at waste loading as low as 18 mass%. Glass ceramics are an attractive choice to achieve waste loading by incorporating these troublesome fission products into durable crystalline phases: oxyapatite, Ln-borosilicate, and powellite by controlling melt composition and cooling rate in the canister. Intentionally crystallizing these components may allow the formation of more durable glass phase by removing a large fraction of components that otherwise would act as modifiers in the glass network. The observed of the phase separation and crystallization sequence upon cooling from a melt as a function of cooling rate and melt composition will be discussed along with the effects of crystallization on melt viscosity (melter pouring) and glass ceramic microstructure on waste form performance.

4:20 PM

(ICACC-S13-041-2015) Ceramic Waste Forms for Immobilization of Waste from Commercial Fuel Reprocessing (Invited)

J. Amoroso*[1]; J. Marra[1]; 1. Savannah River National Laboratory, USA

Developments of waste treatment and immobilization technologies are an integral component to the United States Department of Energy (DOE) Fuel Cycle Research and Development (FCR&D) program. Ceramic waste forms that accommodate a range of waste components are a favorable technology for nuclear waste immobilization. Ceramic waste forms are generally processed using hot pressing or spark plasma sintering, methods that can be prohibitively expensive or impractical at production scales. Melt processing has been investigated as an alternative to solid-state sintering methods. The technology readiness of melt processing is expected to be comparatively advantageous over other solid-state sintering methods given that melter technology is currently in use for High Level Waste (HLW) immobilization in several countries. Progress made towards improving the processing and durability of ceramic waste forms will be discussed.

4:40 PM

(ICACC-S13-042-2015) Development of Silica-Based Waste Form for Radioiodine

J. Matyas*[1]; A. Walter[1]; 1. Pacific Northwest National Lab, USA

The U.S. Department of Energy is currently investigating alternative sorbents for the removal and immobilization of radioiodine from the gas streams in a nuclear fuel reprocessing plant. One of these new sorbents, Ag0-functionalized silica aerogel, shows promise as a potential replacement for Ag-bearing mordenites because of its high selectivity and sorption capacity for iodine. Moreover, a feasible consolidation of iodine-loaded Ag0-functionalized silica aerogels to a durable SiO2-based waste form makes this aerogel an attractive choice for sequestering radioiodine. The presentation will discuss the results from consolidation experiments with hot uniaxial pressing, hot isostatic pressing, and spark plasma sintering, which offer simultaneous application of fast heating rates to temperatures above 1000°C and pressures up to 210 MPa. The discussion will include optimization of starting material (particle size, removal of organic moiety) and process conditions (T, t, p), and testing of different types and concentrations of additives (e.g., silica sol, raw silica aerogel, low-melting glass) to enhance the sintering process with the goal of maximizing iodine loading and retention in the densified product.

FS1: Geopolymers, Chemically Bonded Ceramics, Eco-friendly and Sustainable Materials

Construction Materials II

Room: Oceanview

Session Chairs: Elodie Prud'homme, LGCIE - INSA Lyon; Cengiz Bagci, Hitit University

1:30 PM

(ICACC-FS1-020-2015) Current Progress in the Development of Next Generation Green Manufacturing Technologies (Invited)

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

In the presentation, we will present recent developments on the research and development of green cements, and "greening" of ceramic manufacturing. During part A, we will present recent results on the development of fly ash based cements. It is well known that the alkali activation of Fly Ash to produce cementitious materials is an important area of fundamental research. From environmental perspective, the use of alkali activators, for example NaOH, is an environmental concern as it is electrochemically generated with the concomitant production of harmful Cl2 or HCl gas as by products. Recently, we proposed that it is possible to use activate Fly Ash to produce cementitious network by using low concentration of alkaline solutions (<0.05 M). In this presentation, we will present different results about the successful utilization of this novel technology for fabricating different novel composites by using both Class C and Class F fly ash from different sources. The fundamental chemistry responsible for the cementitious behavior of these novel structures will be discussed. In addition, detailed mechanical property studies, microstructure analysis, and phase analysis will be presented. During part B, we will present recent experimental results to optimize the manufacturing processes by green body engineering.

1:50 PM

(ICACC-FS1-021-2015) Long-term development of mechanical strength of alkali-activated metakaolin (MK), fly ash (FA), slag (H) and hybrids (FA/MK, H/MK)

F. Jirasit*[1]; C. H. Rüscher[2]; L. Lohaus[3]; P. Chindaprasert[4]; 1. RMUTL, Thailand; 2. Leibniz Universität Hannover, Germany; 3. Leibniz Universität Hannover, Germany; 4. Khon Kaen University, Thailand

The room temperature strength development of alkali-activated metakaolin (MK), fly ash (FA), slag (H) and their hybrid systems (FA-MK, H-MK) followed over a period of 2000 days reveal interesting properties for future applications. Using waterglass/MK ratios, which still provides significant amounts of unreacted MK, gains moderate increase in strength for the whole time of observation. With the addition of H the long-term compressive strength observed for MK (30-40 MPa) gradually increases up to 140 MPa after 2000 days for H. This effect is explained by the structure directing effect for the growth of poly-siloxo chains due to the high alkaline earth ion content contributed by the slag. In contrast the addition of FA evokes gradually lower compressive strength at short aging time (60 days). However, at longer times the compressive strength significantly improves the more the higher the FA content is. This is explained by the rather slow reaction of FA compared to

MK in the present systems. Effects of porosity and acid resistance will be discussed.

2:10 PM

(ICACC-FS1-022-2015) Analysis and Correlation of Chemical and Mechanical Characteristics of Fly Ash Geopolymer Concrete

R. Islam*[1]; C. Montes[1]; E. Allouche[1]; 1. Louisiana Tech University, USA

In recent years, EPA has introduced more stringent air quality standards that have made waste products, such as fly ash, more difficult and costly to dispose. Improper handling and disposal of these waste products can cause serious environmental problems such as soil and water contamination. Fly ash based geopolymer offers an opportunity to utilize large volumes of this waste in engineering applications. Therefore, the study of the engineering properties of geopolymer concrete is essential to achieve this goal. For the present study, 60 fly ash samples collected from power generation stations in the United States and abroad were analyzed and tested as raw materials for geopolymer concrete. The data resulting from this experimental program was divided in two sets, the first consisting of 50 samples for data analysis and modeling and the second consisting of the 10 remaining samples for validation purposes. All samples were analyzed via X-Ray Fluorescence (XRF) and X-Ray Diffraction (XRD) for oxide and phase composition. These chemical properties were used to predict the mechanical strength of geopolymer concrete (GPC). The data collected were used to develop equations to predict key properties of geopolymer concrete such as compressive and flexural strength, and static elastic modulus, which can be used as design parameters for geopolymer concrete structures.

2:30 PM

(ICACC-FS1-023-2015) Study of consolidated materials based on alkali-activated blast furnace slag (Invited)

E. Prud'homme*[1]; M. Michel[2]; J. Ambroise[1]; 1. LGCIE - INSA Lyon, France; 2. LCGIE - Université Lyon I, France

With environmental regulations, building field has to reduce its environmental impact. In this context, cements with high degree of OPC substitution have been developed over many years. One of these substitutes is blast furnace slag (BFS), which is a co-product of steel industry, mainly composed of SiO2, Al2O3 and CaO, and has the particularity to be latent hydraulic material. Performances of BFS cement are very good in long term, but could be improved at early age due to its low activation. Global objective is to focus specifically on BFS to evaluate its potential activator (salt, hydroxide …) at short term for cement application. Previous work has already shown the high reactivity of BFS in basic media, by studying dissolution/precipitation reactions of suspensions, raising the possibility of forming materials by alkali activation. In this study, the ternary BSF-SiNa-NaOH is investigated to form materials at room temperature, which are compared in consolidation kinetics, mechanical properties and carbonation durability. Materials characterizations were realized from 0 to 28 days using in-situ infrared spectroscopy, DTA-TGA, XRD, mercury porosity and SEM. Best materials present a good stability in carbonation, a compressive strength of 80MPa and a Young's modulus of 60GPa. This suggests possible use in combination with granular or fibrous additions to form composite material with high performances.

3:10 PM

(ICACC-FS1-024-2015) Preparation of geopolymer-type mortar and lightweight concrete from copper floatation waste and coal combustion by products (Invited)

T. Jadambaa[1]; M. Amgalan[1]; D. Batmunkh[1]; Z. Tsoodol[1]; B. Uyat[1]; J. Tsedev[2]; C. H. Rüscher*[3]; 1. Institute of Chemistry and Chemical Technology, Mongolian Academy of Sciences, Mongolia; 2. Mongolian University of Science and Technology, Mongolia; 3. University of Hannover, Germany

The copper floatation plant in Erdenet (Mongolia) produces up to 25 million tonnes of floatation waste per annum. To utilize this flotation waste and mitigate the dust hazard, the waste was used as a fine aggregate for alkali-activated mortar and lightweight concrete. Here we describe the preparation and properties of alkali-activated mortars and lightweight concrete based on two types of wastes (copper floatation waste and flyash and pond ash from Mongolian thermal power stations in Ulaanbaatar and Darkhan. All these starting materials were characterized by XRF, granulometry, XRD, SEM and gamma-ray spectroscopy. Alkali-activated geopolymer-type mortars and lightweight concretes were formed by substituting these raw materials for construction sand aggregate. Substitution of construction sand by Erdenet floatation waste in the geopolymer mortar and in the lightweight concrete produces materials with physical and mechanical properties comparable with the samples containing construction sand. The 7-day compressive strength of alkali-activated mortar containing 70% flyash and 30% floatation waste was 22.0 (4.69) MPa, while for the corresponding mortar prepared with construction sand it was 21.2 (5.5) MPa. Lightweight concrete of the same composition prepared with floatation waste had a compressive strength of 2.8 MPa.

3:30 PM

(ICACC-FS1-025-2015) Thermomechanical stability of portland cement with steel slag waste contents

H. A. Colorado*[1]; S. A. Colorado[2]; J. Posada[1]; 1. Universidad de Antioquia, Colombia; 2. Instituto Tecnologico Metropolitano, Colombia

Steel slag is a hazardous waste of concern to the slag industry around the world. The main goal of this research is to study the thermomechanical stability of Portland cement with high loading of Colombian steel slag. The manufacturing process is conducted entirely at room temperature. Steel slag waste was added up to 80wt% to cement, which is very beneficial to the environment. The effect of the steel slag concentration on the compressive strength, density, and microstructure is presented. Microstructure was evaluated by scanning electron microscopy (SEM) and x-ray diffraction (XRD). Weibull statistics is also presented.

3:50 PM

(ICACC-FS1-026-2015) Portland cement with battery waste contents

H. A. Colorado*[1]; A. Norena[2]; 1. Universidad de Antioquia, Colombia; 2. I+D Recycling Solutions, Colombia

Waste from alkaline and carbon batteries is used in this research in combination with ordinary Portland cement. Waste is mostly composed of zinc, manganese and iron oxides. The aim of this research is to find new applications for this waste. The waste was introduced in the cement in different loadings and diverse characterization was conducted with this aim. The effect of this waste on the compressive strength, density, and microstructure is presented. Microstructure was evaluated by scanning electron microscopy (SEM) and x-ray diffraction (XRD).

4:10 PM

(ICACC-FS1-027-2015) The role of temperature on properties of ternary composite matrix

M. Boháč*[1]; R. Novotný[1]; J. Másilko[1]; F. Frajkorová[1]; E. Bartonickova[1]; M. Palou[1]; 1. Brno University of Technology, Faculty of Chemistry, Czech Republic

The aim of the study was the role of temperature on early hydration and phase composition of composite matrix consisting of cement and eco-friendly and sustainable metakaolin and blast-furnace slag assuming its application for different building and construction materials with extended durability. Early hydration of matrix was studied at 30 °C, 40 °C, 50 °C and 60 °C by isothermal calorimetry. The phase composition of matrix cured at 60 °C was monitored by XRD and DTA-TG during initial 7 hours. The hydration of composite matrix is strongly dependent on temperature. The processes of formation of amorphous calciumsilicate hydrates, calcium hydroxide and ettringite are characterized by independent peaks on calorimetric curves. The 1st peak is attributed to combination of exothermic wetting and formation of gelatinous coating. The 2nd peak characterizes the nucleation and crystallization of calcium-silicate hydrates and calcium hydroxide. The 3rd peak denotes the renewed crystallization of ettringite. The 4th is related to conversion of ettringite to hemicarbonate aluminate hydrate. Activation energies for each process were calculated and linear trend of heat flow maxima on temperature was revealed. Early properties of composite matrix and especially the rate of formation and morphology of aluminate hydrates are significantly influenced by presence of excessive amount of reactive alumina from metakaolin.

4:30 PM

(ICACC-FS1-028-2015) Sustainability of Geopolymeric bricks production process (Invited)

R. Cioffi[1]; C. Borrelli[1]; C. Ferone*[1]; A. Petrillo[2]; 1. University Parthenope, Italy; 2. University Parthenope, Italy

Brick represents one of the most used materials for the construction of buildings, but the rising demand of building materials and increased construction and demolition wastes have encouraged the development of new building materials. However, the traditional means of brick production causes several environmental and human health impacts, so there is a clear need of searching and replacing for more efficient and durable alternatives far beyond the limitations of the conventional brick production. The purpose of this article is to identify impacts during the entire life cycle and describes the basic operations of the geopolymeric bricks manufacturing in the Campania region plants. The analysis is performed using life cycle assessment (LCA) methodology, which is a method used to identify and quantify the environmental performance of a process or a product from “cradle to grave” approach. LCA methodology supplies a quantitative basis for assessing potential improvements in environmental performance of a system throughout the life cycle. Study results have revealed that the Geopolymeric brick making process consumes less energy and involves low cost in terms of raw materials. The production of the former is compared to conventional bricks and their development which is an important step to reach better performance and environmental friendly materials.

FS2: Advanced Ceramic Materials and Processing for Photonics and Energy

Solar Cells

Room: Tomoka A

Session Chairs: Yasuhiro Tachibana, RMIT University; Giovanni Fanchini, University of Western Ontario

1:30 PM

(ICACC-FS2-001-2015) Solution processed organic/inorganic photovoltaics (Invited)

C. Luscombe*[1]; 1. University of Washington, USA

Due to the decreased availability of fossil fuels and greater understanding of the long-term global effects of CO2 and other greenhouse gas emissions, significant interest is being generated in the area of alternative energy resources. One of the most promising renewable resources lies in photovoltaics (PV) for electricity generation. Traditional, inorganic PV have shown championship efficiencies of up to 44%, and most commercially available units provide conversion efficiencies of about 25%. While extensive production of these devices could help alleviate current energy demands, high production costs have hindered product output. One way to lower the cost of devices is to manufacture devices using high throughput, roll to roll processing. In this talk, synthetic strategies to form solution processible organic/inorganic hybrid nanoparticles will be discussed along with their thin film properties and photophysical properties.

2:00 PM

(ICACC-FS2-002-2015) Charge separation and recombination processes in bare and dye-sensitized TiO2 nanoparticles (Invited)

R. Katoh*[1]; 1. Nihon university, Japan

We have so far studied charge generation and recombination processes in bare and dye-sensitized TiO2 nanoparticles by using wide-wavelength-range (400-2500 nm), highly sensitive transient absorption (TA) spectroscopy and time-resolved microwave conductivity (TRMC) technique. Following three topics will be presented. (1) Assignment of absorption spectra of active species We obtained absorption spectra of active species in nanocrystalline TiO2 films through TA measurements. Three active species, trapped hole and electron, and conducting electron in the spectra can be identified. (2) Recombination rate and trapping dynamics Recombination rate and trapping dynamics of electron can be discussed from decay profiles in TA and TRMC signals. We studied various types of TiO2 samples, including single crystals to discuss the origin of slow recombination rate. (3) Estimation of charge separation efficiency Since the signal in TRMC measurements is proportional to conductivity (mobility x number of charge), charge separation efficiencies can be estimated. We have applied this technique to visible light sensitive photo-catalysts and dye-sensitized TiO2 films.

2:30 PM

(ICACC-FS2-003-2015) Interfacing organic and carbon-based nanomaterials towards their applications in sustainable energy

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

From the 1996 Nobel Prize for Chemistry, recognizing the synthesis of fullerene, to the 2010 Nobel Prize for Physics, awarded to the discovery of graphene, carbon-based nanomaterials have evolved into one of the hottest area in materials science. Utilization of large-area graphene thin films as transparent conductors in solar cells and energy-efficient light emitting devices may take significant advantage of a deeper understanding of their electronic and optical properties at the nanoscale. Applications exploiting the extremely high thermal conductivity of these materials are also emerging. A common denominator between many application-oriented graphene-based thin films is in the necessity of understanding their properties when they are interfaced with organic materials, including conducting polymers, organometallic nanoclusters and small polyaromatic molecules. In this presentation, I will review what our group has learned on the physical properties of graphene laminates, graphene-organic nanocomposites and graphene-based organic solar cells. Although all of these properties are reminiscent of the fundamental physics of individual graphene layers, a number of other concepts, related to their nanocomposite nature, are required to design large-area graphene thin films suitable for practical uses.

3:20 PM

(ICACC-FS2-004-2015) Ultrafast spectroscopic study on interfacial electron transfer in some sensitized solar cell systems (Invited)

A. Furube*[1]; 1. National Institute of Advanced Industrial Science and Technology, Japan

To investigate ultrafast electron injection processes in the dye-sensitized solar cells (DSSCs) and other relating solar cell systems, we have developed transient absorption spectroscopic systems with a ~200 fs time resolution in the wavelength region between 400 nm and ca. 5 μm. We can observe transient absorption signals from not only dye molecules but also injected electrons in nano-crystalline semiconductors (usually TiO2). Using this technique, we have elucidated electron injection dynamics from (i) dye molecules, (ii) gold nanoparticles, and (iii) CdSe quantum dots into TiO2 nanoparticle film. These systems work as a photo-electrode in solar cell systems by combining with suitable electrolyte and a counter electrode. In these sensitized solar cell systems, electron injection was found to occur in femtosecond or picosecond timescale. On the other hand, back electron transfer (i.e. charge recombination) was found to be variable depending on the system; it was generally very slow in the dye-sensitized solar cell system (microseconds or slower) while it was in picosecond timescale for the major part in the case of gold or CdSe sensitized solar cell systems. One of the mechanisms seems to be the larger contact area for nanoparticle sensitization systems, which induce strong electronic interaction at the interface.

3:50 PM

(ICACC-FS2-005-2015) Carbon nanotubes / TiO_2 composite systems for high efficiency dye sensitized solar cells

D. Benetti*[1]; K. Dembele[1]; C. Trudeau[3]; S. Cloutier[3]; A. Vomiero[2]; F. Rosei[1]; 1. INRS, Canada; 2. University of Brescia, Italy; 3. École de technologie supérieure, Canada

Dye sensitized solar cells (DSSCs) represent a viable low-cost alternative to conventional photovoltaic devices. One-dimensional (1D) structures like carbon nanotubes (CNTs) can improve electron injection from the excited state of dye and boost charge collection in devices under illumination. Conformal coverage of CNTs by TiO_2 nanoparticles is a key factor for maximizing cell performances. We investigated the effect of addition of functionalized CNTs into TiO_2 mesoporous thick films on photoconversion efficiency of DSSCs. We functionalized CNTs using a strong acid modification that improves their dispersion into the TiO_2 matrix and their ability to graft to TiO_2 nanoparticles. A simple mixing approach results in homogeneous CNT dispersion into the TiO_2 matrix. Optimized device increased the short-circuit photocurrent (J_{sc}) and the photoconversion efficiency by 32% and 31%, respectively, compared to bare TiO_2 cell, for maximum efficiency of 7.97%. We attribute the improved performances to the combined effect of increased dye loading and reduced charge recombination (as clarified by the impedance spectroscopy), due to the conformal coverage of CNTs, which allows fast and efficient charge collection in operating solar cells.

4:10 PM

(ICACC-FS2-006-2015) Perovskite materials on Silicon for photovoltaics (Invited)

R. Nechache*[1]; 1. Institut National de la Recherche Scientifiqure (INRS), Canada

Since the discovery of the bulk photovoltaic (PV) effect in ferroelectrics, there has been a growing interest in perovskite materials for energy related applications, including PV and water splitting. In such materials, the spontaneous polarization-induced electric field promotes the required separation of photo-excited carriers and allows photovoltages higher than their bandgap, which lead to efficiencies that can exceed the maximum possible in a semiconductor p–n junction solar cells. Among these materials, Bi2FeCrO6 is highly promising due to its high conversion efficiency of 8.1% under 1 Sun in thin film form. The optical properties of these thin films can be modulated to match with crystalline silicon and other thin film devices such as CIS if it is used as a top cell in a tandem junction. The market would be much more disposed to adopt an “enhanced existing PV technology” rather than an all new perovskite oxide technology. The development of wide-gap top cells for tandem junctions based on silicon and thin film PV cells is a key challenge for future generation PV devices. Such cells does not yet exist at efficiencies suitable for commercialization, and the perovskite oxide solar cells could prove to be compatible. Here, we deals with the major challenges related with epitaxial growth of BFCO films on Silicon with good polar and optical properties and the results will be discussed in details.

4:40 PM

(ICACC-FS2-007-2015) Development of semiconductor quantum dot sensitized solar cells

Y. Tachibana*[1]; 1. RMIT University, Australia

Semiconductor quantum dot (QD) is one of the most attractive nanomaterials for solar energy conversion devices. With their relatively large extinction coefficients and a wide light absorption range over visible wavelengths, QDs can be effective light absorbers. However, despite these attractive properties, controlling exciton states and charge separation and recombination dynamics has been challenging. For example, the excited electron and hole can readily be trapped by the surface states, losing initial excited energy. Charge separation of QD-TiO2 interface is relatively slow compared to dye sensitized system, which may compete with charge trapping process or exciton state decays. In this presentation, we will show quantitative analysis of charge trapping in QDs and demonstrate relationship of the QD nanostructures with the interfacial electron transfer reactions. Several types of QDs with a narrow size distribution are synthesized to control the potential energy levels of the conduction and valence bands. We then analysed influence of QD surface states on the interfacial charge transfer dynamics. The interfacial structure is modified to control the dynamics. The relationship between the QD surface/interfacial structure and solar cell performance will be discussed.

FS5: Single Crystalline Materials for Electrical, Optical and Medical Applications

New Directions I

Room: Tomoka C

Session Chairs: Klaus Becker, TU Braunschweig; Detlef Klimm, Leibniz Institute for Crystal Growth

1:30 PM

(ICACC-FS5-027-2015) Solid state electrochemistry: a tool for synthesis and characterization of solids (Invited)

C. Delmas*[1]; M. Guignard[1]; D. Carlier[1]; J. Darriet[1]; 1. CNRS, France

Researches on battery materials have considerably increased during the last 30 years due to the huge development of lithium-ion batteries for portable devices. The next goal is the development of batteries for electric vehicles and their use into the grid. To improve the properties one has to discover new electrode materials, which generally consist of nano-crystals with a very well defined composition and structure. Solid state chemistry is a key point to discover these materials. In this context, solid state electrochemistry, using electrochemical cell, will be a key point to characterize the material and also to synthesize new metastable phases. The cell voltage is equal to the difference in Fermi level between the two electrodes. If one electrode exhibits a constant voltage it can acts as reference and therefore, the cell voltage reflects all structure modifications which occurs on the material upon intercalation. The change is cell voltage depends on: (i) the electronic band filling, (ii) the change in the band structure due to change in composition, (iii) the modification of the Magdelung energy. In this presentation, we report about the NaxVO2, systems with a special focus on the phase diagram and the synthesis of new metastable phases. The physical properties will be also presented.

2:00 PM

(ICACC-FS5-028-2015) Single-Crystal Growth of Solid Electrolyte LixLa(1-x)/3NbO3 by Unidirectional Solidification Method (Invited)

Y. Fujiwara*[1]; K. Hoshikawa[1]; K. Kohama[2]; 1. Shinshu University, Japan; 2. Toyota Motor Corp., Japan

Lithium-ion secondary batteries, now in wide use, present safety problems due to their use of a flammable organic electrolyte. Solid lithium-ion secondary batteries in which both the active material and the electrolyte were nonflammable ceramics would greatly improve safety. The ion conduction that is central to the functioning of all solid lithium-ion secondary batteries has been studied in a material that is almost a ceramic, i.e. a polycrystalline material, prepared by sintering. However, it is difficult to measure the ion conductance of single crystal grains and grain boundaries separately in a ceramics. A bulk single crystal of such an electrolyte, would permit the determination of the ion conduction mechanism of the crystalline electrolyte material itself. In this presentation, we report here the growth and characterization of single- crystal LixLa(1-x)/3NbO3 with a diameter of 20 mm and an approximate length of 100 mm, grown by unidirectional solidification using a crucible translation rate of 0.5 to 1.0 mm/h. The ion conductivity of a single crystal of LixLa(1-x)/3)NbO3 (x = 0.1) was 2.0×10-4 S/cm, which is five times greater than that of a sintered ceramic sample made from raw materials with the same composition.

2:30 PM

(ICACC-FS5-029-2015) Reactive Atmospheres for Oxide Crystal Growth (Invited)

D. Klimm*[1]; R. Bertram[1]; S. Ganschow[1]; Z. Galazka[1]; D. Schulz[1]; R. Uecker[1]; 1. Leibniz Institute for Crystal Growth, Germany

At the high melting points $T_f >> 1000°C$ of most oxide compounds chemical reaction rates are high and equilibrium is reached within split seconds. Then equilibrium thermodynamics is a reliable tool for the description of the crystal growth system. All chemical elements Me can assume several valence states m, and can be transferred between them by redox reactions 2 $MeO_{m/2}$ + 0.5 O_2 = 2 $MeO_{(m+1)/2}$. If the volatility of the MeO_x is negligible; the Gibbs energy change $\Delta G = RT \ln[p_{O2}]$ for each reaction is a linear function of T, and plots of subsequent MeO_x redox reactions are separating predominance fields where only one valence state prevails (Ellingham diagrams) [1]. For some oxides predominance fields are spanning a broad range of p_{O2}. Then crystal growth can be performed in almost arbitrary atmosphere if the crucible material remains stable. Crucible metals Pt, Ir, W tend to get oxidized if p_{O2} is too high, and this tendency increases in that order. Contrary, Ga_2O_3, ZnO, SnO_2 loose oxygen if p_{O2} is low. FeO or Cu_2O must be kept in a narrow predominance field $p_{O2}(T)$ to avoid oxidation to higher oxides or reduction to the metal. For some crucible/crystal combinations "reactive atmospheres" with self-adjusting $p_{O2}(T)$ are a useful way to maintain chemical stability over an extended temperature range [2].

3:20 PM

(ICACC-FS5-030-2015) Simultaneous generation of multiple nonlinear processes in patterned ferroelectrics (Invited)

M. O. Ramirez*[1]; L. Mateos[1]; P. Molina[1]; L. E. Bausa[1]; 1. Universidad Autonoma Madrid, Spain

Advanced multi-photon devices with large spatial and spectral tunable response are ever more required in several scientific and technologically relevant fronts. Here, careful processing based on e-beam lithography and poling has been employed to demonstrate a step forward in the range of multi-harmonic generation with currently available broadband sources in the VIS-NIR. We experimentally show the possibility to obtain multiple nonlinear processes generated in a conical geometry by using a single solid state system. Such observations were made feasible by combining multiple quasi-phase matching interactions in fully dense two dimensional patterned ferroelectric micro-structures. The systems exhibit broad spectral tunability and does not require any angle or thermal alignment, thus fulfilling the compactness, robustness and versatility requirements for integrated on-chip optical devices. The ability to control the spatial and spectral distribution of several photons simultaneously on a compact system represents a step towards novel nonlinear color fan devices, and will enable new experiments on, for example, quantum optics or optical imaging.

3:50 PM

(ICACC-FS5-031-2015) A High-Temperature Optical Spectroscopy Study of Lithium Niobate, $LiNbO_3$ (Invited)

J. Shi[1]; K. D. Becker*[1]; 1. TU Braunschweig, Germany

At room temperature, undoped single crystalline lithium niobate, $LiNbO_3$ (LN), is fully transparent in the visible and in the near UV and IR range. However, depending on ambient conditions, transparency can be impaired significantly. The present study presents an in-situ optical spectroscopy study of LN single crystals with different Li:Nb ratios in a wide range of temperature and oxygen partial pressures. Due to its sensitivity to electronic transitions of ions and defects, optical spectroscopy in the UV-vis-NIR range performed under in-situ conditions is a powerful technique for the study of band gap energies and electronic defects in transparent oxide single crystals. At elevated temperatures, two distinct processes have been found to influence and determine the window of optical transparency of LN. (i) With increasing temperatures in air, the optical absorption edge shifts to lower energies with a temperature dependence of the gap energy of $dE_g/dT = -(1.30\pm0.01)\ 10^{-3}$ eV/K. (ii) In reducing atmospheres, the material gets colored and the optical absorption spectra are dominated by a band at about 0.95 eV due to small polarons. Its intensity follows an oxygen partial pressure dependence of the form $(P_{O2})^m$ with $m = -(0.23 \pm 0.01)$. This m-value is in excellent agreement the value of –1/4 predicted on the basis of point defect thermodynamics for the proposed chemical reduction model of LN.

4:20 PM

(ICACC-FS5-032-2015) Discussion on polycrystals over single crystals for optical devices

M. Prakasam*[1]; A. Largeteau[2]; 1. ICMCB-CNRS, France; 2. ICMCB-CNRS, France

Conventional transparent materials have a strong absorption in the infrared region making them unsuitable in this spectral range. Crystal growth processes are usually very time-consuming and needs sophisticated/ expensive machines. Polycrystalline nature of the ceramics is prone to diffusing light, which primarily arises from residual pores, grain boundaries, secondary phases and birefringency (anisotropic materials). Rapid sintering techniques such as Spark Plasma Sintering (SPS) helps in obtaining maximum densification in short duration of time at comparatively lesser sintering temperatures in comparison to other classical sintering. Simultaneous application of pressure and the help of Joules heating aids in avoiding Ostwald's ripening. Most of the current transparent ceramics are limited only to cubic materials, currently extended to non-cubic materials as well though in early stages. Conventionally optically transparent ceramics are often fabricated by either hot-isostatic pressing (HIP), or hot pressing (HP) or vacuum sintering at very high temperatures using ultrapure ultrafine powders. We at ICMCB have demonstrated successfully the fabrication of transparent ceramics of both cubic and non-cubic crystal structured materials by spark plasma sintering (SPS). The fabrication methodology their possible device applications in comparison to single crystals will be discussed in detail.

4:40 PM

(ICACC-FS5-033-2015) Magnetic phase transitions of hexagonal RMnO3 studied by Raman spectroscopy

T. Nguyen[1]; X. Chen[2]; S. Cheong[3]; T. Noh[4]; N. Sung[5]; B. Cho[5]; I. Yang*[1]; 1. Ewha Womans University, Korea (the Republic of); 2. Konkuk University, Korea (the Republic of); 3. Rutgers University, USA; 4. Seoul National University, Korea (the Republic of); 5. Gwangju Institute of Science and Technology, Korea (the Republic of)

Magnetic phase transitions are usually investigated by temperature dependent magnetization measurements. We present a Raman study of magnetic phase transitions of hexagonal manganite RMnO3 (R = rare earths) single crystal and thin film and compare directly with the results of magnetic measurements. Our temperature dependent Raman study of spin-wave (magnon) scattering provides an accurate method for investigating magnetic phase transitions. For single crystal LuMnO3, our optical method provides results as good as magnetization measurements; it can deduce not only Néel temperature, but also weak spin reorientation transition temperature. For RMnO3 thin films, our optical method gives much more accurate value of Néel temperature than magnetization measurements. Spin-wave (magnon) measurement by Raman is useful for investigating magnetic phase transitions of thin film samples especially, in which magnetization measurements would be due to effect of substrate.

Posters

Session B

Room: Ocean Center Arena

(ICACC-S2-P066-2015) Effects of local nonuniform deformation in SiC/SiC on failure behaviors of EBCs

A. Otsuka*[1]; T. Kuribara[1]; H. Kakisawa[1]; Y. Kagawa[1]; 1. The University of Tokyo, Japan

When woven fabric SiC/SiC composite are loaded, inhomogeneous stress/strain distribution occurs at a surface due to woven fabric structure. Deformation and failure behaviors of environmental barrier coatings (EBCs) . This local stress/strain distribution strongly affects unique stress/strain distribution in oxide EBCs. In the present study, mullite/Si/(SiC/SiC) model EBC system is tensile tested at room temperature and high temperatures (above 1000oC). Surface strain distribution of coating is measured using DIC from sequential images obtained by a specially designed UV illumination optical system. The result suggests that local stress/strain distribution due to woven fabric fiber structure plays an important role on cracking behavior of EBC layer: this tendency occurs independent of test temperature. The crack evolution process differs from that usually observed in brittle coating on ductile substrate. Discussions are made on unique failure behavior of EBC layer and local stress/strain inhomogeneity.

(ICACC-S2-P067-2015) Effect of particle in-flight behavior on the microstructure and mechanical property of La2Ce2O7 thermal barrier coatings

K. Liu*[1]; Y. Kang[1]; Y. Wang[1]; J. Tang[1]; Y. Bai[1]; 1. Xi'an Jiaotong University, China

Lanthanum-Cerium Oxide (La2Ce2O7, LC) coatings were deposited by supersonic and conventional atmospheric plasma spraying. The influence of in-flight behavior of particles on the microstructure of coatings was studied. It was found that the argon flow rate was the most important factor that influenced the velocity of particles, followed by the current and hydrogen flow rate, however the main factors of affecting the particles temperature was the hydrogen flow rate, followed by the current and argon flow rate. The lattice parameter, content of unmelted particles, porosity and crack length of LC coatings deposited at different spray conditions were calculated. It was found that the increase of melting index of in-flight particles increased the lattice parameters of as-sprayed coatings while decreased the content of unmelted particles and the average length of horizontal cracks. The hardness, the elastic modulus and the fracture toughness of the coatings were measured by indentation methods. As a result, the hardness and the elastic modulus of the coatings were decreased with the defects content increasing. However, the fracture toughness increased firstly and then decreased with the defect content increasing due to the composition of the as-spraying coatings.

(ICACC-S2-P068-2015) Influence of In-flight behavior of YSZ Particles on the Microstructure and Thermal Insulation Performance of Thermal Barrier Coatings

J. Tang*[1]; Q. Fu[1]; Z. Han[1]; Y. Bai[1]; 1. Xi'an Jiaotong University, China

In this work, in-flight velocity and surface temperature of nanoscale yttria-stabilised zirconia (YSZ) powders in the plasma jet were monitored by the Spray Watch 2i system. The influnce of in-flight behavior of feedstock powders on the microstructure and thermal insulation perfermance were investigated. The results indicated that the porosity, content of unmelted particles and the thermal insulation performance were reduced with the in-flight velocity and surface temperature increased. The porosity was 3.79 %, content of unmelted particles was 11.86 % and thermal insulation performance was 91 °C as the velocity and surface temperature were in the range of 380 – 400 m/s and 3200 – 3350 °C. The porosity, content of unmelted particles and thermal insulation performance were 2.85 %, 5.50 % and 69 °C, respectively, when the velocity and surface temperature were improved to 430 – 460 m/s and 3500 – 3650 °C.

(ICACC-S2-P069-2015) A Transmission Electron Microscopy Study of The Microstructure And Interface of Zirconia-based Thermal Barrier Coatings

Y. Wang*[1]; Y. Bai[1]; H. Z. Han[1]; 1. State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, China

Yttria-stabilized zirconia (YSZ)-based thermal barrier coatings (TBCs) were deposited by supersonic atmospheric plasma spraying (SAPS) and conventional atmospheric plasma spraying (APS). The microstructural feature of APS-/SAPS-coatings was comparatively studied by high-resolution transmission electron microscopy (HRTEM) in order to gain a physical insight into the formation process of finer multilayered microstructures of SAPS-coating. Results showed that, due to the great improvement of velocity and temperature of in-flight particles, the average height and width of columnar crystals of SAPS-coating were 0.71±0.08 and 0.31±0.04 μm, which was much smaller than that of APS-coating (2.10±0.10 and 0.48±0.07 μm). The preferential growth direction of SAPS-columnar crystals was [101] under rapid solidification due to the growth unit model of coordination polyhedron. A 3-nm-thick amorphous film was discovered at the splat/splat interface for both APS-/SAPS-coatings. The growth mechanism of amorphous, nucleation, growth competition combined with preferential growth induced formation columnar crystals has been proposed.

(ICACC-S2-P070-2015) Development of stable and tough Si base bondcoat layer for EBCs on SiC/SiC substrate

S. Magata*[1]; Y. Arai[1]; H. Kakisawa[1]; Y. Kagawa[1]; 1. The University of Tokyo, Japan

When oxide environmental barrier coating (EBC) system are subjected above melting point of Si bond coat, melting and solidification of Si results in formation of coarse and dense polycrystalline Si. In addition, amorphous SiO2 and crystobalite are formed as a result of oxidation. Formation of cristobalite causes microcracking in Si bond coat layer. Fracture toughness of coarse grain Si bond coat is quite low, and therefore, formed microcracks are easily link to form long delamination cracks. Improvement of chemical stability and toughness in Si bond coat is effective way to prevent formation of delamination cracks. In the present study, some Si-base ceramic powders are incorporated into polycrystalline Si and effects of the additional powders on toughness of Si bond coat layer and long term chemical stability of the powders, including reaction product, are discussed.

(ICACC-S2-P071-2015) Ti-Al-Si-Cr-N nanocomposite coatings deposited by magnetron sputtering process with single alloying targets

H. Lee*[1]; K. Moon[1]; 1. KITECH, Korea (the Republic of)

Ti-Al-Si-Cr alloying target were prepared by powder metallurgy of mechanical alloying and spark plasma sintering. And the properties of the sintered alloys were investigated to find out their usefulness as sputtering targets. The investigation on the alloying target showed that their microstructure was nano-sized about 20-30 nm and all the elements were homogeneously distributed. And their mechanical properties were enough high to be used as a target materials. Ti-Al based nanocomposite coatings were deposited by magnetron sputtering method with the prepared targets. The composition of the coating was almost same with that of the target. Their microstructures and mechanical properties were investigated by XRD, SEM, EPMA, Nano-indenter, TEM, ball on disk, salt spray test. The easiness of the nanocomposite structure was reviewed with alloying properties between alloying elements. Also, the effect of the element on the microstructure and mechanical properties of the Ti-Al based nanocomposite coatings were reviewed in this study.

(ICACC-S3-P072-2015) Preliminary Studies about bi-layer interconnect including lanthanum strontium titanate (LST) for application of solid oxide fuel cell

H. Yoon*[1]; S. Park[1]; N. Sammes[1]; J. Chung[1]; 1. Pohang University of Science and Technology(POSTECH), Korea (the Republic of)

Lanthanum strontium titanate (LST) having n-type conducting behavior show high electrical conductivity and excellent stability in reducing atmosphere, so it is promising candidate for SOFC interconnect. But the LST also exhibit low conductivity in oxidising atmophere. In SOFC system, it is inevitable that the part exposed to oxidising atmosphere have low conductivity when LST layer is applied singly as interconnect. So, S. Gopalan el al. proposed novel concept called bi-layer structure which consists of one p-type layer exposed to cathodic gas (air) and an n-type layer exposed to anodic gas (fuel). In addition, the bi-layer interconnect could be composed of ceramic such as lanthanum strontium titanate and lanthanum strontium manganite. In this study, we tried to form bi-layer with $La_{0.8}Sr_{0.2}MnO_3$, $La_{0.6}Sr_{0.4}CoO_3$ and $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ on LST layer and they show ASR value with 0.0565 Ω cm2, 0.3568 Ω cm2 and 0.1377 Ω cm2 at 900 °C, respectively.

(ICACC-S3-P073-2015) Tubular Ceramic Fuel Cell Stack

A. Hanifi*[1]; T. H. Etsell[1]; P. Sarkar[2]; 1. University of Alberta, Edmonton, Canada; 2. Alberta Innovates - Technology Futures, Canada

Ceramic fuel cells convert the chemical energy of a fuel to electrical power. The main advantages of this type of fuel cell are their high efficiency, fuel flexibility and minimal contribution to pollution of the environment. The two main ceramic fuel cell designs are planar and tubular configurations. Even though tubular fuel cells show lower power density compared with their planar counterparts, they are more advantageous as they do not require sealing, possess improved thermomechanical properties, have higher thermal cycling ability and require less start up/shut down time. Recently a tubular ceramic fuel cell stack incorporating anode supported tubular cells has been developed. This stack uses six ~100 mm long tubular tapered (bottom OD ~9 mm & top OD ~10 mm) cells, heated by a coil resistance heater and enclosed inside a stainless steel shell as shown in Figure 1. This research presents the fabrication procedure for this stack and its performance.

(ICACC-S3-P074-2015) Oxygen Nonstoichiometry of $LaNi_xM_{1-x}O_{3-\delta}$ (M = Fe, Co and x = 0.6, 0.4)

R. A. Budiman*[1]; S. Hashimoto[2]; T. Nakamura[3]; K. Yashiro[1]; K. Amezawa[3]; T. Kawada[1]; 1. Tohoku University, Japan; 2. Tohoku University, Japan; 3. Tohoku University, Japan

The $LaNi_xFe_{1-x}O_{3-\delta}$ and $LaNi_xCo_{1-x}O_{3-\delta}$ are the promising cathode material for solid oxide fuel cell. Determination the defect chemical of perovskite type oxide material is needed in order to clarify the transport and catalytic properties. Thermogravimetry and coloumetric titration was performed to obtain the oxygen nonstoichiometry data. However, to understand the defect chemical, the knowledge of the electronic conduction mechanism is also important. Therefore, the electrical conductivity and thermoelectric power measurement was performed to obtain the information of electronic conduction mechanism. Thereafter, the defect chemical model of $LaNi_{1-x}Fe_xO_{3-\delta}$ and $LaNi_xCo_{1-x}O_{3-\delta}$ will be developed based on those measurements.

(ICACC-S3-P075-2015) Effects of TiO_2 Addition on Microstructure and Ionic Conductivity of Gadolinia-Doped Ceria

M. F. Dias[1]; E. N. Muccillo*[1]; 1. Energy and Nuclear Research Institute, Brazil

Ceria containing trivalent rare-earths is a solid electrolyte with higher ionic conductivity than the standard yttria fully-stabilized zirconia ionic conductor. This property turns these ceria-based ionic conductors promising materials for application in solid oxide fuel cells operating at intermediate temperatures (500-700 C). One of the most utilized approaches to optimize the electrical conductivity and other properties of these materials is the introduction of a second additive. In this work, ceria-20 mol% gadolinia with additions of TiO_2 was prepared by solid state reaction. The main purpose was to investigate the effects of the additive on densification, microstructure and electrical conductivity of the solid electrolyte. Sintered pellets were characterized by apparent density, X-ray diffraction, Raman spectroscopy, scanning electron microscopy and electrical conductivity by impedance spectroscopy. The additive was found to influence all studied properties. Increase of densification was obtained with TiO_2 addition. This additive promotes increase of the blocking of charge carriers at the grain boundaries due to solute exsolution and formation of the pyrochlore $Gd_2Ti_2O_7$ phase at grain boundaries for contents in excess of the solubility limit.

(ICACC-S3-P076-2015) Characteristics of protective LSM coatings on Cr-contained steels used as metallic interconnectors of intermediated temperature solid oxide fuel cells

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

The chromium-contained ferritic stainless steels are widely employed as metallic interconnectors in intermediated temperature solid oxide fuel cells. However, the chromium content of these steels would cause obvious degradation phenomena due to the chromium-poisoning of cathode and oxidation of interconnector. Therefore, many coating techniques were adopted to fabricate a protective layer onto the surfaces of metallic interconnectors in order to decrease the growth chromium oxide and evaporation of chromium trioxide and chromium hydroxide. Among these techniques, atmospheric plasma spraying (APS) process is considered as a promising candidate due to its high deposition rate, flexibility and low cost. In this study, LSM coatings are coated onto Crofer 22 H, Crofer 22 APU and SS441 via APS process. The obtained LSM layers reveal relatively dense microstructure and high purity of crystallography phase due to the employed process parameters. After about 2300 hrs ageing at 800 oC in air, the initial and final area specific resistance (ASR) values of the coated Crofer 22 APU sample with pre-oxidation treatment are 1.91 and 3.31 mΩcm2, respectively. The smallest increasing rate of ASR in this study is only about 0.000613 mΩcm2/hr. The ASR values of the coated interconnectors were measured by a four-probe DC technique.

(ICACC-S3-P077-2015) Electrical and structural characterization of Mn-Co spinel protective coatings for SOFC interconnects

S. Molin[1]; D. Boccaccini[1]; M. Chen[1]; S. Cabanas-Polo[2]; A. R. Boccaccini[2]; M. Bindi[3]; P. Leone[4]; A. De Miranda[5]; F. Smeacetto*[5]; 1. Technical University of Denmark, Denmark; 2. University of Erlangen-Nuremberg, Germany; 3. Edison S.p.A., Italy; 4. Politecnico di Torino, Italy; 5. Politecnico di Torino, Italy

Steel interconnects of Solid Oxide Fuel Cells require protective coatings to stop chromium evaporation from the forming corrosion products – chromium oxide and chromium manganese spinel scales. One of the best materials found to date to block chromium evaporation on the oxygen side of the interconnect is the (Mn,Co)3O4 spinel. Though this material has been studied intensively, still no clear correlation exists between the coating thickness, density, preparation method and its protective properties. In this work Mn-Co based coatings prepared by different methods were evaluated electrically, mechanically and structurally. For the preparation of the coatings, electrophoretic deposition, thermal evaporation and magnetron sputtering methods were used to prepare both thin and relatively thick coatings (from 1 μm to 10 μm). For all coatings Crofer 22 APU steel was used as a substrate and coated samples were studied first electrically for 5000 hours at 800°C under a 500 mA cm-2 current load to determine their Area Specific Resistance. After electrical studies samples were analyzed mechanically by nanoindentation of the cross-sections to determine properties of the interfaces and structurally by Scanning Electron Microscopy to determine chromium diffusion and oxide scale thickness.

(ICACC-S3-P078-2015) Effects of 12% CO2 in Air on LSM/YSZ Cathodes during 1000 h SOFC Tests

J. S. Hardy*[1]; C. A. Coyle[1]; N. L. Canfield[1]; J. Stevenson[1]; 1. Pacific Northwest National Laboratory, USA

Button cells with LSM/YSZ cathodes were tested at 800, 850, 900, and 950°C in cathode air containing 0% and 12% CO2. At each temperature, six cells were operated at a constant current approximating an operating voltage of 800 mV. Of the six cells at each temperature, two were tested in cathode air with no CO2 during the entire 1000 hour test, two were tested in cathode air containing 12% CO2 during the entire test, and two were tested in cathode air in which the CO2 level was alternated between 0% and 12% every ~250 hours. Triple exponential decay equations were fit to the operating voltage as a function of time over each continuous segment of data. This made it possible to calculate the instantaneous degradation rate as a function of time over the entire test duration based on the derivatives of the best fit curves. Comparisons of degradation rates with and without added CO2 will be discussed in conjunction with SEM/EDS analysis.

(ICACC-S5-P079-2015) Enlarging Pore Size in Electrospun Scaffolds by Positive Voltage and Negative Voltage Electrospinning for Enhancing Cell Infiltration

Q. Zhao*[1]; M. Wang[1]; 1. The University of Hong Kong, Hong Kong

A major problem for electrospun tissue engineering scaffolds is their small pore size, which limit cell infiltration, impeding clinical applications of scaffolds. Most of current methods for enlarging pore size in electrospun scaffolds affect the nanofibrous structure or scaffold mechanical properties. This study investigated a new approach for enlarging pore size without causing aforementioned problems. Dual-source dual power electrospinning was employed to fabricate intermeshed nanofibrous membranes, and power supplies of negative voltage (NV) and positive voltage (PV) were used to produce polymer fibers with different electrical charges (polarity and magnitude). Scaffolds composed of PLGA nanofibers were electrospun using different polarity combinations (NV+NV, PV+PV, PV+NV) and different applied voltages (±10, ±15 and ±20 KV). The electrical charge of resultant scaffolds was measured subsequently. It was found that PLGA scaffolds made by high voltages (either PV or NV) would bear corresponding charges which were retained at about 30% of its initial charge value after one week. The porous structure was different for scaffolds made in different conditions. Scaffold made by PV+NV showed enlarged average pore size. Cell culture experiments were conducted to assess cell infiltration in different scaffolds.

(ICACC-S5-P080-2015) Effect of reactivity of dicalcium phosphate dihydrate (DCPD) by hybridization with hydroxyapatite (HA)

Y. Takemura*[1]; M. Tafu[1]; T. Toshima[1]; T. Chohji[2]; 1. National Institute of Technology, Toyama College, Japan; 2. National Institute of Technology, Kagoshima College, Japan

Dicalcium phosphate dihydrate (DCPD) reacts with fluoride ions in an aqueous solution and forms fluorapatite (FAp). In previous study, we have appeared that DCPD does not react with fluoride directly but forms nano-scale precursor particles on surface of the DCPD. The time need to form the precursor particle is delayed by co-existing ions. These are problems to apply DCPD to various applications. Results of our previous studies show that the nano-particles are hydroxyapatite (HA) -like calcium phosphate. The purpose of this study is to investigate effect of HA on improve reactivity of the DCPD with fluoride ions. In this study, we compared between mixing HA with the DCPD and coating of HA on the surface of DCPD particles. For coating of HA, the DCPD soaked into SBF (simulated body fluid, Kokubo solution) . From results of characterization, we found that co-exist of HA is able to accelerate the reaction time of the DCPD with fluoride ions In case of mixing HA, morphology of the DCPD was changed. In case of coating of HA on the DCPD particle, morphology of the DCPD was not changed after reaction with fluoride ions. The optimum amount of HA in the DCPD by coating is smaller than it by mixing one. We concluded that coating of HA on the DCPD is applicable to various application of it such as water treatment, dental phosphate cements.

(ICACC-S5-P081-2015) High-performance, Reaction Sintered Lithium Disilicate Glass-ceramics

T. Zhao[1]; Y. Qin[1]; B. Wang[1]; J. Yang*[1]; 1. Xi'an Jiaotong University, China

A novel method of reaction sintering combined with hot-pressing technology was developed to prepare Li2Si2O5 glass-ceramics with high flexural strength and fracture toughness. Li2SiO3 crystal, SiO2 and Li2Si2O5 glass were used as the starting powders. The results show that via an interaction between Li2SiO3 crystals and SiO2 glass, rod-like Li2Si2O5 crystals with length of up to tens microns could be obtained, which were several times longer than those directly crystallized from the Li2Si2O5 parent glass. Through adjusting the Li2Si2O5 glass content, Li2Si2O5 glass-ceramics displayed a denser microstructure with the bimodal distribution consisting of large elongated Li2Si2O5 grains formed during the reaction and smaller precipitates of the Li2Si2O5 glass powder. Although the crystallinity decreased with increasing the Li2Si2O5 glass content, the Li2Si2O5 glass-ceramics exhibited high flexural strength (350 ± 13 MPa) and high fracture toughness (3.3 ± 0.14 MPa.m1/2).

(ICACC-S5-P082-2015) Effect of Ca and Mg Ion Irradiation on Bioactivity of Hydroxyapatite Ceramics

S. Kobayashi*[1]; T. Izawa[2]; Y. Teranishi[3]; 1. Tokyo Metropolitan University, Japan; 2. Tokyo Metropolitan University, Japan; 3. Tokyo Metropolitan Industrial Technology Research Institute, Japan

Bioactive ceramics has high biocompatibility and attracts attention as bone implant materials. Among them, hydroxyapatite (HA) is a main component of autologous bone and has bone bonding ability through the bone-like apatite layer. The bone-like apatite layer is formed by interaction between HA surface and ions in body environment. Thus, bone-like apatite layer formation is controlled by a microstructure of HA surface. In this study, ion irradiation method was used in order to control bioactivity of hydroxyapatite (HA), that is apatite formation on the HA surface. Bioactivity of hydroxyapatite that was irradiated with Ca or Mg ion at different ion dose and depth was investigated by soaking in simulated body fluid (SBF). The HA irradiated with Ca ion at different ion dose and depth showed acicular apatite formation on the surface after soaking in SBF at all ion irradiation condition. However, apatite formation rate was different. Apatite formation on the HA irradiated with Mg ion became lower with increasing Mg ion dose. Thus, the apatite formation of HA surface can be controlled by changing ion species, dose and depth. This means that the change in microstructure of HA can control the bioactivity appropriate for use site.

(ICACC-S5-P083-2015) Mechanical properties of β-tricalcium phosphate

B. Mehdikhani*[1]; 1. 1Standard Research Institute, Iran (the Islamic Republic of)

Nano-size β-tricalcium phosphate (B-TCP) powders with average grain size of 70-100 nm were prepared by the wet chemical precipitation method with calcium nitrate and di-ammonium hydrogen phosphate as calcium and phosphorus precursors, respectively. The precipitation process employed was also found to be suitable for the production of sub-micrometre B-TCP powder in situ. The sinterability of the nano-size powders, and the microstructure, mechanical strength of the prepared β-TCP bioceramics were investigated. Bioceramic sample characterization was achieved by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), fourier transform infrared spectroscopy (FTIR) and density measurements. Powders compacted and sintered at 800, 900, 1000 and 1100 degree centigrade showed an increase in relative density from 68% to 93%. The results revealed that the maximum hardness of 240HV was obtained for β-TCP sintered at 1100 degree centigrade.

(ICACC-S5-P084-2015) Synthesis nano bio-ceramic powder β-Ca2P2O7

B. Mehdikhani*[1]; 1. Standard Research Institute, Iran (the Islamic Republic of)

Nano-size beta calcium pyrophosphate(β-Ca2P2O7) powders with average grain size of 80 nm were prepared by sol gel method with calcium nitrate 4-hydrateCa(NO3)2.4H2O and different amount of diammonium hydrogen phosphate (NH4)2HPO4(0.4 and 0.6 molar) as calcium and phosphorus precursors. The pH of the system was maintained up to(pH=10) by the adding of sodium hydroxide. The white precipitate stirred for 2 hour and washed with distilled water and filtered. Filtered cake was dried at 80 degree centigrade and calcined at 600 degree centigrade. The dried and calcined powders were characterized for phase composition using X-ray diffractrometry (XRD) and Fourier transform-infrared spectroscopy (FTIR). The particle size and morphology was studied using scanning electron microscopy (SEM).

(ICACC-S5-127-2015) Assessment of bioactive and resorbable ceramic formulations for 3D printing techniques

S. K. Clarke*[1]; S. O. Matthews[1]; J. E. Lancien[2]; I. Thompson[2]; 1. SCF Processing Ltd, Ireland; 2. Dental Institute, Kings's College, Guys HospitaL, United Kingdom

At present it is possible to print materials ranging from chocolate to plastics using low cost 3D printers. There is growing interest in adapting these standard printers for ceramics printing. However, the availability of ceramics suitable for use in bioactive regeneration applications via 3D printing is limited to say the least. To overcome this issue a comprehensive study was undertaken to establish the optimum ceramic formulation. The study also helped to assess whether this formulation should be mixed with biodegradable plastics and melt printed, or whether ceramic slurries printed at room temperature should be used to produce bioactive and resorbable 3D scaffolds.

(ICACC-S7-P085-2015) Cu(II) reduction without reductants: insights from theory

E. Fois*[1]; D. Barreca[2]; A. Gasparotto[3]; C. Maccato[3]; R. Seraglia[2]; E. Tondello[3]; G. Tabacchi[1]; 1. University of Insubria and INSTM, Italy; 2. CNR-ISTM and INSTM and Padova University, Italy; 3. Padova University and INSTM, Italy

A topic issue in sustainable technologies is the production of Cu_xO (x=1,2) nanomaterials with tailored composition and properties. They can be fabricated through bottom-up processes that involve unexpected changes in the metal oxidation state and open intriguing challenges on the copper redox chemistry. How Cu(II) complexes can lead to Cu(I) species in spite of the absence of any explicit reducing agent is a question only recently answered by investigating the fragmentation of a Cu(II) precursor for Cu oxide nanostructures by computer simulations and ESI-MS with multiple collisional experiments (ESI/MSn). Here we show that a Cu-promoted C H bond activation leads to reduction of the metal center and formation of a Cu(I)-C-NCCN six-membered ring. Such 6-ring moiety is the structural motif for a new family of cyclic Cu(I) adducts, characterized by a bonding scheme that may shed unprecedented light on high-temperature Cu chemistry. In particular, in this contribution we describe how collisions with hot atoms may activate Cu(II) species to a configuration prone to the reduction. Besides its relevance for the fabrication of Cu-oxide nanostructures, the hydrogen-abstraction/proton-delivery/electron-gain mechanism of Cu(II) reduction described herein could be a general property of copper and might help to understand its redox reactivity.

(ICACC-S7-P086-2015) Synthesis and functionalization of SHG active Barium Titanate (BaTiO3): Towards biomedical imaging

C. De Dobbelaere*[1]; W. Vanoppré[2]; K. Elen[3]; E. Slenders[4]; S. Deville[4]; M. Ameloot[4]; A. Hardy[3]; M. K. Van Bael[1]; 1. Universiteit Hasselt, Belgium; 2. Transnational University Limburg, Belgium; 3. IMEC vzw, Belgium; 4. Hasselt University, Belgium

Tetragonal barium titanate (BaTiO3) has a non-centrosymmetric crystal structure, making it capable of emitting SHG-light by frequency doubling. Therefore, Second Harmonic Generation (SHG) microscopy has turned out to be a promising method for visualization in the field of (bio-)medical imaging [1], making e.g. intracellular diffusion monitoring and tracking of proteins accessible. However, nanometer sized particles are necessary for adequate imaging resolutions, their dispersion in aqueous media and cellular uptake. Also, the particles have to be properly functionalized for further attachment to a targeting protein. This work focuses on the synthesis of small BaTiO3 particles capable of generating the second harmonic of excitation (SHG). Oxide particles obtained from different synthesis routes are compared, as crystallinity and SHG activity are very synthesis dependent. Following the synthesis, the surface of the particles is modified with the objective of future linking to a biological sensing protein. The applied surface modification encompasses hydroxylation, followed by silanization of the surface [2]. The SHG activity of few obtained oxides is studied ex-vivo and discussed. In further work, nanobodies will be attached to be applied as a biological sensor [3].

(ICACC-S7-P087-2015) Tailored Lysozyme–ZnO Nanoparticle Conjugates as Nanoantibiotics

N. Tripathy[2]; R. Ahmad*[1]; Y. Hahn[1]; 1. Dept of Earth and Envron Sci, Korea (the Republic of); 2. Chonbuk National University, Korea (the Republic of)

ZnO is well recognized as a multifunctional material bestowed with exceptional optical, semiconducting and piezoelectric characteristics. Zinc ion (Zn2+) is an indispensable trace element for adults; 9.5 and 7.0 mg of Zn2+/day is needed for adult men and women, respectively. The intrinsic properties of ZnO such as presence of surface –OH groups facilitate additional benefits of functionalization with various surface-decorating molecules. Especially, ZnO nanoparticles (ZNPs) possess a wide range of antibacterial activities towards both Gram+ and Gram- bacteria, including major foodborne pathogens, attributed to the generation of reactive oxygen species (ROS) on these oxide surfaces. Also, they have remarkable photocatalytic and photo-oxidizing abilities against chemical/biological species that are predicted to increase the ROS levels.10 Herein, we demonstrate an efficient strategy for synthesizing lysozyme covalently attached to ZNPs (L–ZNP conjugates) in order to achieve enhanced enzyme antimicrobial activity, through a low temperature solution route. Furthermore, the effect of this modification was demonstrated by investigating the antibacterial effectiveness of L–ZNP conjugates against Escherichia coli (E. coli) and Staphylococcus aureus (S. aureus).

(ICACC-S7-P088-2015) Crystalline mesoporous films of titanium oxides with various degree of substoichiometry for fuel cells

K. Bienkowski*[1]; P. Kulesza[1]; 1. University of Warsaw, Poland

The first results of the synthesis of mechanically stable, crystalline mesoporous films of titanium oxides with various stoichiometry, which will be applied either as an anode or a cathode for fuel cell electrodes, will be presented. The composition of TiO2 and substoichiomteric TinO2n-1 Magneli phases which has been obtained in a high temperature and in reductive atmosphere is expected to have a potential to serve as an anode for enhanced oxidation of organic fuel and to be employed as a cathode when modified with the co-catalyst (NiO/Ni) to allow an effective oxygen reduction. These applications require high degrees of conductivity and a large contact area with the reaction media. In addition, highly crystalline oxides are desired in order to optimize the properties such as electroactivity or electronic conductivity. The synthesis approach of substoichiometric TinO2n-1 oxides and the structural characterization in view of their potential application in fuel cell systems will be the objective of the presentation.

(ICACC-S7-P089-2015) A novel planar heterojunctioned perovskite solar cell

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

Hybrid organic/inorganic perovskite as a light absorber in solar cell has attracted recently great attention in photovoltaic research. In this article, lead iodide perovskite (CH3NH3PbI3) and an atomic-thin electron transport layer were used to fabricate a heterojunctioned perovskite solar cell. The atomic-thin layer was synthesized using a chemical vapor deposition process. A low-temperature vapor-assisted solution process was used to deposite the perovskite layer. X-ray diffraction, scanning electron microscope, energy dispersive spectrometer, UV-Visible, differential scanning calorimetry and thermogravimetric analysis were used to characterize the material properties. The resulting solar cells were evaluated using sun light simulator, incident photon-to-electron conversion efficiency, intensity modulated photocurrent/photovoltage spectroscopy, and electrochemical impedance spectroscopy.

(ICACC-S7-P090-2015) Visible Light Hydrogen Evolution on Heptazine- and Triazine-based Polymers and Metal Complex Cocatalysts bound to p-Silicon Photocathodes

F. Podjaski*[1]; K. Schwinghammer[1]; B. Tuffy[1]; V. Lau[1]; J. Vukajlovic[2]; E. Alarcon-Llado[2]; A. Fontcuberta-i-Morral[2]; B. V. Lotsch[1]; 1. Max-Planck-Institute for Solid State Research, Germany; 2. Ecole Polytechnique Fédérale de Lausanne, Switzerland

Since the discovery of water splitting on TiO2 under UV-illumination by Honda and Fujishima in 1970s, a lot of different semiconductor materials and cocatalysts have been investigated to produce hydrogen from water using sunlight. A recent discovery has shown that graphitic carbon nitride, consisting only of abundant elements, is able to perform visible light-driven hydrogen evolution. Our research focuses on developing chemical methods and material engineering for improving hydrogen evolution using semiconductor materials. Materials investigated in our group include heptazine- and triazine-based polymers. Furthermore, we propose pathways to bond metal complex cocatalysts to the surface of p-doped silicon as a photocathode for the hydrogen evolution reaction and show first results on the performance of these hybrid structures.

(ICACC-S7-P091-2015) Influence of residual gas pressure and negative heavy-ion implantation on the properites of nitride high-entropy alloys (TiZrHfVNbTa)N

A. Pogrebnjak*[1]; I. V. Yakushchenko[1]; O. V. Sobol[2]; V. M. Beresnev[3]; O. V. Bondar[1]; Y. Takeda[4]; K. Oyoshi[4]; H. Amekura[4]; K. Kono[4]; 1. Sumy State University, Ukraine; 2. National Technical University "Kharkov Polytechnical Institute", Ukraine; 3. Karazin Kharkiv National University, Ukraine; 4. National Institute for Material Science (NIMS), Japan

In current study nitride high-entropy alloys (TiZrHfVNbTa)N, obtained by the cathodic-vacuum-arc-vapor deposition, were investigated. Influence of deposition parameters and ion implantation on the phase and elemental composition, morphology and properties was investigated. Deposition was made in a Bulat-6 setup, on the steel (12X18H9T) substrates. Negative substrate voltage bias Ub = -150 V, and gas pressure of the nitrogen (N_2) in the range from p = 0.04 Pa to p = 0.4 Pa were used. Using methods of scanning electron microscopy (SEM) and atomic force microscopy (AFM), morphology of the surface was studied. Elemental composition was investigated by energy-dispersive spectroscopy (SEM with EDX). X-ray diffraction (XRD) spectroscopy was used to investigate the phase structure of the coatings. Ion implantation with negative ions Au^- with 60 keV energy was conducted. Dose of 10^{17} ions/cm^2 was used. It was shown, that during deposition of the coatings, significant number of droplet fraction is formed, which leads to increasing of the surface roughness. XRD analysis evidences about presence of FCC and BCC phases, which ratio changes due to change of gas pressure. Ion implantation of the (TiZrHfVNbTa)N coatings leads to selective sputtering of nitrogen atoms, and causes decreasing of texture level in the coatings, as it is evidenced by XRD analysis.

(ICACC-S7-P092-2015) Structural features amorphous-like coatings AlN-TiB_2-$TiSi_2$ after annealing and their impact on physical and mechanical properties changes

A. Pogrebnjak*[1]; A. Demianenko[1]; Y. Takeda[2]; K. Oyoshi[2]; 1. Sumy State University, Ukraine; 2. National Institute for Materials Science, Japan

: The magnetron sputtered coatings on base AlN-TiB_2($TiSi_2$) were investigated. The element composition, structural-phase composition, morphology were investigated before and after annealing of coatings with (900, 1300)°C using SEM/EDS, AFM, SIMS, XRD, 3D Laser, Nanoindenter. The concentrations of elements in the coating were changed after annealing under 900°C and further annealing under 1300°C. At high temperature impact on the coating observed crystallize with the formation crystallite with sizes of 11-25 nm. Statistical analysis of the topography of the surface showed that the average height of the projections is 90 nm. The lateral dimensions of the projections at the base was ~ 200 nm, and the width of the projections at half height - about 70 nm. Annealing at the high temperature leads to a fundamental change in the pattern of the diffraction spectrum. The main component of the coating becomes aluminum oxide Al_2O_3 and up to 30 vol.% remains of AlB_2. Achieving viscoplastic index of 0.07 value when the hardness H = 15.3 GPa, provides high damping properties of the coating, wherein an amorphous structure is promising to use coatings such as diffusion barriers in the form of separate elements or as a layer in contact of multilayer wear resistant coatings.

(ICACC-S7-P093-2015) Thermoplastic properties and structural characterization of organically modified metalloxane bulk materials with optical transparency

O. Shinya*[1]; H. Uchiyama[1]; H. Kozuka[1]; 1. Kansai university, Japan

Organic-inorganic hybrids of high refractive indices are attracting much attention because of their applications as antireflective coatings, optical waveguides, holographic materials, and encapsulants for light-emitting diodes. Here we propose a new type of hybrid materials with high refractive indices and thermoplasticity that are prepared without using organic polymers. Ti(OC4H9n)4 was hydrolyzed in the presence of benzoylacetone (BzAc) in solutions of molar compositions, Ti(OC4H9n)4 : BzAc : H2O : CH3COCH3 = 1 : (1 or 2) : (1 or 10) : 20, followed by concentration and drying at 140oC in flowing N2 gas. The hybrid materials obtained were amorphous, optically transparent and colored in yellow, and had refractive indices around 1.7. They were softened at 30 - 85oC on heating while exhibited no endothermic peak corresponding to the melting of BzAc in DTA curves, indicating that the thermoplasticity originates from the week interaction between the polytitanoxanes. The larger BzAc contents and smaller H2O contents in solutions resulted in higher softening temperatures of the hybrids. GPC analyses showed that the molecular weight of the polytitanoxanes increases with decreasing amount of BzAc and with increasing amount of H2O, suggesting that the higher softening temperature results from the larger molecular weight of polytitanoxanes.

(ICACC-S7-P094-2015) Investigation of the HAP/HPMC/MCC biodegradable tablet for controlled drug delivery

M. Oner*[1]; ÖZGE. Ulu[1]; A. Aktas[2]; O. F. Firat[2]; 1. Yildiz Technical University, Turkey; 2. Deva Pharmaceutical Company, Turkey

Controlled drug delivery systems (CDDS) are one of the frontier areas of science and used for administration of a pharmaceutical compound in a controlled manner to achieve a therapeutic effect in humans or animals. The objectives of the present study was to formulate, characterize, in vitro drug release from blend of HAP/HPMC/MCC biodegradable tablet loaded with cefazolin to achieve the controlled drug release system. Local delivery of cefazolin is desired in conditions such as osteomyelitis, soft-tissue infection and for prevention of post-surgical infections. The placement of an antibiotic containing bio-degradable drug delivery system do not only provide high sustained concentrations locally in the bone and skeletal tissue, but also decreased hospitalization, and avoidance of parenteral administration. Hydroxyapatite (HAP) is known for its excellent biocompatibility due to its similarity in composition to the apatite found in natural bone. Hydroxypropyl methylcellulose (HPMC) has been widely used for pharmaceutical applications because of its nontoxic property, ease of handling, and direct compressible manufacturing. Microcrystalline cellulose (MCC) is insoluble but weakly swellable fillers generally result in decrease release rate. This system demonstrates a potential application in the fields of drug delivery and disease therapy based on its bioactive properties.

(ICACC-S7-P095-2015) Microwave synthesis, structure and optical characterization of metal oxides nanoparticles

A. K. Singh*[1]; U. T. Nakate[2]; 1. Armament Research and Development Establishment, India; 2. Defence Institute of Advanced Technology, India

During the last two decades there is wide spread research activity devoted to nanostructured materials and out of these materials metal oxides are the most widely investigated. The most widely reported synthesis methods are sol-gel, organometallic, hydrothermal, and microwave assisted methods. Microwave irradiation not only provides the energy for heating but also greatly accelerates the nucleation. With microwave irradiation on the reactant solution, temperature and concentration gradients can be avoided leading to uniform nucleation. Microwave synthesis is the novel route of synthesis of metal oxide semiconductor NPs which is a clean, cost-effective, energy-efficient, eco-friendly, rapid, and convenient method of heating and results in higher yields in shorter reaction times. Moreover, it leads to enhanced structural and morphological properties for the nanomaterials. Nanoparticles (NPs) of Cr2O3, SnO2, ZnO, TiO2, ZrO2, were synthesized using microwave-assisted method. Synthesized NPs were characterized for their structure, morphology, and elemental composition using X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS). The synthesized NPs have been found to be in stoichiometric ratio. The synthesized NPs were investigated for their band gap energy using UV-Vis spectroscopy, photo catalytic and photoluminescence behavior.

(ICACC-S7-P128-2015) Highly Conductive and Dispersible Graphene and Its Application in P3HT-Based Solar Cells

T. Mahmoudi[1]; W. Rho*[1]; Y. Hahn[1]; 1. Dept of Earth and Envron Sci, Korea (the Republic of)

For devices application of graphene, the production of highly conductive and dispersible graphene sheets is crucial. Various methods to meet such requirements have been examined, but they still lack solving simultaneously the dispersion and electrical conductivity problem. Recently, several research groups reported utilization of reduced graphene or its derivatives for P3HT-based organic solar cells, but power conversion efficiency is still low (< 2 %). In this paper, we propose a simple reduction method without the need for high-temperature annealing is proposed for highly conductive and dispersible graphene sheets. This method 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 organic solar cell, compared to P3HT-only device (0.18 %) a 16-fold increase in the power conversion efficiency (2.85 %) is obtained, attributed to a substantial increase in short-circuit current density from 0.017 to 12.09 mA/cm2.

(ICACC-S8-P096-2015) Polymer Derived Ceramic Nanocomposites Coating Reinforced with Carbon Nanotube Preforms

H. Yang*[1]; J. McKee[1]; X. Wang[1]; Y. Cai[1]; J. Gou[1]; 1. University of Central Florida, USA

Ceramics have a number of applications as coating material due to their high hardness, wear and corrosion resistance, and the ability to withstand high temperatures. Carbon nanotube has been widely used as reinforcement to improve the mechanical properties and thermal and electrical conductivity. However, the high content of carbon nanotube in ceramic matrix composites is hard to achieve, and the properties are somewhat diluted when carbon nanotubes are not well aligned. These problems can be overcome if ceramic coatings are reinforced by carbon nanotubes with good dispersion and suitable alignment. In this study, the dispersion and alignment of carbon nanotubes were achieved with two different types of carbon nanotube preforms, namely Vertically Aligned Carbon Nanotubes (VACNTs) and Buckypaper. Polymer Derived Ceramic (PDC) was selected as the matrix to fabricate carbon nanotube reinforced ceramic nanocomposites through resin curing and pyrolysis. The SEM images indicates the alignment of carbon nanotubes in the PDC nanocomposites through-thickness or in the in-plane direction. The thermal, electrical and mechanical properties of the PDC nanocomposites were characterized through TGA, electrical conductivity measurements, and Vickers hardness testing.

(ICACC-S8-P097-2015) Influence of the added rare earth oxide on DC volume resistivity at high temperatures of Si_3N_4 ceramics

D. Kawai*[1]; J. Tatami[1]; M. Iijima[1]; T. Takahashi[2]; 1. Yokohama National University, Japan; 2. Kanagawa Academy of Science and Technology, Japan

SiC power devices are expected to be applied to EV/HV, power trains and so on in near future. For these applications, substrates having electrical insulation, high thermal conductivity and high mechanical properties is needed. Si_3N_4 ceramics have been paid attention because of the high fracture toughness and strength. Although the improvement of the thermal conductivity of Si_3N_4 ceramics has been investigated in the recent works, the electrical insulation at high temperatures of Si_3N_4 ceramics has not been clarified yet. In this study, influence of the rare earth oxide added as a sintering aid on DC volume resistivity from room temperature to 300°C of Si_3N_4 ceramics was investigated. Although many Si_3N_4 ceramics prepared by adding rare earth oxide showed superior electrical insulation, the DC volume resistivity of the Si_3N_4 ceramics prepared by adding Sm_2O_3, Eu_2O_3, Yb_2O_3 was lower than that by adding the other rare earth oxides. The samples prepared by adding Yb_2O_3 was the lowest resistivity in this study. It has been reported that Yb-Si-Al-O-N glass include not only Yb^{3+} but also Yb^{2+}. Existence of Yb^{2+} in the Si_3N_4 ceramics prepared by adding Yb_2O_3 was confirmed by the XPS profile analysis. It is suggested that such decrease of DC volume resistivity were caused by the grain boundary glassy phase or crystal phases depending on added rare earth oxides.

(ICACC-S8-P098-2015) Novel Visualizing Technique of the Tips of the Cracks for Indentation Fracture Resistance Method

H. Miyazaki*[1]; Y. Yoshizawa[1]; 1. National Institute of AIST, Japan

Fracture resistance testing by the Indentation Fracture (IF) method is an important evaluation tool for mechanical property of tiny ceramic products such as bearing balls and cutting tools. However, quick and accurate detection of crack tip position using a metallurgical microscope has been difficult, resulting in inferior reproducibility between different laboratories. In our previous studies, the authors proposed a new measuring method using high-powered optics with both a traveling stage and an objective lens with a magnification of 40 or 50. Both domestic and international round-robin tests on the proposed technique have demonstrated good matching between the laboratories. However, the improvement was not so significant for some white ceramics with a weak contrast of the cracks. In this study, a novel technique was developed to enhance the crack contrast. A visualizing solution was applied on the indented surface of ceramic test piece during fracture resistance testing by the indentation fracture (IF) method. The concentration of a commercially available solution was optimized to produce the visualizing solution. This could give a sharp image of the crack tip, reducing errors in reading crack lengths.

(ICACC-S8-P099-2015) Round-Robin Test on Fracture Toughness of Ceramic Substrates for Power Modules

H. Miyazaki*[1]; Y. Yoshizawa[1]; K. Hirao[1]; T. Ohji[1]; 1. National Institute of AIST, Japan

Heat dissipating board for the power modules usually consists of a ceramic substrate such as aluminum nitrides or silicon nitrides sandwiched by cupper 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 the substrate. Then, high fracture toughness of the thin ceramic plate is necessary to prevent thermal fatigue 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. The characteristic of the method is that a small, thin single-edge notched plate is bonded on one side of a metallic beam and the assembly is deformed in three-points bending to introduce the precrack. In this study, domestic round-robin test was conducted using alumina, silicon nitrides and aluminum nitrides to testify both feasibility of the new technique and reproducibility of K_{IC}. It was found that the variations in K_{IC} among the participants were reasonable although some participants often failed in precracking, which required more improvements in both procedure and fixtures. Part of the research work was supported by NEDO, Japan.

(ICACC-S8-P100-2015) Fabrication of transparent and fluorescent Eu-doped β-SiAlON ceramics

T. Tanaka*[1]; J. Tatami[1]; M. Iijima[1]; T. Takahashi[2]; M. Yokouchi[3]; 1. Yokohama National University, Japan; 2. Kanagawa Academy of Science and Technology, Japan; 3. Kanagawa Industrial Technology Center, Japan

In white LED, fluorescent particles are dispersed in a resin. The resin is easy to degrade by heating during operation and much light scattering occurred because of the difference in refractive index between the particles and resin. Transparent and fluorescent bulk ceramics are one of the ideas to solve these problems. In order to obtain transparent bulk ceramics, the improvement of their density and the elimination of the glassy phase are needed because of reducing light scattering and absorbing sources. In this study, transparent and fluorescent Eu-doped β-SiAlON ceramics were fabricated using HfO_2, which enhances densification of β-SiAlON and has similar reflective index to β-SiAlON. The powder mixture of α-Si_3N_4, AlN, Al_2O_3, Eu_2O_3, Y_22O_3 and HfO_2 was molded into a pellet by uniaxial pressing and cold isostatic pressing. The green body was fired at the temperature of 1900 °C for 2 h under 0.9 MPa N_2, followed by hot isostatic pressing at the temperature of 1900°C for 1h under 100 MPa N_2. The relative density of the sintered body was higher than 98.0%. Green emission was observed under UV and blue lights, of which emission and excitation wavelength agreed with the Eu-doped β-SiAlON powder. Visible transmittance of over 50% was achieved in the sample having thickness of 100μm because the HfO_2 additive improved the density and reduced the glassy phase to form c-HfO_2 into which Y_2O_3 and SiO_2 dissolved.

(ICACC-S8-P101-2015) Sintering: Fractal electronics and Brownian motion perspectives

V. Mitić*[2]; V. Paunovic[1]; L. Kocic[1]; S. Jankovic[3]; B. Jordovic[4]; M. Miljkovic[5]; 1. Serbian Academy of Sciences, Serbia; 2. University of Nis, Serbia; 3. Serbian Academy of Sciences, Serbia; 4. University of Kragujevac, Serbia; 5. University of Nis, Serbia

The new correlation between microstructure of doped BaTiO3-ceramics, based on fractal geometry and contact surface probability, has been developed. Using the fractal and statistics of grains contact surface, a reconstruction of microstructure configurations, as grains shapes or intergranular contacts has been done. Furthermore, the area of grains surface was calculated using fractal correction expressed through fractal dimension. The main goal of this research is to apply the fractal analysis and Brownian motion within the structure of electronic thermal capacity. The fractal nature for analysis of the structure of ceramics providing a new approach for modeling and prognosis between the BaTiO3-ceramics structure and dielectric properties and new frontier for higher integration on electronic circuits. Microstructure properties of barium-titanate based materials, expressed in grain boundary contacts, are of basic importance for electric properties of these material in this case special electric thermal capacity.

(ICACC-S8-P102-2015) Hydrothermal Synthesis and Characterization of 0.65Pb (Mg1/3Nb 2/3)O3 - 0.35PbTiO3 nanowires and its Application to Nanogenerators

B. Moorthy*[1]; C. Baek[1]; D. Kim[1]; 1. Korea Advanced Institute of Science and Technology, Korea (the Republic of)

The solid solution of (1-x)Pb (Mg1/3Nb2/3)O3-xPbTiO3(PMN-PT) has been studied for micro and nanodevice applications due to its high piezoelectric properties. Hence, it is used for improving performance of nanogenerators. Recently, synthesis of PMN-PT nanowires has been reported and the piezoelectric coefficient was measured as 381pm/V. This is 15 times higher than the reported value of ZnO nanowires. However, the formation mechanism of PMN-PT nanowires has not been fully explained. Here, the possible reaction mechanism for the formation of PMN-PT nanowires was discussed. The composition with PMN-PT ratio of 65:35 lies near the morphotrotic phase boundary (MPB) and exhibits high piezoelectric coefficient due to co-existence of phases. The 0.65PMN-0.35PT nanowires have been synthesized via hydrothermal method using poly-(ethylene glycol)-200 that serves both as solvent and a capping agent. The influences of PEG-200, KOH concentration, and reaction time on phase evolution and morphology of the synthesized powders have been analyzed by XRD, SEM, and TEM. The synthesized PMN-PT nanowires were used for the fabrication of nanogenerator device to examine the output voltage and current.

(ICACC-S8-P103-2015) Microstructural control of crystal-oriented strontium barium niobate ceramics

T. Tanaka*[1]; S. Tanaka[1]; 1. Nagaoka university of technology, Japan

To control microstructure of ceramics is necessary for improvement of their property. We have fabricated the crystal-oriented strontium barium niobate (Sr0.6Ba0.4Nb2O6, SBN60) ceramics by a magnetic field for optical application. However, for sintering process, the microstructure have not been controlled well. Because, SBN ceramics, which has tetragonal tungsten bronze crystal system, often shows exaggerate grain growth during sintering. This grain growth may be caused by second phase at grain boundary. The objective of this study is to homogenize microstructure of the crystal-oriented SBN60 by heating schedule. In experiment, SBN60 powder was synthesized from a solid reaction of SrCO3, BaCO3 and Nb2O5 powder. The reaction temperature was 1250°C. The well-dispersed slurry was prepared from synthesized powder by ball milling. The powder compact was prepared by a colloidal processing in rotating magnet field. The sintering schedules were controlled as follows. At first, sintering temperature were set at 1250°C - 1300°C for several hours, then temperature was raised up to 1350°C for 2 h. Finally, specimen was sintered by hot isostatic pressing at 1300°C at 190MPa in argon. As a result, the sintering at 1250°C - 1300°C was effective for homogeneous grain growth. This suggests that the crystal phase of SBN60 is stabilized by sintering at 1250°C - 1300°C.

(ICACC-S8-P104-2015) Synthesis and sintering behavior of Y2O3 nanoparticles for transparent ceramics

H. Ma*[1]; W. Jung[1]; S. Jung[1]; D. Kim[1]; 1. KAIST, Korea (the Republic of)

Transparent ceramics have attracted considerable attention as light transmitting material at high temperatures and in corrosive environments. Especially, yttria (Y2O3) ceramic is considered as one of the promising optical materials for laser host materials and infrared-domes due to higher transmittance at IR wavelengths and superior thermal stability. However, it is not easy to produce full density Y2O3 ceramics due to its high melting point. To decrease the sintering temperature, there have been a lot of efforts for preparing Y2O3 powders that sinter better than the original raw material. Many researchers have found that mono dispersed, sub-micrometer equiaxed particles offer uniform agglomeration in packing the green body results in improved sintered density. In this study, we prepared spherical Y2O3 nanoparticles via a homogeneous precipitation in aqueous solutions by reaction with the thermal decomposition products of urea. We studied the effect of particle size and doping on the sintering behavior and transmittance of Y2O3 ceramics.

(ICACC-S8-P105-2015) Synthesis of BaTiO3 core-shell nanoparticles with Sr-doped surface layer

J. Wang*[1]; C. Baek[1]; K. Park[2]; C. Choi[2]; D. Kim[1]; 1. KAIST, Korea (the Republic of); 2. Samsung Electro-Mechenics, Korea (the Republic of)

BaTiO3 has been used as dielectric material in multilayer ceramic capacitor (MLCC) due to its high dielectric constant. The advances in electronic devices require implementation of ultra-high capacity MLCC. As dielectric layer material for MLCC, nano-sized BaTiO3 powder below 200nm has become necessity. While nano-size BaTiO3 powder is essential for miniaturized ultra-high capacity MLCC, BaTiO3 nanoparticle must maintain high dielectric properties despite its size effect. Homogeneous existence of SrTiO3 in BaTiO3 leads to broadening of dielectric permittivity peak. However, mixture of SrTiO3 and BaTiO3 may result inhomogeneous distribution between two components. The synthesis of core-shell structure of two component is one of promising approaches to achieve homogeneous distribution of BaTiO3 and SrTiO3 resulting broadened permittivity peak. Core-shell structure of BaTiO3 core and SrTiO3 shell has been investigated with relatively large BaTiO3 particle size. Thus core-shell structure of BaTiO3 core with size around 100nm and Sr-doped BaTiO3 layer are synthesized. The phase and morphology of Ba1-xSrxTiO3 at BaTiO3 core-shell structure has been investigated via X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM).

(ICACC-S8-P106-2015) Direct observation of particle motions in condensed slurry by confocal laser scanning fluorescent microscopy

Y. Nagasawa*[1]; Z. Kato[1]; S. Tanaka[1]; 1. Nagaoka University of Technology, Japan

Dispersion state of particles in a slurry is important for a colloidal processing of ceramics such as a slip casting method. Usually, rheological or sedimentation tests are carried out for characterization of a slurry dispersion. However, the results must be discussed with the state of particles in the slurry. The objective of this study is to elucidate the dispersed state of the slurry and their influence on rheological characteristics. Here, we directly observed particles in a slurry during sedimentation test and under shear stress by the confocal laser scanning fluorescent microscopy (CLSFM). Silica spheres with 2 micro meter were used as raw materials. These particles were mixed in a prepared glycerol solution. The volume fraction of particles in slurry is in the range from 30 to 50vol%. The refractive index of glycerol solution including a fluorescent dye is matched with silica particles, so that we are able to observe the internal structure directly by CLSFM. The observation result shows that the particles in slurry, which showed shear thinning behavior slightly, became to flocculate with sedimentation very slowly. Cluster of particles formed into a larger agglomeration by incorporating fine particles during sedimentation.

(ICACC-S8-P107-2015) Continuous observation of large pores of alumina at middle stage of sintering by micro-focus X-ray computed tomography

T. Hondo*[1]; Z. Kato[1]; S. Tanaka[1]; 1. Nagaoka University of Technology, Japan

Morphological change of ceramics at middle stage was examined by micro-focus X-ray computed tomography (micro-CT). We focused on morphological change of large pores from powder compact to sintered ceramics in alumina system. In previous study, large amount of large pores and interstices of granules were found in a powder compact. After sintering, some of them became larger and remained as coarse pores in the ceramics. Particularly, the remarkable shrinkage occur by densification at the middle stage of sintering. At the same time, some of the large pores should grow with incorporating small pores. The objective of this study is to elucidate the growth and morphological change of large pores during sintering by observation with micro-CT. In experiment, alumina powder compact was fabricated by dry-pressing using granules. The de-binder process was carried out at 800°C. The sample was cut into a small piece with 1mm x 1mm x 1mm in size and was observed by SEM and micro-CT. We observed the same place of the sample after heat-treatment at each temperature 1300-1550°C, respectively. Lots of pores were observed even after sintering. The number of large pores with > 5μm was increased with sintering. It was also observed that a large pore took in neighboring pores and grew at the heat-treatment temperature 1400-1500°C.

(ICACC-S8-P108-2015) Preparation and characterization of RB-SiC ceramics delivered from phenol resin/SiC composite

A. Shimamura*[1]; K. Naoki[1]; M. Hotta[1]; M. Fukushima[1]; T. Ohji[1]; 1. National Institute of Advanced Industrial Science and Technology (AIST), Japan

Silicon carbide (SiC) has been attracted as an advanced ceramic material because of its superior mechanical properties, low thermal expansion coefficient, wear resistance and corrosion resistance in high thermal temperature. Reaction Bonding-SiC (RB-SiC) is considered one of the most attractive processes from the viewpoints of low processing temperature, good shape capability, and low cost. RB-SiC ceramics are generally fabricated by infiltrating silicon melt into green compacts consisting of carbon black and SiC powders. However, the use of carbon black can easily encounter the difficulty of shape forming, handling and structural rigidity. To solve these problems, organic binder can be employed to prepare green compact with various shapes, i.e., to achieve near net shaping, in which phenol resin is one of the most promised organic binders that can also act the carbon souse after its decomposition at elevated temperature. In this study, we examined various processing factors to prepare green compacts composed of SiC and large amount of phenol resin, where the size and content of SiC particles, and heating rate to curing temperature affected dimensional changes. After carbonization of green compacts, morphologies of carbon layers derived from phenol resin were depending on the processing conditions. Infiltrating of silicon melt into carbonized compacts will be also discussed.

(ICACC-S8-P109-2015) Catalytical effect on Ammonia Borane for nano Boron Nitride materials in Hydrogen energy application

J. Wang*[1]; 1. NSYSU, Taiwan

Boron Nitride material is well known for its excellent thermal and chemical stability. In addition, the nano boron-nitride is an analogy of carbon-carbon but with heteronuclear other than homonuclear characteristics, which potentially can provide greater donor-acceptor functionality. Indeed, BN nanotube and nano-sheet have been developed in contrast to CNT and graphene in carbon-carbon family. Furthermore, ammonia borane is known as a good candidate for Hydrogen release agent. With these intriguing properties, understanding synthesis and processing of nanostructured BN and promoting its properties with respect to nano size, pore size and shape tunability may potentially beneficiate to hydrogen energy application. In this study, we attempt to preliminarily analyze the nano BN products of ammonia borane (H3NBH3) as function of various transition metals such as Ni, Co, Cu, Pt, etc. under thermal pyrolysis. Through product analysis of BN with respect to shape, pore size, and particle size among these catalytical synthesis routes, an optimal synthesis route for a desired nano Boron Nitride materials toward hydrogen release and storage applications can hopefully proposed.

(ICACC-S8-P110-2015) High-Strain-Rate Superplastic Deformation of Nanocrystalline Silicon Nitride Ceramics

R. Wananuruksawong*[1]; Y. Shinoda[1]; T. Akatsu[1]; F. Wakai[1]; 1. Tokyo Institute of Technology, Japan

Silicon nitride (Si3N4) based ceramic possess high toughness, thermal shock resistance and high strength at elevated temperatures. They have been used for high-temperature components as a turbocharger rotor or a grove plug. Since their strong covalent nature of hardness and brittleness makes some difficult and costly issue during machining operation. Superplastic forming is an attractive route for near-net shaping of ceramic components. The limitation of strain rate is one of major causes that superplastic Si3N4 ceramics typically deform at around strain rate of 10-4 s-1 or lower. High-strain-rate superplasticity is challenging process to reduce forming time and a key for industrial applications. In this work, nanocrystalline Si3N4 ceramics containing 6 wt%Y2O3, 3wt% Al2O3 and 2wt% MgO were fully densified at extremely low temperature 1300 °C by spark plasma sintering under pressure 300MPa.The mean grain size of sintered sample was 56±13 nm. High-strain-rate superplasticity in the nanocrystalline Si3N4 sample was attained with a strain rate of 10-2 s-1at 1600 °C under compression. Significant strain hardening as seen in the general superplasticity of Si3N4 ceramics was not observed. Microstructural evolution during deformation was investigated by TEM analysis.

(ICACC-S8-P111-2015) Citrate-nitrate synthesis of IGZO powder: an isothermal titration approach

K. Chuang*[1]; K. Chiu[1]; 1. Industrial Technology Research Institute, Taiwan

Synthesis of indium gallium zinc oxide powder by a citrate-nitrate method using an isothermal titration analysis approach was investigated. The citrate-to-nitrate ratio γ would influence the material characteristic of IGZO powder, like crystalline structure and stoichiometric of composition. However less literature to discuss the design rules of citrate-to-nitrate ratio. In this study, we used an isothermal titration calorimeter to analysis the behavior that chelating agent combine with metal ion. Results show more chelating agent would cause more residual carbon content and decrease the degree of crystallization of IGZO. The binding energy of citrate-metal ion show Ga>In>Zn. The binding curve of titration can be defined an exponential decay formula to predict the suitable the amount of chelating agent with metal nitrate.

(ICACC-S10-P112-2015) First Principles Calculations of Boron Suboxide

J. S. Dunn*[1]; A. B. Rahane[2]; V. Kumar[2]; 1. Army Research Laboratory, USA; 2. Vijay Kumar Foundation, India

Single crystal B6O is the third hardest naturally occurring material after diamond and boron nitride, making it a competitive material for armor, abrasive, and nuclear applications. However, like many structural ceramics, its inherent fracture toughness is low (~4.5MPa*m^0.5). This limitation has been partially resolved in the Si3N4 material system by using an intergranular glassy film (IGF) in combination with a self-reinforced microstructure to maximize energy dissipation during fracture. The Army initiated a program to apply these principles to B4C with limited success. Imperfect glass wetting, high glass viscosity, and strong B4C/glass adhesion resulted in incomplete densification (90% of theoretical). Since B6O and B4C have similar chemistries and crystal structures, these problems are also expected for the B6O material system. The compositional design space for doped-glass systems is very extensive; therefore a method is needed to identify promising regions in order to reduce the number of processing experiments. First principles models based on Density Functional Theory (DFT) offer a promising way to explore the wettability, thermodynamic stability, and the adhesion strength of grain boundary interfaces. In this poster, we present the most recent results for our DFT model of defect-free and doped bulk B6O.

(ICACC-S11-P113-2015) A study on the Ti-Al-Cr-Si-N nanocomposite coatings deposited by magnetron sputtering process with single alloying targets

J. Pyun*[1]; H. Lee[1]; K. Moon[1]; 1. KITECH, Korea (the Republic of)

It is well known that the Cutting performance of the conventional TiAlN coatings can be improved by adding various elements such as Cr, Si and B etc.. This is principally due to the solution hardening, grain refinement and formation of new stable nitrides with high thermal stability in the new quaternary nitrides. Also, the addition of such elements to TiAlN is known to form nano-composite coating with high hardness. Generally, TiAlN-X-Y coatings have been prepared by hybrid process with PVD with multiple target sources or PVD + PECVD with elemental source gas. However, it is not easy to add additional elements to the TiAlN by a proper PVD system. To add the 3rd or 4th elements in TiAlN system with multiple sputtering target sources, coating systems are complex and hard to control. As results, it is not easy to get the high productivity and repeatability. In this study, Ti-Al-Cr-Si alloying targets had been prepared by Planetary Ball Milling (PBM) and spark plasma sintering (SPS) and Ti-Al-X-Y-N coatings had been prepared by magnetron sputtering method with the various alloying targets and their properties had been investigated.

(ICACC-S11-P114-2015) Microstructural and properties of influence of Cu contents (5 ~ 20 wt. %) on Mo-Cu alloys synthesized by planetary ball milling and spark plasma sintering

H. Lee*[1]; K. Moon[1]; P. SHIN[2]; 1. KITECH, Korea (the Republic of); 2. Inha Univ, Korea (the Republic of)

Mo–Cu alloys have been widely used for heat sink materials, vacuum technology, automobile and many other applications due to their excellent physical and electronic properties. Especially, Mo–Cu composites with 5 ~ 20 wt. % copper are widely used for the heavy duty service contacts due to their excellent properties like low coefficient of thermal expansion, wear resistance, high temperature strength and prominent electrical and thermal conductivity. In most of the applications, high - dense Mo–Cu materials with homogeneous microstructure are required for high performance, which has led in turn to attempts to prepare ultra-fine and well-dispersed Mo–Cu powders in different ways, such as spray drying and reduction process, electroless plating technique, mechanical alloying process and gelatification–reduction process. However, most of these methods were accomplished at high temperature (typically degree), resulting in undesirable growth of large Cu phases; furthermore, these methods usually require complicated experimental facilities and procedure. In this study, Mo-Cu alloying were prepared by Planetary Ball Milling (PBM) and spark plasma sintering (SPS) and the effect of Cu with contents of 5 ~ 20 wt. % on the microstructure and properties of Mo-Cu alloy has been investigated.

(ICACC-S11-P115-2015) Alpha-double-prime type Ti-7.5Mo alloy for dental casting applications

J. Chern Lin*[1]; Y. Hsiao[1]; Y. Chen[1]; C. Ju[1]; 1. National Cheng Kung University, Taiwan

A biocompatible, high strength and low modulus alpha-double-prime (α")- type Ti-7.5Mo alloy has been developed in the present authors' laboratory. The present study compares some dental casting-related performance, including castability, machinability and mechanical properties, between α"- type Ti-7.5Mo alloy developed in the present authors' laboratory and popularly-used grade-2 commercially pure titanium (c.p. Ti). The Ti-7.5Mo alloy was prepared in-house using a commercial arc-melting vacuum-pressure type casting system operated in an argon atmosphere. The ingots were re-melted three times to improve chemical homogeneity of the alloy. The experimental data indicate that the as-cast Ti-7.5Mo alloy performs consistently superior to c.p. Ti. Compared to c.p. Ti, the Ti-7.5Mo alloy demonstrates much greater castability values (by 25-100%, depending on the wax paten design) and shorter polishing and cutting time (a measure of machinability). The combination of its much higher strength and lower elastic modulus of Ti-7.5Mo alloy offers a far higher elastic recovery angle (by many times) than that of c.p. Ti, which has great advantages for some dental casting applications such as removable partial denture (RPD). The research is supported by the National Science Council of Taiwan, Republic of China under the research grant NSC102-2622-E-006-041-CC2.

(ICACC-S11-P116-2015) The particle growth mechanism of high-purity silicon carbide powders

Y. Kim*[1]; M. Bang[1]; E. Lee[1]; D. Kim[1]; 1. SUNG KYUN KWAN UNIVERSITY, Korea (the Republic of)

The carbon thermal reduction is commonly used to synthesize for high purity SiC powders. It is synthesized in low-temperature region at 1773K. It is not easy to prepare high-purity coarse α-SiC powder. Therefore, the objective of this study was to produce high-purity coarse α-SiC powder. The particle growth mechanism of high-purity silicon carbide powders was studied. The effects of initial particle size and heat treatment condition on the coarsening of SiC particles were investigated. Micro β-SiC particles grew to uniform coarse α-SiC particles through recrystallization at >2273K. The shape of particles was observed by SEM, and phase-analysis was carried out by XRD.

(ICACC-S11-P117-2015) A Novel High Temperature Continuous Thermal Processing System for Various Applications

D. Bloom*[1]; 1. BTU International, USA

A novel concept for a high temperature thermal processing furnace is presently being evaluated to determine if it can replace a Pusher style furnace. Maximum operating temperature is 1600°C with a product loading of 18 kg over a 380 mm wide by 300 mm long area. Advantages over Pusher include low particle generation; lower cost of ownership; faster thermal ramping of product; improved thermal uniformity; yield improvements through elimination of jamming or cracking of pusher plates; variable production rates; and ability to power on or off quickly. The furnace utilizes a unique transport conveyor that is metal free surrounding the product. The conveyor system can be operated in an indexing fashion, similar to a Pusher or continuously, unlike a Pusher.

(ICACC-S11-P118-2015) CrN/Al2O3/CrN multilayered coatings with excellent mechanical property and corrosion behavior synthesized by a hybrid HIPIMS/ALD process

Z. Wan[1]; P. Song[2]; K. Cho[2]; K. Kim[3]; S. Kwon*[2]; 1. Pusan National University, Korea (the Republic of); 2. Pusan National University, Korea (the Republic of); 3. Pusan National University, Korea (the Republic of)

CrN hard coatings have been widely studied in various applications due to the high hardness, corrosion, wear and anti-oxidation properties. However, the hard coatings present intrinsic defects (columnar structures, pinholes, pores, and discontinuities) that allow contact between the steel and its environment, which can lead to accelerated deterioration through pitting corrosion when substrates are active alloys like steel. In this work, CrN/Al2O3/CrN multilayered coatings were synthesized by a hybrid process of high power impulse magnetron sputtering (HIPIMS) and atomic layer deposition (ALD) techniques, aiming to modify the CrN hard coating properties. Detailed studies on the microstructure, surface roughness, mechanical properties and corrosion behaviors, investigated by SEM, XRD, AFM, polarization curves and the hardness indenter, were used to characterize the influence of Al2O3 interlayer addition. The results indicated that the dense Al2O3 interlayer addition lead to a significant decrease of the average grain size and surface roughness, which greatly improved the mechanical properties and corrosion resistance of the CrN coatings. The thickness increasing of the Al2O3 layer and intercalation position altering to be approaching to the coating surface resulted in better mechanical properties and corrosion resistance.

(ICACC-S11-P119-2015) Plasma-enhanced Atomic Layer Deposition of TiN thin films for Effective Se Barrier in CIGS Solar Cells

E. Yun[2]; S. Kwon[2]; S. Lee[1]; W. Park[1]; K. Kim*[1]; 1. Pusan National University, Korea (the Republic of); 2. Pusan National University, Korea (the Republic of)

Cu (In, Ga) Se2 (CIGS) is a key material for thin film solar cell. During the selenization process, the molybdenum (Mo) back contact, which is commonly used in CIGS solar cells, partly reacts with the selenium (Se) to form the MoSe2 layer. However, thick MoSe2 layer between the effective layer and substrate can lead to the lower efficiency for CIGS solar cells. Thus, in this work, TiN thin film was deposited as a ultrathin barrier layer on the Mo substrate to inhibit the diffusion of the Se by plasma enhanced atomic layer deposition (PEALD). The influence of different TiN thickness on chemical composition, crystallinity, microstructures and efficiency characteristic of CIGS were investigated to evaluate the cell property. The results indicated that the TiN barrier thickness played an important role to suppress the formation of MoSe2 layer and the cell efficiency was greatly improved by applying TiN barrier layer. It can be considered that the TiN worked as the excellent barrier layer to reduced unintentional Se diffusion during the selenization process.

(ICACC-S13-P120-2015) Erosion-corrosion behavior of graphite foil-incorporated carbon-carbon composite in molten fluoride salt

C. Ju*[1]; T. Chen[1]; H. Lin[1]; K. Lee[2]; J. Chern Lin[1]; 1. National Cheng-Kung University, Taiwan; 2. I-Shou University, Taiwan

Despite their excellent high-temperature mechanical properties and chemical compatibility with molten fluoride salts, the inherently high porosity level of carbon-carbon (C-C) composites is one major challenge to the material for such applications. The numerous macrocracks and microcracks in C-C composites are difficult to be completely sealed by conventional techniques such as chemical vapor deposition (CVD) or chemical vapor infiltration (CVI). To overcome the porosity-related molten salt permeation problem, a graphite foil-incorporated carbon-carbon composite has been developed in the authors' laboratory. One purpose of the present study was to investigate the effect of graphite foil incorporation timing on some physical and mechanical properties of the graphite foil-incorporated C-C composite. One other purpose was to evaluate the effect of the graphite foil on erosion-corrosion behavior of the composite in molten fluoride salt. The experimental results indicate that the graphite foil has effectively sealed the C-C composite against permeation of the high-temperature molten salts. Furthermore, the graphite foil remains tightly bonded to the C-C substrate during the entire fabrication processes as well as after subsequent tests. The research is supported by the National Science Council of Taiwan, Republic of China under the research grant NSC102-2221-E-006-059.

(ICACC-S13-P121-2015) The behavior of He-ion irradiation defects in SA-Tyrannohex SiC Fiber-Bonded composite and single crystal 3C-SiC under high temperature environment

J. Hu*[1]; Y. Lin[1]; H. Lin[2]; J. Kai[1]; I. Chiu[1]; 1. National Tsing Hua University, Taiwan; 2. National Tsing Hua University, Taiwan

Silicon carbide (SiC) composite is considered as a candidate for fusion-reactor structural materials due to its low activation and irradiation tolerance at high temperatures. In this study, 2-dimensional SA-Tyrannohex SiC fiber-bonded composite and single crystal 3C-SiC were irradiated by He+ ions at irradiation temperatures at 800, 1000 and 1200°C, respectively. Each specimen were irradiated by 275, 225, and 175KeV He+ ions to reach the He concentration as 15000 appm in the examined area (0.6~0.8μm from the surface), and the depth distribution versus He concentration of incident He ions was calculated by SRIM-2013. The microstructural development of irradiated SiC composite and single crystal SiC were observed by transmission electron microscopy (TEM). Helium bubbles formed in SiC composite only at 800°C and were found mainly in large gains. However, helium bubbles were found in the single crystal SiC samples irradiated at all temperatures and the bubbles showed a band distribution. The width of the band expands at elevated temperature indicated the increasing distance of helium diffused in SiC. Based on this result, we suggest the increased diffusivity of He in SiC at elevated temperature might help He to remove from grain and release from SiC by extra carbon layer that were found between the grains of SiC composite.

(ICACC-S13-P122-2015) TEM and XRD investigation of the point defect-induced swelling in irradiated 3C SiC

H. Lin*[1]; J. Hu[2]; Y. Lin[2]; J. Kai[2]; 1. National Tsing Hua University, Taiwan; 2. National Tsing Hua University, Taiwan

Cubic silicon carbide (3C-SiC) is a promising material for nuclear applications due to its excellent mechanical properties and good corrosion resistance at very high temperatures. In this study, single crystal 3C-SiC samples were irradiated at 400 to 1000°C with 5.1 MeV Si2+ (~20 dpa) to simulate the neutron irradiation in reactors. The microstructure of the irradiated SiC was examined by using transmission electron microscope (TEM). Furthermore, these specimens were also analyzed by Synchrotron XRD at wiggler beam-line BL-17B1 in the National Synchrotron Radiation Research Center (NSRRC), Taiwan. Interstitial clusters, dislocation loops, and Frank loops in 3C-SiC were investigated under TEM. The HRTEM images showed that small loops gradually form inside a cluster along {111} with increasing temperature, and develop into Frank loops with an added atomic layer along {111} at 1000°C.In the Synchrotron XRD results, irradiation-induced swelling at 400-1000°C was measured, and humps on the right side of SiC(002) were observed, which suggested that C+/Si+-Si<100> and/or C+/Si+-C<100> dumbbells gave rise to diffuse scattering. Therefore, we estimated the defect density and verified the defect types, by using Convolutional Multiple Whole Profile fitting (CMWP-fit) program.

(ICACC-S13-P123-2015) Effect of Additive Content on Thermal Properties of Liquid-Phase Sintered SiC Ceramics Sintered with Yttria and Scandia

Y. Na*[1]; K. Lim[1]; S. Lee[1]; Y. Kim[2]; 1. KEPCO NF, Korea (the Republic of); 2. The University of Seoul, Korea (the Republic of)

The effect of additive content on the thermal properties of hot-pressed liquid-phase sintered (LPS)-SiC ceramics with 0.25 to 3 vol% Y2O3 and Sc2O3 additives were investigated. It was found that specimens with 0.5 to 3 vol% additives could be sintered to densities >99.9% of the theoretical density. The SiC ceramics sintered with Y2O3 and Sc2O3 had a bimodal microstructure consisting of large and small equiaxed SiC grains. The average grain size increased with increasing sintering additive content in the starting composition. All specimens showed very high thermal conductivity ranging from 137 to 234 W/mK at room temperature. The phonon mean free path and thermal conductivity increased with the increase in sintering additive content to 1 vol%, thereafter decreased. An optimum Y2O3-Sc2O3 content exists for which the absence of amorphous films at grain boundaries and the confinement of poor-conducting RE-containing phases in the junction areas, resulting the maximum thermal conductivity.

(ICACC-S13-P124-2015) Spark Plasma Sintering for Transuranic Elements

M. Cologna*[1]; V. Tyrpekl[1]; T. Wangle[2]; C. Berkmann[1]; M. Holzhäuzer[1]; J. Somers[1]; 1. JRC-ITU, Germany; 2. Czech Technical University, Czech Republic

Spark Plasma Sintering (SPS) is an emerging technique that enables the synthesis samples with unique properties. Its application to the nuclear fuel synthesis has not been explored extensively. Many questions remain unanswered and the behaviour of actinides under field assisted sintering condition needs to be assessed. Very recently JRC-ITU integrated a first of a kind SPS in a glovebox, which is fully equipped for work with transuranic elements. With this new and unique equipment, a series of samples are being synthesized and a throughout characterisation is being conducted. We will present the first results on the nuclearisation of the equipment, the sintering of UO2 and ThO2 along with corresponding characterization and will provide an outlook of the future developments with a focus on materials for safe operations of nuclear fuels.

(ICACC-FS2-P125-2015) Molecular Co(II) and Co(III) Heteroarylalkenolates as Efficient Precursors for Chemical Vapor Depositions of Co3O4 Nanowires

M. Bueyuekyazi*[1]; C. Hegemann[1]; T. Lehnen[1]; W. Tyrra[1]; S. Mathur[1]; 1. University of Cologne, Germany

Two new cobalt precursors, Co(II)(PyCHCOCF3)2(DMAP)2 (1) and Co(III)(PyCHCOCF3)3 (2), based on Co(II) and Co(III) centers were synthesized using a redox active ligand system.The different chemical configurations of (1) and (2) and differential valence states of cobalt were confirmed by crystal structure determination and comprehensive analytical studies. Whereas (1) could not be studied by NMR due to the paramagnetic nature of the central atom, (2) was unambiguously characterized by multinuclear 1D and 2D NMR experiments in solution. Both compounds are efficient precursors for catalyst-free growth of Co3O4 nanowires on Si and Al2O3 substrates by a chemical vapor deposition process. The different valence states of cobalt species influenced their chemical decomposition pathways in the gas phase, for instance, (1) was partially oxidized (Co2+→Co3+) and (2) underwent reduction (Co3+→Co2+) to form pure cobaltite in both cases that verified the metal-ligand redox interplay. Co3O4 nanowires with nanometric diameters (50-100 nm) were obtained subject to the chosen cobalt precursor. Investigations on the humidity sensing behavior of CVD deposits demonstrated their potential as promising sensor materials.

(ICACC-FS2-P126-2015) Glass-ceramics based on the bulk formation of "anti-glass" spherulites in the TeO2-Nb2O5-Bi2O3 system

M. Shimoda[1]; A. Bertrand[2]; J. Carreaud[2]; G. Delaizir[2]; J. Duclere*[2]; M. Colas[2]; J. Cornette[2]; T. Hayakawa[1]; O. Masson[2]; C. Genevois[3]; E. Véron[3]; M. Allix[3]; P. Thomas[2]; 1. Nagoya Institute of Technology, Japan; 2. Laboratoire de Science des Procédés Céramiques et de Traitements de Surface (SPCTS), France; 3. Conditions Extrêmes et Matériaux : Haute Température et Irradiation (CEMHTI), France

Glass-ceramics in the TeO2-Nb2O5-Bi2O3 system were studied. The kinetics parameters and the Avrami exponent, as well as the nucleation and growth parameters, were determined. The glass-ceramics consist in crystalline spherulites present throughout the bulk. The crystal structure corresponds to a cubic phase, similar to β-Bi2Te4O11, but containing Nb. Such structure is analogous to the "anti-glass" phases described by Trömel. The optical transparency of the bulk materials is progressively reduced with the increase in the density of spherulite/glass matrix interfaces. The photoluminescence (PL) properties of (1% wt) Er2O3-doped compositions, as a function of the devitrification time at T = 380°C, were investigated. A careful analysis of the evolution of the PL signal (4I13/2 - 4I15/2 transition) allows the indirect detection of the first steps of the devitrification. The corresponding time determined from PL measurements match very well with the one directly derived from X-ray diffraction (XRD) data. Finally, the evolution of the integrated PL intensity and lifetime values as a function of the devitrification time is monitored. It is noticed that both quantities show very comparable trends, and that the increase/decrease in the PL intensity is systematically accompanied by a respective increase/decrease of the lifetime value.

Thursday, January 29, 2015

S1: Mechanical Behavior and Performance of Ceramics & Composites

Mechanical Behavior of CMCs

Room: Coquina Salon D

Session Chairs: Randall Hay, Air Force Research Laboratory; Jacques Lamon, CNRS

8:30 AM

(ICACC-S1-049-2015) Investigation of the flexural strength of continuous fiber reinforced ceramic matrix composites (Invited)

J. Lamon*[1]; V. Calard[2]; 1. CNRS, ENS, France; 2. CNRS, University of Bordeaux, France

The paper tackles the important issue of the flexural strength of continuous fibre reinforced ceramic composites and discusses the applicability of equation of elastic beam theory that is often employed. The 3-pt bending behavior of 2D woven SiC/SiC composites was investigated. Tensile tests were also performed for comparison purposes, as well as in order to produce some pertinent material characteristics. The flexural strength was extracted from bending tests results using various methods: (1) the equations of elastic beam theory, (2) finite element analysis of stress-state, (3) stress-strain relations, (4) a fiber bundle-based approach using results from tensile tests. It is shown that the equation of elastic beam theory significantly overestimates the flexural strength of 2D SiC/SiC, whereas the three other approaches converge on 340 MPa.

9:00 AM

(ICACC-S1-050-2015) Delamination and Damage Growth in Ceramic Matrix Composites under Impact Loads

R. S. Kumar*[1]; M. Mordasky[1]; 1. United Technologies Research Center, USA

Ceramic matrix composite (CMC) components in a gas turbine engine environment can be subjected to impact load during operation. Such loads can lead to both ply damage as well as delamination cracks. In the present work computational Finite Element (FE) approach is used to model the impact process in a laminated two-dimensional CMC material. Furthermore, impact experiments are conducted for model calibration and validation. The model considers ply damage mechanisms using a continuum damage approach, whereas the delamination mechanism is modeled explicitly using cohesive-zone FE method. Validation experiments are conducted on CMC beams using a gas-gun impact apparatus. Post-test analyses of the specimen are conducted to quantify the extent of surface and sub-surface damage and the results are compared against corresponding FE analysis.

9:20 AM

(ICACC-S1-051-2015) Investigation and modeling of creep for an all-oxide CMC

K. Artzt*[1]; S. Hackemann[1]; F. Flucht[1]; M. Bartsch[1]; 1. DLR, Germany

All-oxide ceramic matrix composites represent strong candidates for high temperature applications in oxidizing atmosphere, e.g. as combustion liners in gas turbines. This material class has the advantage of inherent oxidation resistance and damage tolerance, but limitations in creep resistance exist and should be included in long-term simulations of components. Data for developing a creep simulation model were acquired in creep experiments on material with quasi-unidirectional fiber architecture. Besides highly anisotropic creep behavior, a significant dependence of strain rate on fiber orientation was revealed under tensile and compressive loading. Additionally, a potential size effect in compression creep was investigated by regarding different specimen's aspect ratio. All results were evaluated with respect to stress and temperature dependences for further usage in simulations. An approach according to Hill, describing anisotropic creep, was taken as basis and modified by an own subroutine to overcome drawbacks. Hill's model - as available in common finite element software – does not distinguish tensile from compressive creep. The new subroutine allows for a compression to tension change in stress, as well as the development of creep anisotropy caused by cumulative strain. Experimental results from tension and compression as well as from four-point bending tests were used for input and validation of the simulation.

9:40 AM

(ICACC-S1-052-2015) 3-D Alumina Grain Growth and Fiber Mechanical Properties in Nextel 610

R. Hay*[1]; K. Keller[2]; T. Tidball[3]; 1. Air Force Research Laboratory, USA; 2. UES, Inc., USA; 3. Wright State University, USA

Nextel 610 alumina fibers were heat-treated at 1100 to 1500°C for 1 to 100 hours in air. Grain-size distributions and orientations were characterized using TEM of longitudinal fiber sections. The tensile strength of heat-treated filaments was also measured. 2-D grain-size distributions and orientations were characterized as ellipses. 3-D grain size and orientation distributions were calculated by fitting oriented ellipsoids distributions to ellipses formed by ellipsoid – section-plane intersections. Standard-deviations of log-normal grain-size distributions increased with average grain-size, which is inconsistent with normal grain growth. The aspect-ratio of plate-like grains and their tendency to orient along the fiber-axis also increased with grain-size. Average 3-D grain-sizes were larger than 2-D sizes for distributions with small standard-deviation, but were smaller for large standard-deviation because of under sampling of small grains. 3-D grain growth kinetics had the same activation energy as that found for 2-D grains, but the growth exponent was larger and the pre-exponential factor much smaller. Expressions for 3-D log-normal grain-size, aspect ratio, and orientation distributions as a function of temperature and time were determined. Methods for determining 3-D grain size distributions are discussed. Relationships between grain-size, fiber strength and other fiber properties are explored.

10:20 AM

(ICACC-S1-053-2015) Optical deformation analysis of alumina based wound highly porous CMCs

S. Hackemann*[1]; J. Wischek[1]; 1. DLR - German Aerospace Center, Germany

All-oxide ceramic matrix composites are promising candidates for long term applications at high temperature and oxidizing environments, which can be found in combustors or turbines. The investigated WHIPOX-CMCs (Wound Highly Porous Oxide) show good toughness and thermoshock resistance. The mechanical behavior is based on the interaction of ceramic fibers embedded by a porous matrix. The winding technique enables variable fiber architecture, but the cross-over lines turned out to be a main source of failure, especially where fiber bundle dominated failure occurs. Optical 3D deformation analysis (ARAMIS-system) of laminates with stacked cross-over lines was conducted. The section of the cross-over lines and their vicinity revealed little deviations in the linear-elastic range, but exceptional high strains towards final failure. The experimental results are the basis for a modified material model. One material law was obtained from unidirectional material data, adopted by crack densities and applied to the structure besides the cross-over lines. The deviating second material law is based on the results of the optical analysis and refers to the cross-over-lines and their vicinity. Further experiments are carried out on samples with alternating and continuously shifted cross-over lines to verify the model with focus on the onset of fiber bundle dominated failure.

10:40 AM

(ICACC-S1-054-2015) Correlation of electrical resistance to CMC stress-strain and fracture behavior under high heat-flux thermal and stress gradients

M. P. Appleby*[1]; G. N. Morscher[1]; D. Zhu[2]; 1. The University of Akron, USA; 2. NASA Glenn Research Center, USA

Because SiC/SiC ceramic matrix composites (CMCs) are under consideration for use as turbine engine hot-section components in extreme environments, it becomes necessary to investigate their performance and damage morphologies under complex loading and environmental conditions. Monitoring of electrical resistance (ER) has been shown as an effective tool for detecting damage accumulation of woven melt-infiltrated SiC/SiC CMCs. However, ER change under complicated thermo-mechanical loading is not well understood. In this study a systematic approach is taken to determine the capabilities of ER as a relevant non-destructive evaluation technique for high heat-flux testing, including thermal gradients and localized stress concentrations. Room temperature and high temperature, laser-based tensile tests were conducted in which stress-dependent damage locations were determined using modal acoustic emission (AE) monitoring and compared to full-field strain mapping using digital image correlation (DIC). This information is then compared with the results of in-situ ER monitoring, post-test ER inspection and fractography in order to correlate ER response to convoluted loading conditions and damage evolution. Environmental barrier coating (EBC) coated SiC/SiC CMCs were also compared for CMC failure and NDE behavior.

11:00 AM

(ICACC-S1-055-2015) Modeling of the mechanical and electrical behaviors of melt-infiltrated SiC/SiC composites

E. Maillet*[1]; M. P. Appleby[1]; C. R. Baker[1]; G. N. Morscher[1]; 1. The University of Akron, USA

Electrical Resistance (ER) measurement has been shown to be a very effective technique for monitoring damage in Ceramic Matrix Composites (CMCs). In particular, ER is exceptionally sensitive to transverse matrix cracking in woven melt-infiltrated CMCs. The increase in ER under tensile loading, however, is not only a function of matrix crack density, but depends also on applied stress and interfacial wear. A cohesive mechanical-electrical model is necessary in order to understand and validate the relations between damage and ER. Here, a micromechanics-based approach was adopted. First, the influence of earlier assumptions regarding friction and interface debond energy on the predicted mechanical behavior will be discussed. Predictions of ER behavior will then be presented for various composite systems and loading schemes.

11:20 AM

(ICACC-S1-056-2015) Failure of Short Carbon Fiber-Dispersed SiC Matrix Composite under bi-axial Tensile Loading Condition

R. Inoue*[1]; Y. Kagawa[2]; 1. The University of Tokyo, Japan; 2. National Institute for Materials Science(NIMS), Japan

Deformation and fracture behaviors of short carbon fiber-dispersed SiC matrix composite (SCF/SiC) under biaxial tensile loading condition are studied. Ring-on-ring tests of SCF/SiC composite are carried out using a disk–shape specimen. Direct microscale observation of tensile outermost surface of the SCF/SiC specimen is done using specially designed fixture and monitoring system. Micro/macro scale strain distribution is also obtained using DIC method. Experimental results show that microcracks nucleate in SiC and Si phase, and perpendicular to fiber axis in a bundle. Under bi-axial tensile loading condition, crack arrest mechanism opperates when angle between crack growth direction and fiber axis in the bundle is close to ~90 degrees. From experimental results, microcrack nucleation, accumulation and origin of macroscopic failure will be discussed.

11:40 AM

(ICACC-S1-057-2015) Electrical Resistivity During Tensile Creep Testing of Different Volume Fraction SiC/SiC Composites

A. Almansour*[1]; E. Maillet[1]; G. N. Morscher[1]; 1. The University of Akron, USA

Ceramic Matrix Composites (CMCs) are promising candidates for high-temperature applications such as hot section and exhaust components of advanced turbine and hypersonic engines. Therefore, the tensile creep behavior of different volume fraction pristine and precracked Hi Nicalon, Hi Nicalon Type S and Tyranno ZMI reinforced minicomposites with BN interphases was determined. Precracking stresses were determined from room temperature monotonic tensile tests. Creep tests were performed in air at 1200 C. Very low fiber volume fraction samples were tested to characterize the behavior and properties of CVI SiC matrix. Electrical resistance evolution was measured using the four-probe method. Strain was measured using LVDT and electrical resistivity monitoring was performed to assess damage development during the test. Finally, the results were compared to previous high temperature fiber testing data and the effects of load-sharing and matrix cracking will be discussed.

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

Environmental Barrier Coatings I

Room: Coquina Salon G

Session Chairs: Dongming Zhu, NASA Glenn Research Center; Yutaka Kagawa

9:00 AM

(ICACC-S2-026-2015) Functionally Graded Mullite-Based Hybrid EBC/TBC Coatings for Si-Based Ceramics in Gas Turbines (Invited)

S. Basu*[1]; V. Sarin[1]; 1. Boston University, USA

SiC/SiC ceramic matrix composites (CMCs) are being used increasingly in the hot-sections of gas turbines, especially for aerospace applications. These CMCs are subject to recession of their surface if exposed to a flow of high-velocity water vapor, and to hot-corrosion when exposed to molten alkali salts. This research involves developing a hybrid system containing an environmental barrier coating (EBC) for protection of the CMC from chemical attack and a thermal barrier coating (TBC) that allows a steep temperature gradient across it to lower the temperature of the CMC for increased lifetimes. The EBC coating is a functionally graded mullite (3Al2O3-2SiO2) deposited by chemical vapor deposition (CVD). The effect of a TBC layer of yttria-stabilized zirconia (YSZ) or HfO2 deposited by air plasma spray (APS) on the EBC is explored. The effect of vertical cracks in the TBC on the EBC layer below it is also simulated.

9:30 AM

(ICACC-S2-027-2015) Structural Stabilization of Advanced EBC with Excellent Thermal Energy Reflection at High Temperatures

M. Tanaka*[1]; T. SASSA[2]; S. HORI[2]; N. KAWASHIMA[1]; S. KITAOKA[1]; M. YOSHIDA[2]; O. SAKURADA[2]; M. HASEGAWA[3]; Y. KAGAWA[4]; 1. Japan Fine Ceramics Center, Japan; 2. Gifu University, Japan; 3. Yokohama National University, Japan; 4. The University of Tokyo, Japan

Environmental barrier coatings (EBCs) for SiC fiber reinforced SiC ceramic matrix composites (CMCs) play a critical role in their application to hot-section components such as next-generation gas-turbine engines. We have previously proposed a new concept for an advanced EBC that can effectively reflect thermal energy in addition to preventing oxidation of the underling CMCs. Such thermal reflectivity can arise from the formation of periodic layered structure consisting of two kinds of oxide materials with a large difference in refractive index. The combination of Y2Ti2O7 and alumina is expected to be candidate for satisfying the above conditions. This advanced EBC should be required to have the excellent stability of the layered structure at high temperatures. Movement of cations through the hetero interface in the EBC subjected to steep oxygen potential gradients at high temperatures induces collapse of the periodic layered structure, resulting in dissipation of the environmental barrier and the thermal reflective functions. In this study, control of mass-transfer by the addition of dopants to the individual oxide layers is discussed for the structural stabilization at high temperature.

9:50 AM

(ICACC-S2-028-2015) Modeling of interactions between cracks in multilayer environmental barrier coatings

S. Sehr*[1]; W. Pro[1]; M. Begley[1]; 1. University of California, Santa Barbara, USA

The complex environmental barrier coatings needed for SiC/SiC composites can fail through multiple initiation modes such as delamination between the layers, mud cracking through the thickness of a layer and flaws within the layers. These modes can operate independently of each other or interact possibly leading to crack arrest. In this study, an Explicit-DEM (Discrete Element Method) based computational model is used to simulate crack patterns and interactions in a representative three-layer EBC. Through the use of a combination of element types, preexisting cracks as well as discontinuities in material behavior can be modeled efficiently. Furthermore, the simulation method makes no assumptions about the crack path a priori and allows the crack progression to occur naturally. The method is parallelizable, resulting in speed increases as compared to serial computations. The results reveal the effects of geometry on crack initiation and growth.

10:30 AM

(ICACC-S2-029-2015) Mechanical Properties of Air Plasma Sprayed Environmental Barrier Coating (EBC) Materials

B. T. Richards*[1]; D. Zhu[2]; H. Wadley[1]; 1. University of Virginia, USA; 2. NASA Glenn Research Center, USA

Development work in Environmental Barrier Coatings (EBCs) for Ceramic Matrix Composites (CMCs) has focused considerably on the identification of materials systems and coating architectures to meet application needs. The evolution of these systems has occurred so quickly that modeling efforts and requisite data for modeling lag considerably behind development. Materials property data exists for many systems in the bulk form, but the effects of deposition on the critical properties of strength and fracture behavior are not well studied. We have plasma sprayed bulk samples of baseline EBC materials (silicon, ytterbium disilicate) and tested the mechanical properties of these materials to elicit differences in strength and toughness. We have also endeavored to assess the mixed-mode fracture resistance, Gc, of silicon in a baseline EBC applied to SiC/SiC CMC via four point bend test. These results are compared to previously determined properties of the comparable bulk material.

10:50 AM

(ICACC-S2-030-2015) The effect of rare earth-based environmental barrier coatings (EBC) on the oxidation behaviour of a melt infiltrated (MI) SiC/SiC matrix composite

N. Al Nasiri*[1]; D. D. Jayaseelan[1]; W. E. Lee[1]; 1. Imperial College London, United Kingdom

Ceramic matrix composites (CMC) have received significant attention from many researchers for being excellent candidates for gas turbine applications. Using CMCs led to a significant improvement in fuel consumption and thrust to weight ratio in comparison to metal based alloys. In addition, the low density of CMCs allows potential weight savings of up to 30% comparing to Ni-based super alloys. However, Si-based ceramics lack of environmental durability in high velocity combustion environments. Si-based ceramics have excellent oxidation resistance due to the formation of a protective silica layer when it reacts with dry air. On the other hand, the same silica layer will react with water vapour to form gaseous silicon hydroxide leading to high recession of Si-based ceramics. In order to avoid the recession in water vapour environment, an external barrier coating is needed. Five different environmental barrier coatings (EBC) were selected and the diffusion rate of oxygen was obtained at temperatures up to 1350C. The oxidation behaviour of the MI SiC/SiC composite was studied at 900C to 1300C and the oxidation thickness versus time was obtained.

11:10 AM

(ICACC-S2-031-2015) Thermochemistry of Rare Earth Silicates for Environmental Barrier Applications

G. Costa*[1]; N. S. Jacobson[1]; 1. NASA Glenn Research Center, USA

Rare earth silicates are promising candidates as environmental protective coatings (EBCs) for silica-forming ceramics and composites in combustion environments since they are predicted to have lower reactivity with the water vapor combustion products. The reactivity of rare earth silicates is assessed by the thermodynamic activity of the silica component which is best measured by Knudsen effusion mass spectrometry (KEMS). Here, we discuss a novel method based on a reducing agent to increase the partial pressure of SiO(g) which is then used to calculate thermodynamic activity of silica in Y2O3-SiO2 and Yb2O3-SiO2 systems. After the KEMS measurements, samples were probed by X-ray diffraction and their phase content was calculated from Rietveld refinement.

S3: 12th International Symposium on Solid Oxide Fuel Cells (SOFC): Materials, Science and Technology

Electrical and Mechanical Reliability / Electrochemical Performance and Stability

Room: Crystal
Session Chairs: John Olenick, ENrG Incorporated; Jochen Schilm, Fraunhofer Gesellschaft

8:30 AM

(ICACC-S3-043-2015) Tailoring Chemo-Mechanical Coupling to Enhance Durability of Mixed Conducting Perovskite Electrodes (Invited)

N. H. Perry*[1]; D. Marrocchelli[2]; J. Kim[2]; S. R. Bishop[1]; H. L. Tuller[2]; 1. Kyushu University, Japan; 2. Massachusetts Institute of Technology, USA

Large chemo-mechanical coupling, e.g., a high chemical coefficient of expansion (CCE), is undesirable for an oxide in an operating fuel cell: strains generated during changes in oxygen content can lead to catastrophic mechanical failure. In this work we studied chemical expansion of gallate and titanate mixed conducting perovskites, to identify factors that can lower CCEs in electrodes. CCEs of bulk $(La,Sr)(Ga,Ni)O_{3-\delta}$ (LSGN) and $Sr(Ti,Fe)O_{3-\alpha}$ (STF) were determined experimentally by *in situ* thermogravimetric analysis and dilatometry, with *in situ* X-ray diffraction tracking accompanying structural changes. Density functional theory and molecular dynamics simulations enabled atomistic examination of the roles of charge localization and lattice relaxation around oxygen vacancies in chemical expansion. In LSGN it was found experimentally that lowering charge localization on multivalent Ni (via increased concentration) lowered the CCE, in agreement with theory. Also the lattice symmetry gradually increased during expansion. In both STF and LSGN the CCE was strongly temperature-dependent. The effective oxygen vacancy radius in LSGN was smaller than that in STF. Four (non-exhaustive) factors therefore may be tuned to lower CCEs for enhanced durability: charge localization, crystal structure symmetry, temperature during oxygen activity excursions, and the effective size of oxygen vacancies.

9:00 AM

(ICACC-S3-044-2015) Mechanical Damping and Dielectric Relaxation of 8 mol% YSZ

P. Gao*[1]; G. Brankovic[2]; Z. Brankovic[2]; M. Radovic[3]; 1. Texas A&M University, USA; 2. University of Belgrade, Serbia; 3. Texas A&M University, USA

8 mol% Yittria Stabilized Zirconia (YSZ) with high ionic conductivity is currently essential material for highly-efficient and environmentally-friendly energy technologies, including solid oxide fuel cells (SOFCs) and batteries. 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 addition, electrical polarization and impedance spectroscopy 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.

9:20 AM

(ICACC-S3-045-2015) Elastic Properties and Mechanical Loss of Doped Cerias Determined by Resonant Ultrasound Spectroscopy

A. M. Bolon*[1]; P. Gao[2]; M. Radovic[1]; 1. Texas A&M University, USA; 2. Texas A&M University, USA

Cerias doped with aliovalent cations, such as gadolinia doped ceria (GDC) are excellent ionic conductors that are commonly used as electrolyte materials for Solid Oxide Fuel Cells. The type of doping cation (gadolinia, lanthana, samaria, yttria, and zirconia) and the concentration can have a significant effect on the energy dissipation (or mechanical loss) in ceria. Mechanical loss and activation energy of defect motion of pure and different doped cerias were determined using Resonant Ultrasound Spectroscopy (RUS) in the 25 – 1000 °C temperature range and Dynamic Mechanical Analysis (DMA) in the 25 – 550 °C temperature range. The mechanical loss, Q-1 was determined as a full width 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 Q-1 and the loss modulus show two frequency dependent maximum at different temperatures for different doped cerias while the elastic moduli decrease almost linearly with temperature. This phenomenon is discussed in light of the anelastic relaxation of oxygen vacancy-dopant associates by oxygen vacancy hopping.

9:40 AM

(ICACC-S3-046-2015) Mechanical Properties of Ni-YSZ Anode Materials for Solid Oxide Fuel Cells

D. Ni*[1]; B. Charlas[1]; K. Kwok[1]; H. L. Frandsen[1]; 1. Technical University of Denmark, Denmark

Solid Oxide Fuel Cells (SOFCs) are subjected to significant stresses during production and operation. The various stress generating mechanisms impose strength requirements for SOFC materials, and thus the mechanical properties of the critical load bearing components at operational conditions need to be characterized in order to ensure reliable operation. In anode supported SOFCs, Ni-YSZ anode materials provide the major mechanical support. In this study, the effect of reduction conditions on microstructural stability and high temperature mechanical properties, e.g. elastic modulus, bending strength of the Ni-YSZ anode materials were investigated firstly. Both the elastic modulus and bending strength were determined by 4 point bending test. The statistical distribution of strength was determined from a large number of samples (+30) at each reduction condition and temperature for high statistical validity. The high number of experiments was achieved by use of a novel method, where up to 16 samples can be tested at a time. The strength of each of the samples was accurately determined by batch wise finite element simulations.

10:20 AM

(ICACC-S3-047-2015) Two-stage performance and durability evaluation of anode-supported solid oxide fuel cell with 15,000 hours operation

T. Lin*[1]; W. Kao[1]; H. Kuo[1]; R. Lee[2]; S. Cheng[2]; 1. Institute of Nuclear Energy Research, Taiwan; 2. Institute of Nuclear Energy Research, Taiwan

An anode-supported solid oxide fuel cell consisting of a NiO-YSZ anode, YSZ electrolyte, and YSZ-LSM || LSM composite cathodes has been investigated. The cell is fabricated with a 10 × 10 cm^{-2} commercially available size and has been electrochemically tested. The open circuit voltage is greater than 1.1 V at 800 °C, suggesting a firm cell structure. The power densities are 173, 257, and 364 mW cm^{-2} at 700, 750, and 800 °C, respectively. The durability evaluation is conducted for 15,000 hours with 14 thermal cycles. During the first stage test with fixed current density of 300 mA cm^{-2}, the degradation rate is 0.4 %/Khr for 6761 hours operation. At the second stage, operation with 400 mA cm^{-2} was executed for 8241 hours to further investigate the electrochemical property and the degradation rate is 1.07 %/Khr. The cell shows consistent power output, indicating the stable cell structure as well as the compatible performance behavior. Some expected thermal cycling operations were conducted. However, the open circuit voltage exceeded 1.0 V whenever the cell was operated again. It is evidenced that the operational conditions with lower current density or higher cell voltage can prolong the cell lifetime but somehow decrease the output power of the cell.

10:40 AM

(ICACC-S3-048-2015) Electrochemical performance of thermal sprayed metal supported solid oxide fuel cells

M. Gupta*[1]; A. Weber[2]; N. Markocsan[1]; M. Gindrat[3]; 1. University West, Sweden; 2. Karlsruher Institut für Technologie (KIT), Germany; 3. Oerlikon Metco, Switzerland

Solid Oxide Fuel Cells (SOFCs) are electrochemical energy converters which provide high net efficiencies above 50% as well as clean and low level emissions. However, high material and production costs are key barriers to the widespread commercialization of SOFCs. Thermal spray technique may provide an alternative for the production of SOFCs. The objective of this work was to evaluate the electrochemical performance of half-cells produced by thermal spraying. In this work, anode was deposited on a porous metallic support by atmospheric plasma spraying and consisted of a mixture of nickel, Yttria Stabilized Zirconia (YSZ) and a pore former. A YSZ electrolyte was deposited by low pressure plasma spray technique called Plasma Spray-Thin Film (PS-TF) which can produce thin and dense coatings at high deposition rates. A LSCF-cathode was screen-printed for testing. The tests were performed in a temperature range of 600-800°C at atmospheric pressure under various gas compositions of H2, H2O and N2 on the anode side and of O2 and N2 on the cathode side. Current-voltage characteristics and impedance spectra were measured. The impact of spray parameters and applied layer thicknesses on the gas tightness of the electrolyte and the area specific resistance of the cell will be discussed. The results show that the applied thermal spraying techniques could be a promising alternative for producing SOFCs.

11:00 AM

(ICACC-S3-049-2015) Improving Power Density of Solid Oxide Fuel Cells: Role of Contact Resistance

L. Zhang*[1]; L. Zhu[1]; A. V. Virkar[1]; 1. Univeristy of Utah, USA

Numerous studies have been reported on improving power density of solid oxide fuel cells (SOFCs). Improved cell structure and more active cathode materials have led to better performance of thin electrolyte, anode-supported cells. However, in the past decade, significant further improvement has not been achieved. Recent work in our group has shown that minimizing the ohmic loss is essential to further improve the performance of anode-supported SOFCs. The study showed that around 48% of the ohmic resistance is due to poor interlayer contact which occurs in anode-supported cells with graded electrodes. Pores or cracks between layers in such structures in SOFCs are the source of the contact resistance. Finite element analysis (FEA) has been used to determine the contact resistance between layers. By maintaining the same delamination area, we varied the size of each individual crack. Preliminary results showed that as much as 25% increase in ohmic resistance occurs due to around 30% of delaminated region. The origin and the role of delamination region on the cell performance will be discussed.

11:20 AM

(ICACC-S3-050-2015) Development of LT-SOFCs: Limiting Factors and Concepts for Achieving High Performance at Low Temperatures

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

Considerable work has been reported on solid oxide fuel cells (SOFC) over the past decade. While progress has been made, there has not been significant further gains in performance beyond ~2 W.cm^(-2) at 800°C achieved about fifteen years ago and ~ 0.2-0.4 W.cm^(-2) at 500°C reported about ten years ago, despite using a number of different cathodes. A parametric model has been developed to estimate polarization losses based on out-of-cell measurements using micro-fabricated electrodes, microstructural measurements on cells, and cell electrochemical performance measurements. The objective of this presentation is to identify dominant losses in low temperature solid oxide fuel cells (LTSOFCs) using the parametric model. Calculations show that the limiting factors are the ohmic loss, followed by cathode and anode activation polarizations which are closely related to the electrode grain size. In fact, at 800°C, even in thin YSZ electrolyte anode-supported cells, the dominant factor is the ohmic loss, associated with cell components other than the electrolyte. It is also shown that by using thin ceria-based electrolyte and using nanostructured electrodes, cell performance well over 1 W.cm^(-2) can be realized at temperatures lower than 500°C.

11:40 AM

(ICACC-S3-051-2015) Development of high performance anode-supported solid oxide fuel cells with optimized components

H. Shimada*[1]; T. Suzuki[1]; Y. Fujishiro[1]; 1. National Institute of Advanced Industrial Sience and Technology (AIST), Japan

High power density anode-supported solid oxide fuel cells (SOFCs) were developed in which microstructure-controlled electrodes and an optimized ceria interlayer. For commercialization of SOFCs, high power density operation is essential to cost reduction. To improve in anode performance, we controlled the porosity of nickel/yttria-stabilized zirconia anodes by using pore former and optimizing sintering temperature. For cathode side, we investigated the effect of cathode composition on performance, and also attempted to densify ceria interlayer to reduce the internal resistance. The prepared cells were characterized using scanning electron microscopy. In electrochemical measurements, current-voltage measurements and electrochemical impedance spectroscopy were performed in the intermediate temperature range. In conclusion, our cells achieved more than 2 W/cm2 at 800 degrees C.

S5: Next Generation Bioceramics and Biocomposites

Bioceramics II

Room: Coquina Salon F

Session Chairs: Anna Tampieri, CNR ISTEC (Faenza, Italy); Laurie Gower, University of Florida

8:30 AM

(ICACC-S5-010-2015) Smart bio-inspired nano-composites for tissue regeneration (Invited)

A. Tampieri*[1]; M. Sandri[1]; S. Sprio[1]; S. Panseri[1]; 1. CNR ISTEC (Faenza, Italy), Italy

New regenerative approaches for the healing of diseased tissues and organs aim at minimizing surgical invasivity to recover tissue functionality. The formation of human bones is governed by self-assembling and organization of collagen molecules in a complex 3-D structure, acting as a template for simultaneous mineralization with nanocrystalline, ion-substituted apatite. Since a decade, the reproduction of the conditions of bone formation allowed to settle a biomimetic synthesis process generating hybrid constructs where the nucleation of the mineral phase is directed by the chemical features and physical confinement imposed by the self-organizing polymeric matrix, so that the mineral phase has physical, chemical and ultra-structural resemblance with mineral bone, thus triggering, in vivo, the cascade of events leading to tissue regeneration. The possibility of tailoring the mineralization extent also enabled the synthesis of graded constructs mimicking different areas of multi-functional articular regions. Pinning on this recent development, it is illustrated how bone- and osteochondral-mimicking devices with intrinsic superparamagnetic properties can be obtained nucleating Fe-HA on assembling Collagen fibers; these new devices possess an increased osteogenic ability under the influence of a static magnetic field.

9:00 AM

(ICACC-S5-011-2015) Combining Soft and Hard Biomimetic Processing to Emulate Bone's Nano- and Micro-Structure (Invited)

B. Wingender[1]; P. Bradley[2]; J. Ruberti[2]; L. Gower*[1]; 1. University of Florida, USA; 2. Northeastern University, USA

Bone is a hierarchically structured organic-inorganic composite. At the nanostructural level, bone consists of collagen fibrils that are embedded with uniaxially-aligned nanocrystals of hydroxyapatite. At the microstructural level, bone has a lamellar architecture with each layer comprised of densely packed, aligned collagen fibrils. Gower's lab has developed a biomimetic mineralization process that enables the intrafibrillar mineralization to be achieved. Polyanionic additives (e.g. polyaspartate or osteopontin) are used to sequester ions/clusters which phase separate into nanodroplets/particles of a hydrated amorphous mineral precursor. These polymer-induced liquid-precursor (PILP) droplets infiltrate into the interstices of collagen fibrils, and upon solidification and crystallization, lead to an interpenetrating collagen-hydroxyapatite composite that emulates bone's nanostructure. Ruberti's lab has developed 'molecular crowding' techniques that lead to highly aligned, dense collagen scaffolds. We are now combining our soft and hard biomimetic processing techniques to collectively synthesize lamellar composites that emulate bone's hierarchical structure at the nano- and micro-structural levels. Our long-range goal is to build biomimetic bone composites that are both load-bearing and bioresorbable, to yield the next generation bone substitute.

9:20 AM

(ICACC-S5-012-2015) Synthesis of hollow silica flowers and titania nano-flowers for biomedical applications (Invited)

S. Chen[2]; N. Hanagata[2]; J. Wu[3]; A. Osaka*[1]; 1. Okayama University, Japan; 2. National Institute for Materials Science, Japan; 3. Zhejiang University, China

Ceramic nano-flowers (NF) are advantageous due to their large surface area as well as better handling than nano-particles. This presentation introduces two for biomedical uses, such as titania and hollow silica nano-flowers because of their biological advantages: e.g., sol-gel titania was characterized with anti-blood clotting properties while silica and silicate glasses exhibited significance effects in osteoconductivity due to gene stimulation by dissolved silicate fragments. Flower-like materials are characterized with nano-scale sub-units whose assembly provides some synergy effects in biological performance over their sub-units. Silica hollow flowers were synthesized with semi-globular apatite agglomerates as the template deposited on Ca-containing chitosan-silicate (3-glycidoxypropyl trimethoxysilane) hybrid films developed on a sheet of poly(dimethylsiloxane). Titania flowers were prepared from simple H2O2 oxidation of pure titanium under the presence of organic agents like hexamethylenetetramine and HNO3. Those two ceramic NFs were characterized with their microstructure dependent on the preparation conditions, in vitro bioactivity, and the silica NFs exhibited good proliferation of osteoblast MC3T3-E1 cells and sustained release behavior for BMP-2.

9:40 AM

(ICACC-S5-013-2015) Rare Earth Nanoceria in Wound healing (Invited)

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

Wound healing is a major challenge and specially, chronic non-healing diabetic wounds possess a significant clinical problem. Diabetic wounds have been shown to have increased inflammation during the wound healing response. Our Previous data indicated that Cerium Oxide Nanoparticles (CNPs) treatment can improve healing in skin wounds of mice. It is shown that CNPs induce wound healing by controlling the reactive oxygen species in the cell. However, the exact mechanisms by CNPs improve wound repair is not clear. We hypothesize that CNPs can attenuate inflammation in diabetic fibroblast by altering various gene expressions. As an example, in the diabetic wounds, MiR-146a was significantly down-regulated in diabetic fibroblast compared to non-diabetic fibroblast. Dermal fibroblasts treated with CNPs significantly up-regulated the gene expression in both diabetic fibroblast and non-diabetic fibroblast. These findings explore the mechanisms of CNPs on wound repair on cellular level.

10:20 AM

(ICACC-S5-014-2015) Potential of Bioactive Glass as Synthetic Scaffolds in the Repair of Structural Bone Defects (Invited)

M. N. Rahaman*[1]; L. F. Bonewald[2]; S. Bal[3]; W. Huang[4]; 1. Missouri University of Science & Technology, USA; 2. University of Missouri-Kansas City, USA; 3. University of Missouri-Columbia, USA; 4. Tongji University, China

The repair of large defects in structural bone, such as segmental defects in the long bones of the limbs, remains a challenging clinical problem. Bioactive glass has attractive properties as a scaffold material for structural bone repair but its mechanical reliability in vivo is a concern. Recent reports have shown the ability to create silicate and borate-based bioactive glass scaffolds by robotic deposition which have with compressive strength comparable to human cortical bone and the capacity of the scaffolds to heal osseous defects in a non-loaded rodent calvarial defect model. When implanted in critical size segmental defects in rat femurs or rabbit tibiae, those strong porous scaffolds integrated with bone and healed the defects. The potential of using bioactive glass as synthetic scaffolds for healing large defects in structural bone will be discussed.

10:40 AM

(ICACC-S5-015-2015) Emulsion Electrospun Scaffolds Made by Negative Voltage Electrospinning for Controlled Release of Growth Factors

Q. Zhao*[1]; M. Wang[1]; 1. The University of Hong Kong, Hong Kong

High positive voltages are used in conventional emulsion electrospinning when incorporating growth factors (GFs) in tissue engineering scaffolds. Undesirable GF release behaviors are observed for such scaffolds. High negative voltages may be applied in emulsion electrospinning for incorporating GFs bearing positive charges such as basic fibroblast growth factor (bFGF), minimizing possible electrospinning damages to GF and modulating GF release behavior. In this study, negative voltage emulsion electrospinning was investigated, forming bFGF-incorporated nanofibrous scaffolds. A bFGF-containing aqueous solution was firstly mixed with a PLGA solution (1:10) to form an emulsion. The emulsion was subjected to either positive voltage (10, 15, or 20 KV) or negative voltage (-10, -15, or -20 KV) for electrospinning. The scaffolds formed were characterized using various techniques. Nanofibers in all scaffolds exhibited core-shell structures, with the bFGF-containing water phase forming the fiber core. The scaffolds carried electrical charges and the intensity and retention time of the charges increased with an increase in applied voltage. In vitro scaffold degradation tests and in vitro bFGF release tests were conducted separately for scaffolds. Results showed the bFGF release behavior was modulated by negative voltage electrospinning, indicating the charge effect.

11:00 AM

(ICACC-S5-016-2015) Functionally Graded Ceramics for Next-generation Dental Restorations (Invited)

Y. Zhang*[1]; 1. New York University College of Dentistry, USA

Ceramics have become increasingly popular as restorative materials because of their superior esthetics, inertness and biocompatibility. However, ceramics are brittle and subject to premature failure. Yttria stabilized tetragonal zirconia polycrystal (Y-TZP) has become the predominant material choice for all-ceramic restorations due to its outstanding mechanical properties. However, clinical studies have revealed that while zirconia frameworks are very fracture resistant, chipping and delamination of the porcelain veneer are frequent problems. Recent advances in materials science have demonstrated that veneer failure may be substantially mitigated by controlled gradients of elastic modulus within the restoration layer. Using glass powders of various compositions and commercial fine-grained zirconia materials, we have successfully fabricated functionally graded structures with low modulus glass-ceramics at both the top and bottom surfaces, sandwiching a high modulus, strong zirconia interior. Our studies have demonstrated that such graded structures exhibit significantly higher resistance to fatigue sliding-contact and flexural damage relative to porcelain-veneered and monolithic Y-TZP. This is because the gradient diminishes the intensity of tensile stresses and simultaneously transfers these stresses from the layer surface into the interior, away from the source of failure-inducing surface flaws.

11:20 AM

(ICACC-S5-017-2015) In Vitro Degradation and Conversion of Melt-derived Bioactive Glass Microfibers in Simulated Body Fluid

M. N. Rahaman*[1]; X. Liu[1]; D. E. Day[1]; 1. Missouri University of Science & Technology, USA

Melt-derived borate bioactive glass microfibers are showing a considerable capacity to heal chronic soft tissue wounds in humans and animals. In the present study, the degradation and conversion of borate (13-93B3) and silicate (45S5) bioactive glass microfibers (diameter = 0.2–5 microns) to hydroxyapatite (HA) were evaluated in vitro as a function of immersion time in a simulated body fluid (SBF) at 37 °C. While the 13-93B3 microfibers converted more rapidly to amorphous calcium phosphate (ACP) than the 45S5 microfibers, the ACP formed on the 13-93B3 fibers crystallized more slowly to HA than the ACP formed on the 45S5 fibers. Doping the borate 13-93B3 glass with biologically relevant metal ions (less than 1–2 wt% CuO; ZnO; Fe_2O_3; SrO) had little effect on the degradation of the parent glass microfibers and their conversion to ACP but it inhibited the crystallization of the ACP to HA. The consequences of the results in the design of bioactive glasses for optimum healing of soft tissue wounds and bone will be discussed.

11:40 AM

(ICACC-S5-018-2015) Thick gelatin/hydroxyapatite composite coatings produced by electrophoretic deposition

F. Frajkorová*[1]; B. Ferrari[2]; J. Sedláček[3]; E. Molero[2]; 1. Faculty of Chemistry, Brno University of Technology, Czech Republic, Czech Republic; 2. Instituto de Ceramica y Vidrio, CSIC, Spain; 3. Institute of Inorganic Chemistry, Slovak Academy of Sciences, Slovakia

Biodegradable polymers and bioactive ceramics are being combined in a variety of novel materials for tissue engineering scaffolds. Recently, the use of biopolymers that gelate on cooling has received a great attention to the production of coatings. In this work, the incorporating of hydroxyapatite (HA) into a gelatin coating on stainless steel substrate using colloidal processing technology was developed. Titania (Ti) buffer layer prepared by dip coating was inserted to improve the bonding strength between gelatin/HA layer and stainless steel substrate. To obtain the homogeneous Ti layers the dip coating process was optimized in term of the suspension viscosity and the withdrawal rate. The suspensions composed of 1 vol% of HA and three different additions of gelatin were formulated with a focus on rheological properties for codeposition of both phases by electrophoretic deposition (EPD). EPD process was performed at ambient and also at the gelling temperature of the suspension. While at the room temperature not electrophoretic growth of the layers was observed, the thermal gelation of gelatin promotes the growth of the homogeneous coating. The coatings were characterised by scanning electron microscope (SEM) and thermogravimetric analysis (TGA). To evaluate in vitro bioactivity the samples were immersed in simulated body fluid (SBF).

S7: 9th International Symposium on Nanostructured Materials: Innovative Synthesis and Processing of Nanostructured, Nanocomposite and Hybrid Functional Materials for Energy, Health and Sustainability

Solution Synthesis, Functionalization and Assembly of Metal Oxide Nano-materials I

Room: Coquina Salon B

Session Chairs: Mualla Oner, Yldz Technical University; Federico Rosei, INRS

8:30 AM

(ICACC-S7-033-2015) Complex shape and composition metals and metal-in-ceramic nano-composites (Invited)

G. Westin*[1]; 1. Uppsala University, Sweden

Low cost synthesis of highly complex nano-materials is a requisite for practical application in many areas including renewable energy. Solution based processing routes provide means for synthesis of for multi-phase, multi-elemental nano-materials in one or few steps and are therefore of great interest for practical exploitation. Here we describe low cost, salt based solution routes to nano-composites consisting of metal-in-ceramic nano-composites. The metal inclusions are of a wide range of metals and alloys being in controllable sizes in the range 1-10 nm. They can be formed in a variety of ceramic matrixes with loadings up to over 80%. The effects of thermal treatment and processing of various alloyed nano-particles will be described as well as applications of these nano-composites as thin and ultra-thin films on flat or nano-structured substrates or highly porous foams and sponges. Further, low cost, salt based solution routes to nano-structured metal and alloys will be described. The process has been used for synthesis of mainly Co, Ni and Cu based metals, but here further developments are described. The materials are prepared as thin- and ultra-thin films on flat or nano-structured substrates as well as highly porous sponges. Various properties will be described.

9:00 AM

(ICACC-S7-034-2015) High current multilayered and nanocomposite $YBa_2Cu_3O_7$ superconductor thin films and coated conductors derived from chemical solutions (Invited)

X. Obradors*[1]; T. Puig[1]; M. Coll[1]; V. R. Vlad[2]; J. Gázquez[1]; A. Palau[1]; S. Ricart[1]; C. F. Sánchez[1]; A. Calleja[2]; M. Vilardell[2]; X. Granados[1]; P. Cayado[1]; C. Pop[1]; L. Soler[1]; V. Rouco[1]; F. Vallés[1]; B. Villarejo[1]; R. Guzmán[1]; A. Queraltó[1]; A. Perez del Pino[1]; 1. ICMAB - CSIC, Spain; 2. Oxolutia, Spain

In this presentation we will review first recent advances in understanding the processing paths towards epitaxial buffer layers and YBCO film grown from Trifluoroacetate metallorganic precursors. Ink Jet Printing has allowed obtaining sharp oxide multilayers with accurate control of the interfacial nanostructure. Comparison of furnace thermal annealing with RTA and laser heating has allowed clarified the epitaxial growth mechanisms while in-situ resistance measurements of YBCO film growth has allowed investigating the influence of processing parameters on nucleation, growth and oxygenation. On the other hand, we will report on YBCO nanocomposite growth (BaZrO3, Y2O3, BaCeO3 and Ba2(Ta,Y)O6 second phase nanoparticles) obtained using complex metallorganic solutions or preparing colloidal solutions. Highly effective novel vortex pinning mechanisms, coupling superconducting pairing to lattice strain has been proposed. The nanoscale strain is evaluated from X-ray diffraction line broadening while HRTEM and STEM investigation evidences a ramified shape of nanostrained regions. Our work stresses that CSD is a bottom-up approach with a strong potential to create cost-effectively novel complex functional materials with outstanding performances.

9:30 AM

(ICACC-S7-035-2015) Microwave assisted synthesis of monodispersed Y2O3 and Y2O3:Eu3+ particles

A. M. Khachatourian[1]; C. Vogt[3]; F. Golestanifard[2]; H. Sarpoolaky[2]; M. S. Toprak*[1]; 1. KTH Royal Institute of Technology, Sweden; 2. Iran University of Science and Technology (IUST), Iran (the Islamic Republic of); 3. KTH Royal Institute of Technology, Sweden

Monodisperse spherical Y2O3 and Y2O3:Eu3+ particles with particle size between 100 nm and 350 nm were successfully prepared by microwave assisted urea precipitation method followed by a thermoechemical treatment. Fast microwave heating, controlled decomposition of urea and burst nucleation of metal ions in aqueous solution led to the formation of non-aggregated spherical particles with monodispersed size. The particle size and monodispersity was controlled by adjusting the urea / metal ions ratio, the metal ions concentration, the reaction time and the temperature. X-ray diffraction (XRD) analysis indicated that the as prepared particles have the Y(OH)CO3 composition, which converted to highly crystalline cubic Y2O3 after calcination at temperatures above 600°C. The calcined Y2O3 particles preserved the spherical morphology of the as prepared particles and were exhibiting a polycrystalline structure. The size of the crystallites increased from ~8 nm to ~37 nm with the increase in the calcination temperature from 500°C to 900°C. Furthermore, Y2O3:Eu3+ particles had the morphology and polycrystalline structure of the Y2O3 host particles. Photoluminescence (PL) analysis of Y2O3:Eu3+ particles showed a strong red emission peak at 613 nm of Eu3+ ions under UV excitation (235nm). All these characteristics are critical in many application areas such as display devices, fluorescent lamps and bioimaging.

Solution Synthesis, Functionalization and Assembly of Metal Oxide Nano-materials II

Room: Coquina Salon B

Session Chairs: Gunnar Westin, Uppsala University; Xavier Obradors, ICMAB - CSIC

10:30 AM

(ICACC-S7-036-2015) The role of surfaces and interfaces in multifunctional materials (Invited)

F. Rosei*[1]; 1. INRS, Canada

The bottom–up approach is considered a potential alternative for low cost manufacturing of nanostructured materials. It is based on the concept of self–assembly of nanostructures on a substrate, and is emerging as an alternative paradigm for traditional top down fabrication used in the semiconductor industry. We demonstrate various strategies to control nanostructure assembly (both organic and inorganic) at the nanoscale. Depending on the specific material system under investigation, we developed various approaches, which include, in particular: (i) control of size and luminescence properties of semiconductor nanostructures, synthesized by reactive laser ablation; (ii) we developed new experimental tools and comparison with simulations are presented to gain atomic scale insight into the surface processes that govern nucleation, growth and assembly; (iii) we devised new strategies for synthesizing multifunctional materials for electronics and photovoltaics; (iv) we developed a nanoscale surface modification which allows to control cell growth [19], including antibacterial effects.

11:00 AM

(ICACC-S7-037-2015) Aqueous chemical solution deposition of $LuFeO_3$ ultra high-k films

S. Gielis*[1]; M. Ivanov[2]; N. Peys[1]; J. van den Ham[1]; N. Pavlovic[1]; P. Robaeys[3]; M. Nesladek[3]; J. Banys[2]; A. Hardy[1]; M. K. Van Bael[1]; 1. Hasselt University - IMEC vzw (div. IMOMEC), Belgium; 2. Vilnius University, Lithuania; 3. Hasselt University - IMEC vzw (div. IMOMEC), Belgium

Ultra high-k materials are very attractive for the use in applications such as thin-film capacitors. Due to their extremely high dielectric constant (k>10000), they can possibly be used for the miniaturization of the energy storage devices and the increase of their energy density. For orthorhombic $LuFeO_3$ (LFO) ceramics, a dielectric constant of 10000 (frequency ≤ 1kHz) has been reported at room temperature. Nevertheless, research on the deposition of LFO thin films, indispensable for the thin film applications envisaged, is still very scarce, especially when it comes to wet chemical deposition. We prepared a stable aqueous Lu/Fe multimetal ion precursor by mixing citrato complex-based Fe and Lu solutions in the desired ratio. Prior to thin film deposition, the thermal decomposition of the precursor and the phase formation process towards bulk, crystalline LFO were studied. It was shown that phase-pure orthorhombic LFO could be formed at 900°C, indicating a high temperature requirement. These insights, combined with a profound study on the key deposition and process parameters, were successfully employed for the formation of orthorhombic LFO thin films on Si_3N_4. Impedance spectroscopy analyses did confirm their associated ultra high dielectric constant (> 10000) at room temperature for frequencies lower than or equal to 1kHz.

11:20 AM

(ICACC-S7-038-2015) Preparation and characterization of hydroxyapatite reinforced polyhydroxyalkanoate composites (Invited)

M. Oner*[1]; B. Ilhan[1]; T. Bekat[1]; 1. Chemical Engineering Department, Turkey

In recent decades, hydroxyapatite (HAP)-reinforced biopolyester composites have received considerable attention because of their potential approach to the bone treatment, guided tissue regeneration, tissue engineering scaffolds and drug delivery. Biodegradable polymers, especially thermoplastic polyesters such as microbial polyhydroxyalkanoates (PHAs), have become a focus of interest in this field. The aim of this study was to fabricate and characterize polyhydroxyalkanoates/nano-hydroxyapatite composites. Hydroxyapatite (HAP) crystals were produced by wet chemical synthesis under controlled temperature, pH, and atmospheric conditions. The obtained crystals were used to produce composites. PHA/HAP nanocomposites were prepared by melt mixing method. A twin screw extruder (Rondol Microlab, England) with L/D ratio 20 was used for preparing nanocomposites. Materials at different production conditions were analysed using various techniques. Processing parameters of the composite can be optimized through production trials which lead to good mechanical properties.

11:50 AM

(ICACC-S7-039-2015) Nanostructured titanium surfaces with Sr doped calcium phosphate coating

S. Issa*[1]; P. Dubot[1]; L. Jordan[2]; 1. * MCMC, Institut de Chimie et Des Matériaux Paris-Est, ICMPE-CNRS, France; 2. Université Paris 7, France

Functionalization of implants surface is important for their osseointegration. Titanium is widely used in dental implantology and surface modifications are sometimes needed to improve osteoblasts colonization. Calcium phosphate coatings are known to enhance implant osseointegration but some problems concerning effectiveness and durability can happene. The objective is to study the adsorption of strontium doped calcium phosphate compounds onto the nanostructured TiO2 surface. Titania nanotubes arrays were fabricated by anodisation of titanium samples in a fluoride-based solution. Calcium phosphate and Sr doped CaP have been adsorbed using pulsed electrodeposition. Surface nanostructuration allows getting specific reactive sites on TiO2 surfaces that don't exist on passive oxide layer. SEM microscopy reveals that the most reactive sites on nanostructured surfaces were the nanotube edges where the deposits mostly grow. Ca cations were substituted by Sr due to the positive properties of Sr in enhancing bone formation. Results by XPS and Infrared Spectroscopy revealed that for pure CaP coating, the deposited CaP phase was amorphous apatite-like compound (ACP). In the case of Sr2+ doped CaP, we observe Ca1-xSrxHPO4 compound that is more resorbable than ACP. Such depositions could be considered as controlled bioactive coatings on titnium surface that have positive effects when used for new implant design.

S8: 9th International Symposium on Advanced Processing and Manufacturing Technologies for Structural and Multifunctional Materials and Systems (APMT9)

Integration and Joining

Room: Coquina Salon A

Session Chairs: Kevin Ewsuk, Sandia National Laboratories; Michael Halbig, NASA Glenn Research Center

8:30 AM

(ICACC-S8-045-2015) Characterization and Modeling of Glass Chemistry-Structure-Property Relations To Develop Advanced Glass Composite Joining Materials (Invited)

K. Ewsuk*[1]; 1. Sandia National Laboratories, USA

Glass composites are being developed as new, improved performance and reliability joining/sealing materials (e.g., in glass-to-metal seals and solid oxide fuel cells). Particle-filled glass composites (FGCs) offer enhanced manufacturability, performance, and reliability by combining the inherent processability of a glass with the physical stability, design flexibility, and enhanced performance and stability of a crystalline solid. FGC seal materials are being developed, employing: 1) experimentally-validated molecular modeling to understand and control glass chemistry and structure; and 2) property and process modeling to optimize FGC design, manufacturability, and performance. This paper will introduce FGC sealing materials, and review the coupled modeling and experimental work underway to understand and control critical glass chemistry-structure relationships that will ultimately be employed to optimize interface bonding and joining. 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.

9:00 AM

(ICACC-S8-046-2015) Challenges in the Development of High Temperature Joining and Characterization Technologies for SiC-Based Materials

M. C. Halbig*[1]; M. Singh[2]; J. Lang[1]; 1. NASA Glenn Research Center, USA; 2. Ohio Aerospace Institute, USA

As interest in fiber reinforced SiC-based composite materials continues to grow due to advancements in their properties, new integration technologies with increased capabilities will be critically needed. Although manufacturability and strength capabilities of these materials are improved, there remain limitations in the sizes and shapes that can be fabricated. Advanced joining technologies are enabling for the fabrication of large and complex shaped silicon carbide-based ceramic and ceramic matrix composite components to be utilized in high temperature extreme environment applications. In this presentation, a number of joining methods will be discussed along with each one's benefits and shortcomings. New strategies will be presented for improving the high temperature stability, strength, and ease of manufacturing. Characterization approaches were pursued that provide an understanding of the processing-microstructure-property relations. Microstructural analysis of the joining interface was conducted using scanning and transmission electron microscopes to identify phases and evaluate bond quality. Stress analyses and results from mechanical test methods will be presented. The need for new standardized joint tests will be emphasized.

9:20 AM

(ICACC-S8-047-2015) Microstructural Observation of Interfaces in Diffusion Bonded Silicon Carbide Ceramics by TEM

H. Tsuda*[1]; S. Mori[1]; M. C. Halbig[2]; M. Singh[3]; R. Asthana[4]; 1. Osaka Prefecture University, Japan; 2. NASA, USA; 3. Ohio Aerospace Institute, USA; 4. University of Wisconsin-Stout, USA

Silicon carbide (SiC) is an enabling material for high-temperature structural and extreme environment applications due to its excellent high-temperature mechanical properties, oxidation resistance, and thermal stability. Advanced cost effective joining and integration approaches for SiC-based materials have been developed to fabricate large and complex shaped components and reported in the literature. However, in most cases, detailed microstructural observation of the bonded area by Transmission Electron Microscopy (TEM) has not been carried out due to difficulty in preparing TEM samples. Recently, we have successfully prepared TEM samples from diffusion bonded regions in CVD-SiC and fiber bonded ceramic (SA-Tyrannohex) by Focused Ion Beam (FIB) system. In these systems, PVD-Ti, metallic Ti foil, and Mo-B foil were used as joint interlayers. Detailed analysis of interfaces using SEM, elemental analysis, and TEM were conducted. In this presentation, microstructural details from different interlayer materials were investigated. The effects of microstructures of individual Ti interlayers and fiber orientation of SA-THX on the resulting phases, and the effects of thermal expansion coefficient of various phases on the formation of microcracks will also be discussed.

9:40 AM

(ICACC-S8-048-2015) Joining of alumina using a alumina-zirconia interlayer under low mechanical pressure

M. Hotta*[1]; N. Kondo[1]; H. Kita[1]; T. Ohji[1]; 1. National Institute of Advanced Industrial Science and Technology (AIST), Japan

Alumina was joined with insert material of alumina-20wt% zirconia composite at a temperature of 1700oC for a holding time of 8 h at a mechanical pressure of 0.05 MPa. Some zirconia grains at insert were incorporated into alumina grains at the parent alumina in the border between joint and parent regions. Flexural strengths of the alumina joint had 234 and 138 MPa at room temperature and 1200oC, respectively, which were similar to those of the parent alumina.

10:20 AM

(ICACC-S8-049-2015) Principles of formation and manufacturing of corrosion resistant boride-based coatings

E. Medvedovski*[1]; 1. Endurance Technologies Inc., Canada

Possibilities and principles of the formation of corrosion resistant non-oxide based coatings on the metallic substrates are considered and formulated. In particular, the compounds based on the metals of IVb – VIb and VIII groups and the non-metallic elements of IIIa - Va groups with strong covalent bonds and high thermodynamic potential should be considered. The principles of the coating formation through gas phase deposition and thermal diffusion of boron into metallic substrate and consequent metal boride formation are reported. The boride-based thermal diffusion coatings obtained demonstrated a high level of corrosion resistance in the high temperature/ high pressure water steam and in acidic environments simulating oil field and petrochemical service conditions.

10:40 AM

(ICACC-S8-050-2015) Development of a Plasma Arc Welding Technique for joining SiC based Composites

J. Watts*[1]; G. Hilmas[1]; W. G. Fahrenholtz[1]; S. Landwehr[2]; 1. Missouri University of Science and 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.

11:00 AM

(ICACC-S8-051-2015) Laser Alloying and Dispersing Processes for the Modification of Ceramic Surfaces

M. Rohde*[1]; H. Seifert[1]; 1. Karlsruhe Institut for Technology, Germany

Laser supported processes can be used to modify the electrical and thermal properties of ceramic substrates locally. These processes are characterised by a strong thermal interaction between the laser beam and the ceramic surface. During the dynamic melting process metal particles are introduced into the melt pool in order to modify the physical properties. The interface between the metal and the ceramic can be designed by using selected combinations of metal- and metal-oxide-powders and also by a thermal post-processing. The application of nano-particles during the laser-dispersing process resulted in completely different characteristics of the micro-structure and the electrical properties compared to the conventional metal powders. The micron sized metal particles are embedded within the ceramic matrix as particle agglomerates or as distinct metal phase the nano-particle phase covers the grain boundaries of the ceramics leading to network of nano-scaled electrically conducting “wires”. The resulting electrical resistance of the laser tracks can be adjusted from semi-conducting to metallic behavior. The laser modification can be adapted for selective wetting of the ceramic surfaces at high temperatures in order to utilize the metalized surface in a laser supported joining process.

11:20 AM

(ICACC-S8-052-2015) New Combined Method of MPS and FEM for Simulating Friction Stir Processing

H. Serizawa*[1]; F. Miyasaka[2]; 1. Osaka University, Japan; 2. Osaka University, Japan

Friction Stir Processing (FSP) has been developed as one of the surface modification techniques and various surface composites such as Al-SiC, Mg-SiC and so on, were reported. Most of these researches mainly discussed about the microstructural changes and the residual stress produced by FPS has not been studied precisely. It seems to be caused by the unclearness of plastic flow effect on the residual stress. In addition, the heat generated in FSP affects the residual stress. Recently, the moving particle semi-implicit (MPS) method has been applied for simulating the flow behavior in friction stir welding (FSW). However, only a small region can be modelled by MPS due to the computational time. On the other hand, finite element method (FEM) is one of the most powerful tools for predicting the residual stress produced in various thermal processes. So, in this research, as a first step for estimating the residual stress in FSP, a new combined method of MPS and FEM was developed and its applicability was examined through the butt joining process of Al plates by FSW. The computational results suggested that the transient temperature distributions could be precisely predicted by using this combined method. Also, it was revealed that the longitudinal plastic strain near the tool was not governed by only the temperature distributions and the influence of plastic flow should be taken into account.

11:40 AM

(ICACC-S8-053-2015) Laser-Induced Periodic Surface Structures (LIPSS) on Ceramic Materials Using Ultrashort Pulse Filamentation

K. D. Behler*[1]; A. Valenzuela[2]; C. Munson[3]; M. Weidman[4]; M. Richardson[4]; 1. U.S. Army Research Laboratory, USA; 2. U.S. Army Research Laboratory, USA; 3. U.S. Army Research Laboratory, USA; 4. University of Central Florida, USA

Laser-induced filaments can ablate solid material at distances greater than that practicably achieved through linear optics. Advances in solid-state lasers allow for delivery of light pulses with sub-picosecond duration and intensities that access the nonlinear optics regime. In this non-linear regime, filaments are formed where the focusing of air molecules is balanced by defocusing of free electrons, creating a propagating intense laser pulse over great distances. Short- and ultrashort-pulsed lasers have been shown to produce sub-micron laser-induced periodic surface structures (LIPSS) on metals, polymers and semiconductors. These parallel ridges typically have peak-to-peak distances slightly less than the incident laser wavelength. It has been observed that multi-scale structures can be imparted upon these surfaces as well as ceramic materials. In this study we present results showing filament generated LIPSS on boron carbide, silicon carbide, tungsten carbide and other ceramics materials and compare them to more well-known and studied polymers (PVC and PC) and metals (aluminum, copper, steel and titanium). The ceramics tested required many more pulses for a detectable ablation region and demonstrated two regimes of LIPSS with high spatial frequency (~200 nm) in the central, crater region and low spatial frequency (~650 nm) in the outlying, rim region.

S9: Porous Ceramics: Novel Developments and Applications

Modeling and Properties of Porous Ceramics

Room: Coquina Salon H

Session Chair: Sawao Honda, Nagoya Institute of Technology

8:30 AM

(ICACC-S9-024-2015) Modeling of Freeze-Cast Alumina Structures Using Solidification Theory and the Two-Phase Stefan Problem

S. M. Miller*[1]; X. Xiao[2]; K. Faber[1]; 1. Northwestern University, USA; 2. Argonne National Laboratory, USA

Freeze casting is a popular and straightforward method to create porous ceramics. However, fabrication parameters to tailor pore network properties are not well defined. In this study pore network characteristics such as pore size, specific surface area, and tortuosity determined using X-ray computed tomography scans of water- and camphene-based freeze-cast alumina samples are presented. The pore network characteristics are linked to temporally- and spatially-dependent temperature profiles recorded during solidification. These profiles are compared to calculated values using the two-phase Stefan problem for directional solidification of a warm liquid from a cold surface as a function of temperature processing parameters. Additionally, freezing front velocity measurements and the resulting pore network characteristics are compared to traditional solidification theory of pure and binary materials for both lamellar and dendritic microstructures. Results indicate that freeze casting is satisfactorily modeled using a basis of solidification theory and the two-phase Stefan problem. Additionally, inclusion of the physical and thermal properties of the ceramic particles in the slurry is found to be unnecessary, as directional freeze casting can be described using theories formulated for solidification of the dispersion medium alone.

8:50 AM

(ICACC-S9-025-2015) A Numerical Study of a High Temperature Thermal Energy Storage System Using Graphite Foam Infiltrated with MgCl2

A. Gyekenyesi*[1]; A. Wroblewski[2]; 1. Ohio Aerospace Institute, USA; 2. Cleveland State University, USA

Because phase change materials (PCM) utilized for thermal energy storage (TES) have notoriously low thermal conductivities, TES systems based only on stand-alone PCMs may experience large internal thermal gradients and slow reaction times making them impractical for most applications. To improve the conductivity, porous high thermal conductivity graphite foams are infiltrated with a PCM. For high temperature applications, such as Concentrated Solar Power (CSP) Systems, the PCM is typically a molten salt. Here, finite element analyses (FEA) are conducted to study graphite foam/MgCl2 latent heat TES systems. The numerical simulations allow for the comparisons of a stand-alone PCM and a graphite foam/PCM composite system. The results show the history of the melt-fronts as well as the overall energy stored during an 8 hour charge period. Based on both 2D and 3D FEA results, the increased conductivity due to the graphite foam allows the composite to attain overall energy absorptions that are an order of magnitude greater than for the PCM alone.

9:10 AM

(ICACC-S9-026-2015) Effect of Grain Size on the Properties of Porous Alumina

S. Honda*[1]; G. Grabarski[2]; Y. Daiko[1]; S. Hashimoto[1]; B. NAIT-ALI[2]; D. Smith[2]; Y. Iwamoto[1]; 1. Nagoya Institute of Technology, Japan; 2. Center Europeen de la Ceramique, France

To study the effect of grain size on properties of porous ceramics, the porous alumina were fabricated using the different starting grain size by pulse electric current sintering. These porous alumina could be sintered without the grain growth from starting grain size. Permeability, fracture strength and thermal conductivity of porous alumina with different porosity were measured, the thermal resistance of grain boundary was evaluated by temperature dependence of thermal conductivity. These properties of porous alumina were showed clearly dependence to the grain size.

9:30 AM

(ICACC-S9-027-2015) 2D and 3D periodic hybridmaterial structures made of ceramic building blocks

T. Fey*[1]; P. Greil[1]; M. Götz[1]; B. Diepold[1]; 1. Friedrich-Alexander Universität Erlangen (FAU), Germany

Cellular structures like foams exhibit a heterogeneous, non-periodic structure with a non-uniform cell and strut size distribution. Generative processing techniques like 3D-direct printing of cellular ceramic structures can lead to nearly mono-modular distributed cell and strut sizes but with lack of mechanical properties due to a layer wise build up technique. As reported [1], [2] the 2D-arrangement of alumina cubes to periodic cellular structure formation was optimized by vibration assistance for uniform packing with different unit cell symmetry (cubic, monocline). Vacuum infiltration with epoxy resin of these periodic structures generates ceramic-polymer composites with a crack deflecting behavior in compact tension test. Different crystalline 3D-structures were build up with a novel pick-and-placing technique with auto arrangement of the building blocks following a predefined CAD-file and epoxy infiltration. Besides mech. properties of the hybrid material the positioning and repeat accuracy for different structures was determined.

9:50 AM

(ICACC-S9-028-2015) Evaluation of Thermal Protection System (TPS) Properties of Carbon Foam

S. C. Sharma*[1]; T. S. Lakshmanan[1]; V. K. Vaidyan[2]; 1. Vikram Sarabhai Space Centre, India; 2. University of Kerala, India

Carbon foam offers a low density thermal protection system (TPS) for high heat flux regions of a reusable launch vehicle (RLV). Sacrificial substrate method was used to process the carbon foams of varying density in the range of 0.110 to 0.232 g/cc. Foams were carbonized at 1000 0C and 1900 0C. TPS behavior of the carbon foam was evaluated in terms of its thermostructural integrity and its response to the designed heat flux profile. Thermal response was first computed for 10, 20 and 30 mm thick C-foam TPS panels of different density and thermal conductivity using Fourier heat conduction expression. Back-wall temperature of the TPS panels of equal thickness but of different density, varied within a narrow temperature range. However, TPS panels made of 1900 0C carbonized foam which showed appreciably (36%) more thermal conductivity as compared to 1000 0C carbonized foam, recorded noticeably higher back-wall temperature. Computed thermal response was subsequently validated using the Kinetic Heat Simulation test on the processed foams.

Mechanical Properties of Porous Ceramics

Room: Coquina Salon H
Session Chair: Abhaya Bakshi, Saint-Gobain

10:30 AM

(ICACC-S9-029-2015) Mechanical characterization of porous ceramics (Invited)

A. A. Shamkin*[1]; A. N. Levandovskiy[1]; J. W. Zimmermann[2]; 1. OOO Corning SNG, Russian Federation; 2. Corning Incorporated, USA

In this work elastic moduli prediction for porous ceramic using FEM is considered. Assuming material orthotropy all 9 independent elastic constants can be estimated for specific tomography based sample, which size should be big enough to demonstrate representative properties. Work also focuses on representative volume element (RVE) size determination in particular when initial sample is shape limited (thin ceramic honeycomb walls). The technique allows understanding mechanical response on porous media properties at microlevel. The response is hard to study experimentally. The comparison between modeled and experimentally measured values of Young's modulus for macrosamples shows good agreement for different porosity cordierite. The work demonstrates the capabilities of mechanical characterization of porous ceramics.

10:50 AM

(ICACC-S9-030-2015) Experimental verification of bending test on porous ceramics

S. Honda*[1]; K. Yasuda[2]; H. Kita[3]; M. Takahashi[4]; Y. Takahashi[5]; J. Tatami[6]; S. Tanaka[7]; H. Muto[8]; S. Yamamoto[9]; 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. Yokohama National University, Japan; 7. Nagaoka Unversity of Technology, Japan; 8. Toyohashi University of Technology, Japan; 9. Asuzac, Japan

Round Robin test was carried out for bending strength of porous ceramics by nine organizations in Japan. For each bending type (three or four point) were carefully carried out using porous ceramics with different components and microstructure. The stiffness of testing machine and symmetry of applied loading was checked each testing. The difference of average bending strength in the same testing condition among the organization performed bending test was several MPa. The average fracture strength of three point bending test was larger than that of four point test. The average fracture location of samples after three point bending test was almost underneath of upper loading point, however, that of four point test tend to dislocated to the center of upper span due to the misaligned of specimen. Most of the samples showed elastic deformation and followed by brittle fracture, however, one sample which had large pore size showed non-linear stress-strain curve before fracture. This work was supported in part by METI, Japan..

11:20 AM

(ICACC-S9-031-2015) 3 dimensional observation of porous ceramics by x-ray computer tomography

S. Tanaka*[1]; K. Yasuda[2]; H. Kita[3]; M. Takahashi[4]; Y. Takahashi[5]; J. Tatami[6]; S. Honda[7]; H. Muto[8]; S. Yamamoto[9]; 1. Nagaoka University of Technology, Japan; 2. Tokyo Tech, Japan; 3. Nagoya Univ., Japan; 4. Ehime Univ., Japan; 5. Noritake Co. Ltd., Japan; 6. Yokohama Nat'l Univ., Japan; 7. Nagoya Tech., Japan; 8. Toyohashi Univ. Tech., Japan; 9. Asuzac, Japan

Porous ceramics with micro pores have been applied for functional materials such as electrolyte for fuel cell, gas or liquid filter, and heat insulator, etc. The properties are (strongly) influenced by the internal structure including the amount, shape and network of pores, and the wall structure between pores. However, the influence of internal structure on distribution of mechanical property has not been understood well. The objective of this study is to observe the internal structures of various porous ceramics by micro-focus x-ray computer tomography (μ-CT) and other method, and to discuss their influence of internal structures on distributions of mechanical property. Porous Al2O3 ceramics and porous NiO/YSZ ceramics were used. Porous Al2O3 ceramics have a continuous porosity of 30 vol% and the pore sizes varied in the range from several to several hundred micro meter. The samples were cut in small pieces with 1mm x 1mm x 1mm for observation by the μ-CT. The 3D networks of pores were observed clearly in various porous ceramics by the μ-CT. Particularly, structures consisting of large pores and necking structures of particles with several hundred micro meter were observed in the samples, which showed a non-linear deformation before brittle fracture in stress-strain curve. This work was supported in part by METI, Japan.

11:40 AM

(ICACC-S9-032-2015) Strength Distribution of Various Porous Ceramics

K. Yasuda*[1]; H. KITA[2]; M. TAKAHASHI[3]; Y. TAKAHASHI[4]; J. TATAMI[5]; S. TANAKA[6]; S. Honda[7]; H. MUTO[8]; S. YAMAMOTO[9]; 1. Tokyo Institute of Technology, Japan; 2. Nagoya Univ., Japan; 3. Ehime Univ., Japan; 4. Noritake Company Limited, Japan; 5. Yokohama Nat'l Univ., Japan; 6. Nagaoka Univ.Tech., Japan; 7. Nagoya Tech., Japan; 8. Toyohashi Univ. Tech., Japan; 9. Asuzac, Japan

Porous ceramics have been widely used in engineering applications, for example, electrodes in solid oxide fuel cells, exhaust gas filters in automobiles, catalysis carriers in chemical plants, filtration films for water purification, and humidity sensors etc. However, little attention has been paid to strength reliability of the porous ceramics although its failure may cause serious lack of function of advanced engineering systems. To characterize the strength distribution, a round robin tests were conducted by 9 organizations in Japan. The samples include 4 types of porous alumina and 4 types of NiO/YSZ electrodes, and they were tested by 3- point and 4- point bending, respectively. During bending tests, most of samples showed elastic deformation, and followed by brittle fracture, however, one alumina sample had a non-linear deformation before brittle fracture. With and without non-linearity in stress/strain curves, the bending strength data can be analyzed by Weibull distribution. The onset stress for non-linearity in stress/strain curve was tested by Weibull distribution as well. This work was supported in part by METI, Japan.

S10: Virtual Materials (Computational) Design and Ceramic Genome

Ceramic Genome and Modeling of Structure and Property II

Room: Coquina Salon C

Session Chairs: Hans Seifert, Karlsruhe Institute of Technology; Leonhard Mayrhofer, Fraunhofer IWM

8:30 AM

(ICACC-S10-008-2015) Systematics of Grain Boundary Transitions and Diagrams (Invited)

N. Zhou[1]; J. Luo*[1]; 1. UCSD, USA

Phase transitions are one of the most important physical phenomena in materials science. Phase diagrams are one of the most useful materials design tools. In classical thermodynamics, a variety of binary phase diagrams can be constructed systematically using simple regular solution models. In this study, we utilize the Wynblatt-Chatain multilayer grain boundary adsorption model to systematically map out various grain boundary transitions. In particular, a normalized segregation strength is defined, which is the key parameter that controls the grain boundary transition behaviors. The effects of misorientation can also be represented to the first order of approximation. Grain boundary "phase" (complexion) diagrams are systematically constructed as a function of three normalized parameters. Furthermore, we refine the model to consider the effects of interfacial disorder. These grain boundary diagrams, as an analogy to bulk phase diagrams, can be used as tools to accelerate materials design in the spirit of the Materials Genome initiative.

9:00 AM

(ICACC-S10-009-2015) Theoretical prediction of the extremely low thermal conductivity of Mg2Al4Si5O18 with the rattler-in-cage crystal structure

Y. Li*[1]; J. Wang[1]; 1. Institute of Metal Research, China

One of the challenges in developing thermal insulation material addresses on searching novel lightweight low thermal conductivity

ceramic without rare-earth element. Mg2Al4Si5O18 engaged our attention for its very low density and its special rattler-in-cage crystal structure. First-principle calculations were performed to predict mechanical and lattice thermal conductivity of hexagonal and orthorhombic phases of Mg2Al4Si5O18. The thermal conductivities of both Mg2Al4Si5O18 phases are lower than the most rare-earth containing silicates, phosphates, zirconates. According to Debye approximation and Slack model, the lattice thermal conductivity at room temperature is about 2.6 W/m.K at room temperature. The high temperature limit of thermal conductivity is as low as 1.3 W/m.K. This work suggests that Mg2Al4Si5O18 is a promising aluminosilicate with extremely low thermal conductivity.

9:20 AM

(ICACC-S10-010-2015) Doping of CeO_2 as a tunable buffer layer for coated superconductors: A DFT study of mechanical and electronic properties

D. E. Vanpoucke*[1]; S. Cottenier[1]; P. Bultinck[2]; V. Van Speybroeck[1]; I. Van Driessche[2]; 1. Ghent University, Belgium; 2. Ghent University, Belgium

Ceramic superconductors (CSC) are, just like roof tiles and flower pots, brittle by nature. To fabricate flexible superconducting wires, they are grown as a layered architecture on a metal substrate. Buffer layers are used to prevent metal diffusion and improve lattice matching between the CSC and the substrate. CeO_2 is one example of such a buffer layer. To prevent the formation of micro cracks during the fabrication process, doping of CeO_2 has been suggested. In this work, we study the influence of dopants (both tetravalent and aliovalent) on the mechanical and structural properties of CeO_2 by means of density functional theory (DFT). For tetravalent dopants, a clearly different behavior is found for the group IVa and IVb elements – with the latter acting as stable dopants (i.e. leading to uniform doping) and the former as unstable. This difference is linked to the dopant electronic structure. For all dopants, an inverse relation is observed between the bulk modulus and thermal expansion coefficient. The presence of charge compensating oxygen vacancies is found to modify the dopant influence significantly, often counteracting it. Oxygen vacancies lead to non-linear lattice parameter modifications and strongly reduce the material's bulk modulus. Based on the study of these idealized systems, new dopants are suggested for applications.

9:40 AM

(ICACC-S10-011-2015) Thermodynamic investigation of the perovskite electrical conductivity

S. Darvish[1]; M. Mora[1]; Y. Zhong*[1]; 1. Florida International University, USA

Many efforts have been done to understand the fundamental mechanism determining the electrical conductivity of perovskites. In the current work, electrical conductivity of strontium doped lanthanum manganite were measured in-situ by interface 1000TM potentiostat from room temperature to 1100 °C in different atmospheres. Computational thermodynamic calculation on the quantitative defect chemistry prediction based on CALPHAD approach by using La-Sr-Mn-O database will be done and comparing with experimental data. The effect of stoichiometry, P(O2), temperature, etc. to the conductivity will be mapped out.

10:20 AM

(ICACC-S10-012-2015) Atomistic modeling of 2D and 3D nanocrystalline graphenic carbons: Structure and elastic properties (Invited)

B. Farbos[2]; J. Da Costa[3]; P. Weisbecker[1]; C. Germain[3]; H. E. Fischer[4]; G. L. Vignoles[2]; J. Leyssale*[1]; 1. CNRS, France; 2. Univ. Bordeaux, France; 3. Univ. Bordeaux, France; 4. Institut Laue Langevin, France

The exceptional properties - mechanical, thermal or electonic - of graphite and graphene are well-known. However many carbons or nanocarbons, deriving from these ideal structures have crystallite sizes of a few nm only. It is often the case of carbons obtained by chemical vapor deposition (CVD) - either 2D like graphenes or 3D like pyrolytic carbons (PyC) found in composite materials. The properties of such materials having a ratio of crystallites over defects close to one are poorly known. In this talk we will present the Image Guided Atomistic Reconstruction (IGAR) method we have recently developed to produce realistic atomistic representations of such materials. This method, based on a combination of high resolution TEM (HR-TEM) image processing and molecular dynamics simulation, will be applied to different highly textured pyrocarbons (PyC). We will show that the obtained models are both able to render correctly the nanoscale structure (diffraction data in real and reciprocal spaces) and texture (HR-TEM images) of the different materials. We will then discuss the relationship existing between the nano-structure/texture of the materials and their elastic properties obtained by tensile test simulations. These results will be compared to those obtained for polycrystalline graphene models obtained in a similar way.

10:50 AM

(ICACC-S10-013-2015) Theoretical prediction of magnetic state of the new MAX phases: (Ti1/3Cr2/3)3AlC2

J. Wang*[1]; J. Wang[1]; 1. Institute of Metal Research, China

Mn+1AXn (MAX) phases are a group of nanolaminated ceramics with layered structure containing Mn+1Xn rigid layers which are intercalated by A-group atomic layers. Magnetic MAX phases attracted extensive attentions for both of the potential applications and fundamental sciences in spintronics due to the relationship between magnetism and nanolaminated crystal structure. Previous theoretical and experimental researches showed that magnetism mainly appeared in the Cr or Mn containing MAX phases. In this work, we studied the magnetic state of the newly discovered MAX phases (Ti1/3Cr2/3)3AlC2 by using the first-principles method. This compound contains two types of transition metal elements, Ti and Cr, and has ordered occupations of Ti in the 2a and Cr in the 4f Wyckoff positions of a M3AlC2 lattice. The strong correlation among the Ti or Cr 3d electrons is taken into account from the Hubbard-like correction (GGA+U). The magnetic orders of the moments of the Ti and Cr atoms are considered to involve three states: ferromagnetic (FM), antiferromagnetic (AFM) and nonmagnetic (NM). The theoretical results show that magnetism of (Ti1/3Cr2/3)3AlC2 is totally originated from the Cr 3d electrons. FM configuration is the ground state of (Ti1/3Cr2/3)3AlC2. The predicated magnetic state of (Ti1/3Cr2/3)3AlC2 is validated by the experimental measurement.

11:10 AM

(ICACC-S10-014-2015) Elastic and Electronic Properties of Ti2Al(CxN1-x) Solid Solutions

S. R. Aryal*[1]; L. Ouyang[1]; W. Ching[2]; 1. Tennessee State Universirty, USA; 2. University of Missouri Kansas City, USA

Elastic stiffness coefficients and mechanical bulk properties of Ti2Al(CxN1-x) solid solutions are calculated using ab initio methods on 4 x 4 x 1 supercell models. Changes in elastic properties are nonlinear and linear elastic anisotropy increases with increasing C content. Elastic constant C11 is significantly larger than C33 for all x. C11 is minimum at x = 0.56 whereas C33 appears decreasing relatively smoothly with increasing C concentration. For larger N concentration, shear anisotropy is small with C44 larger than C66 and it decreases with increasing C resulting in no shear anisotropy at x = 0.69. A sharp rise in shear anisotropy results in beyond x = 0.69 with C66 larger than C44. The bulk modulus K displays a steady decrease from nitride (x = 0) to carbide (x = 1) as expected. Decrease in shear modulus G flattens out at x = 0.62 whereas Young's modulus E decreases almost linearly with x. The reasons for such complicated variations in mechanical properties of Ti2Al(CxN1-x) solid solutions will be explained in terms of difference in the electronic structure and bonding between carbides and nitrides in complex MAX phase compounds.

11:30 AM

(ICACC-S10-015-2015) Numerical simulation of mixed conductive/radiative heat transfer in highly porous materials

G. L. Vignoles*[1]; 1. University Bordeaux, France

Heat transfer properties from ambient up to extremely high temperatures are a key feature of advanced thermal protection and thermal exchange materials – like ceramic foams or fibrous media. Because of their porous nature, heat transfer occurs by conduction in solids and by radiation trough pores. The precise knowledge of the thermal behavior of these materials in these conditions is an issue. Based on a novel computational simulation tool for heat transfer in such materials, effective conduction and diffusion tensors may be obtained in large 3D blocks as produced e.g. by X-ray CMT or image synthesis. The application to ideal and real material images (fibrous media) is described and discussed, principally in terms of the influence of the diffusion/radiation ratio on the effective (large-scale) diffusivity tensor; we show that some ideal media may exhibit a somewhat "pathological" behavior as compared to real media.

S11: Advanced Materials and Innovative Processing Ideas for the Production Root Technology

New Concept & Emerging Technology

Room: Coquina Salon E

Session Chairs: Jochen Schneider, RWTH Aachen Univeristy; Byung-Koog Jang, National Institute for Materials Science (NIMS)

8:30 AM

(ICACC-S11-001-2015) Quantum mechanically guided materials design approaches for industrial coating applications (Invited)

J. M. Schneider*[1]; 1. RWTH Aachen Univeristy, Germany

The combinatorial approach, combining combinatorial materials synthesis of thin film composition-spreads with high-throughput property characterization has proven to be a powerful tool to delineate composition-structure-property relationships, and hence to efficiently identify composition windows with enhanced properties. These results are relevant for the design of coating and bulk materials. Furthermore, and most importantly for materials design, theoretical models and hypotheses can be critically appraised. The combination of modern electronic structure calculations with the highly efficient combinatorial thin film composition-spread method constitutes an effective tool for knowledge based materials design of hard and wear resistant coatings. Besides the elastic property and phase stability also the interaction of the coating with the ambient can be described based on quantum mechanics. In the talk predictions of the interaction of coated tool surfaces with gases contained in the atmosphere as well as materials to be formed are discussed. Coatings used for forming operations of Al and Polymers are investigated and initial experimental data characterizing these interactions will be discussed.

9:00 AM

(ICACC-S11-002-2015) Removal of ceramic binder system using a hybrid supercritical fluid-assisted extraction technique

S. O. Matthews*[1]; J. E. Lancien[1]; J. Matthews[1]; 1. SCF Processing Ltd, Ireland

Supercritical fluid technology has been successfully used to extrude and injection mold ceramic parts. These parts can be porous or solid on-demand, and higher levels of ceramic loadings can be achieved when compared to conventional techniques. One of the rate limiting steps in ceramic injection molding is the removal of the binder system. Conventional techniques such as solvent dissolution, aqueous dissolution and thermal pyrolysis are used as the industry standard. These techniques all have their limitations such as long debind time, debind surface defects and the handling and/or the environmental hazard of the waste product. Supercritical fluid extraction has been successfully used to remove the binder system with reduced debind times. As this type of extraction is from the outside-in part defects are reduced. This paper will introduce a new hybrid technique that combines solvent dissolution with supercritical extraction. Examples will be given to highlight that it is now possible to debind in significantly shorter times when compared to the other extraction techniques, whilst maintaining good part quality. This technique has the added advantage that the binder system can be reused and recycled.

9:20 AM

(ICACC-S11-003-2015) Thermal Properties and Fabrication of ZrO2 Based Composites by Rare-Earth Oxides Addition

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

Partially stabilized zirconia of ZrO2-4mol%Y2O3 exhibits outstanding properties, such as low thermal conductivity, low Young's modulus, and a relatively high thermal expansion coefficient. This work describes the influence of Gd2O3 addition on the thermal conductivity of ZrO2-4mol% Y2O3 ceramics is fabricated by spark plasma sintering. The additions of Gd2O3 in the ZrO2 matrix are 0, 1, 3 and 5 mol%. Sintering was conducted at 1100C or 1500C for 20 min under pressure of 30MPa under a vacuum of 10-2 Pa. The thermal diffusivity and thermal conductivity of sintered YSZ decreased with increasing Gd2O3 addition. In addition, we report the formation and thermal properties of the fluorite-pyrochlore composite structure in the La2(ZrxCe1−x)2O7 system. This composite structure is composed of coarse Ce-rich fluorite and fine Zr-rich pyrochlore grains. The low thermal conductivity of La2(ZrxCe1−x)2O7 is attributed to phonon scattering by phase boundaries or a change in thermal conductivity of each constituent phase.

Shaping & Thermal Process

Room: Coquina Salon E

Session Chairs: Tadachika Nakayama, Nagaoka University of Technology; Kyoung Il Moon, KITECH

10:20 AM

(ICACC-S11-004-2015) Creation of ceramics micro components and fine coated layers by using nanoparticles paste stereolithography and thermal spraying (Invited)

S. Kirihara*[1]; 1. Osaka University, Japan

Nanoparticles paste stereolithography had been developed to realize 3D ceramics modeling. The slurry pastes of photosensitive liquid resins with ceramics particles dispersions were spread on a glass substrate, and micro patterns were drown by ultra violet laser scanning to create cross sectional solid layers. After these layers stacking, formed composite precursors were dewaxed and sintered to obtain full ceramics components with micro geometric patterns. Subsequently, nanoparticles paste thermal spraying had been developed to realize 2D ceramics coating without structural defects. Thixotropic resin paste of rheological flows with ceramics nanoparticles were sputtered by compressed air jet, and formed micro mists blew into the arc plasma. Through introductions of various ceramics pastes, functionally graded layers including designed compositional and structural distributions were created successfully. These ceramics micro structures and functionally graded layers will be applied to micro devices and large components.

10:50 AM

(ICACC-S11-005-2015) Laminated Structure is One of the Most Important Industry Root Technologies in Ceramics

K. Yasuda*[1]; T. NAKAYAMA[2]; S. TANAKA[2]; 1. Tokyo Institute of Technology, Japan; 2. Nagaoka University of Technology, Japan

Laminated structure is widely used in ceramic products, such as thin film/substrate systems, multilayer capacitors and inductors, gas sensors, thermal barrier coating in gas turbine engines, piezoelectric actuators, and ceramic coating for cutting tools etc. In addition to this, laminated composites exhibits higher toughness, compared with monolithic ceramics. Processing for the laminated structures is automatic, clean, and easy, so that it must be one of the most important industry root technologies in ceramics. However, due to combination with different materials, the difference in thermal expansion coefficient may cause internal stress of each layer during temperature change in processing and/or in service. In this presentation, we discuss how to estimate the internal stress of the laminated structure and to guarantee reliability of the structure. This work was partly supported by scientific research funds from JSPS (A: 24246108, C: 25420706).

11:10 AM

(ICACC-S11-006-2015) Modeling of fluid flow in tape casting of thin ceramics: analytical approaches and numerical investigations

M. Jabbari*[1]; J. H. Hattel[1]; 1. Technical University of Denmark, Denmark

Tape casting has been used for many years to produce thin layers of ceramics that can be used as single layers or can be stacked and laminated into multilayered structures. Many startup products such as multilayered inductors, multilayered varistors, piezoelectrics, ceramic fuel cells and lithium ion battery components are dependent upon tape casting technology and this has increased the interest for doing fluid flow analysis to control and enhance the quality of the final tapes. CFD analysis of the ceramic slurries during tape casting is an efficient mean to elucidate the physical parameters crucial to the process. A review of the development of the tape casting process with particular focus on modelling the material flow is presented and in this context the current state of the art in this field is examined and future potential discussed.

11:30 AM

(ICACC-S11-007-2015) Carbonization of Polyacrylonitrile (PAN) studied by TGA-GC-MS and TGA-FTIR

E. Post*[1]; 1. NETZSCH Geraetebau GmbH, Germany

Polyacrylonitrile (PAN) is a semi-crystalline polymer with the formula (C3H3N)n. Under "normal" melting conditions it decomposes before melting though it belongs to thermoplastics. Due to its versatile properties it has a large range of applications, e.g. textiles, membranes etc. It is also used to produce high quality carbon fibers by pyrolysis of the PAN. During this pyrolysis process several toxic gaseous products can occur. With a TGA-GC-MS instrument the pyrolysis of PAN was investigated and the heavier molecules/gaseous products were identified. The GC-MS measurements were performed in quasi-continuous mode and cryo mode. The quasi-continuous mode allows a better time correlation of the GC-MS data to the TGA results. The cryo mode offers the higher GC separation and better identification of the different evolved substances. The smaller gaseous molecules as HCN, NH3 etc. were easier identified by FTIR, which was also coupled to a TGA apparatus. The pyrolysis of PAN was investigated by TGA-GC-MS and TGA-FTIR. The evolved gases will be shown versus weight loss and temperature at different heating rates.

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

Structural-property Relationships of Existing Systems III

Room: Ponce DeLeon
Session Chair: Luke Walker, GT Advanced Technology

8:30 AM

(ICACC-S12-047-2015) Effects of Sintering Temperature and Cooling Rate on Microstructure and Mechanical Properties of Spark Plasma Sintered ZrB2-SiC

F. Gai*[1]; L. S. Walker[1]; E. L. Corral[1]; 1. The University of Arizona, USA

ZrB2-SiC is an ultra-high temperature ceramic (UHTC) composite that has potential applications as leading edge materials in hypersonic vehicles. Spark Plasma Sintering (SPS) offers significant processing advantages, which allows ZrB2-SiC powder compacts to be densified at a lower sintering temperature with a shorter hold time compare to conventional sintering techniques. In order to produce high quality UHTCs with SPS, effect of sintering temperature and cooling rate on structures and properties must be known. We investigate influences of sintering temperature and cooling rate for SPS ZrB2-SiC sintered at temperatures of 1750°C to 2000°C and cooling rates from 10°C/minute to 210°C/minute. Hardness of specimens is obtained by Vickers hardness micro-indentation. Flexural strength and fracture toughness of selected specimens cooled at increasing cooling rate are obtained using an Instron mechanical tester; and x-ray diffraction method is used to investigate the residual stress within these specimens. Grain size of specimens is characterized from scanning electron microscopy (SEM) images. Among selected sintering temperatures and cooling rates in this experiment, we are able to optimize mechanical properties when the specimen is sintered at 1800°C and cooled at 100°C/minute.

8:50 AM

(ICACC-S12-048-2015) Evaluation of oxidation resistance of ZrB2-SiC-ZrC ceramics at temperatures above 1973K

Y. Kubota*[1]; H. Tanaka[1]; Y. Kogo[1]; Y. Arai[2]; K. Goto[3]; 1. Tokyo University of Science, Japan; 2. University of Tokyo, Japan; 3. Institute of Space and Astronautical Science, Japan

The oxidation behavior of four different compositions of ZrB2-16vol%SiC-ZrC, which is one of the candidate UHTCs, was examined so as to identify the optimal composition for oxidation resistance at temperatures above 1973K. The compositions of these materials were 20vol%-ZrB2 and 64vol%-ZrC in Material A, 34vol%-ZrB2 and 50vol%-ZrC in Material B, 50vol%-ZrB2 and 34vol%-ZrC in Material C, and 64vol%-ZrB2 and 20vol%-ZrC in Material D. The oxidation resistance of these materials was evaluated by the measurement of thickness of oxide layers. The thickness was measured by observation using SEM-EDX after heat-treatments at temperature above 1927K for 10min. SiO2-rich layer, SiO2+ZrO2 layer and ZrO2-rich layer were observed in each material. The total thickness of these oxide layers in Material C and D was 100~110μm, which was lower than that in Material A and B; 140~150μm. The total thickness of the oxide layer decreased with decreasing amount of ZrO2 because of its high oxygen permeability. The amount of ZrO2 formed after oxidation in Material C and D was less than that in Material A and B. It is because ZrC, which was contained larger amount in Material A and B, is expected more actively oxidized than ZrB2 at temperature above 1923K. Consequently, ZrB2-SiC-ZrC indicated high oxygen resistance when the volume percent of ZrC was lower than that of ZrB2.

9:10 AM

(ICACC-S12-049-2015) Densification and Mechanical Properties of Direct Current Sintered High Purity ZrB2 Ultrahigh Temperature Ceramics

D. Pham*[1]; E. L. Corral[1]; 1. University of Arizona, USA

Zirconium diboride (ZrB2) is an ultra-high temperature ceramic (UHTC) with properties that make it ideal for use as thermal protection system (TPS) materials. Direct current sintering (DCS) of UHTCs is advantageous as it allows densification at lower temperatures with total densification times under 30 minutes. Various processing methods and sintering additives are used to make fully dense ZrB2, however, the effects on the mechanical behavior of highly pure ZrB2 using (DCS) needs further investigation. This study focuses on understanding the mechanical properties of ZrB2 after DCS as a function of powder processing and oxygen reducing agents to produce high density and low oxygen impurity ZrB2. Powder is processed with minor additions of carbon or boron carbide (<1wt%) to produce high purity ceramics with smaller grain size and higher Vicker's hardness and flexural strength compared to nominally processed ZrB2. High purity ZrB2 (B4C additions) has exceptional flexural strength (~630MPa) with a fracture toughness of 3.2MPa*m1/2 at a grain size of 3.5μm.

9:30 AM

(ICACC-S12-050-2015) Thermo-Chemical Compatibility of Hafnium Diboride with Alumina and Yttrium Aluminum Garnet at 1500°C in Air

S. Winder[1]; M. Ruggles-Wrenn*[1]; T. Parthasarathy[2]; T. Key[2]; C. Carney[3]; 1. Air Force Institute of Technology, USA; 2. UES Inc., USA; 3. Air Force Research Laboratory, USA

Due to its high thermal conductivity and oxidation resistance, both at very high temperatures, hafnium diboride (HfB_2) is being considered for use as leading edge material on sharp-bodied reentry vehicles. In structural applications HfB_2 is likely to operate at elevated temperature in proximity to other refractory materials. The thermo-chemical compatibility of HfB_2 with $Y_3Al_5O_{12}$ (YAG) and Al_2O_3 was examined in multiple contact combinations during furnace heat treatment exposures at 1500°C in air. It was found that alumina was stable with HfB_2 in all experiments, while YAG was unstable except when separated from HfB_2 using alumina as interlayer. The reaction products were characterized using optical, SEM, XRD and EDX. The results will be presented along with a discussion of possible mechanisms.

Novel Processing Methods

Room: Ponce DeLeon
Session Chair: Lin Zhang, Brown University

10:20 AM

(ICACC-S12-051-2015) Processing of ZrB2-MoSi2 Granules for Dual Architectural Toughening of ZrB2-Based Ceramics

L. Pienti*[1]; F. Monteverde[1]; L. Silvestroni[1]; D. Sciti[1]; R. J. Grohsmeyer[2]; G. Hilmas[2]; W. G. Fahrenholtz[2]; 1. CNR - ISTEC, Italy; 2. Missouri University of Science and Technology, USA

ZrB2-based composites possess high strength, but low fracture toughness. Common efforts to toughen borides include incorporation of elongated reinforcing phases (SiC chopped fibers, SiC whiskers) or in-situ development of SiC platelet-reinforced materials, but often the improvement of fracture toughness is accompanied by a decrease of strength, due to a change in the defect population. In this frame, a new approach to engineer microstructure and consequently improve the elevated temperature mechanical properties of ZrB2-based composites based on a dual composite (DC) architecture was studied. DC ceramic architectures were produced with 100-300 μm-sized granules of ZrB2 with an engineered quantity of MoSi2, uniformly dispersed in a ZrB2 matrix containing a different volume fraction of MoSi2. ZrB2 particle size and MoSi2 quantity were chosen to optimize the mechanical property relationship of the individual ZrB2-MoSi2 composites in the matrix and granules. This work focuses on the processing of ZrB2-MoSi2-based granules, both through freeze granulation and high solids-loaded polymer extrusion, from the preparation of the suspensions to the microstructural analysis of the granules. At the same time, the monolithic matrix ZrB2-MoSi2 was microstructurally and thermo-mechanically characterized.

10:40 AM

(ICACC-S12-052-2015) Effect of Processing Conditions, $MoSi_2$ Content, and ZrB_2 Particle Size on the Microstructure and Mechanical Properties of ZrB_2-$MoSi_2$ Particulate Composites

R. J. Grohsmeyer*[1]; G. Hilmas[1]; W. G. Fahrenholtz[1]; L. Pienti[2]; F. Monteverde[2]; L. Silvestroni[2]; D. Sciti[2]; 1. Missouri University of Science and Technology, USA; 2. CNR-ISTEC, Italy

Molybdenum disilicide ($MoSi_2$) is an effective sintering aid, oxidation inhibitor, and high-temperature strengthener of zirconium diboride (ZrB_2)-based composites for structural applications at temperatures up to 1500°C in air. Because of these attributes and its high-temperature ductility, $MoSi_2$ is being investigated for use with ZrB_2 in dual composite (DC) architectures. In designing such multiscale architectures, mechanical property information for each subcomposite is critical. This research has found that high-temperature mechanical properties are very dependent on specific densification parameters and resulting microstructure. However, the multiple reactions that occur during sintering are not fully understood. The extensive decomposition of $MoSi_2$, limited solid solubility of Mo in the ZrB_2 phase, and the formation of other phases strongly affect HT strength, plasticity and elastic modulus. These issues are dependent on the maximum hot pressing temperature and isothermal hold duration at T_{max}. In the interest of finer property control during densification, a systematic study of 12 monolithic ZrB_2-$MoSi_2$ particulate composites of varying $MoSi_2$ content and ZrB_2 particle size has been conducted, relating densification characteristics, resultant microstructural trends and phases, and mechanical properties at RT and 1500°C.

11:00 AM

(ICACC-S12-053-2015) Ultra High Temperature Ceramics as Conductive Die Materials for High Pressure and High Temperature Direct Current/Spark Plasma Sintering

L. S. Walker*[1]; 1. GT Advanced Technology, USA

Direct Current Sintering (DCS) also known as spark plasma sintering (SPS) has allowed the development of revolutionary material systems with nano-crystalline grain structures and non-equilibrium phases but operating pressures are generally limited to ~100 MPa using isotropic graphite tooling. Co-bonded WC tooling has been adopted for high pressure applications up to and beyond 500 MPa but is limited in temperature to <800°C due to creep and deformation. Ultra High Temperature Ceramics (UHTCs) represent an ideal tooling material due to their unique material properties of high strength, creep resistance and electrical conductivity. This study involves the UHTC material selection for high temperature tooling, processing and densification optimization of the tooling materials, near net shape densification of tooling components, and testing of the final tooling assembly to densify nanocystalline materials at high temperatures and pressures.

11:20 AM

(ICACC-S12-054-2015) Influence of Current Density on Specimen Temperature and Grain Growth Mechanisms of Spark Plasma Sintered ZrB2-SiC

F. Gai*[1]; W. R. Pinc[1]; E. L. Corral[1]; 1. The University of Arizona, USA

ZrB2-SiC is an ultra-high temperature ceramic (UHTC) composite that has potential applications as leading edge materials in hypersonic vehicles due to its excellent stability at elevated temperature. Conventional sintering techniques with radiant heating method are both time consuming and energy intensive. Spark plasma sintering uses joule heating method and generates heat internally from the pulse DC current, which allows ZrB2-SiC powder compacts to be densified rapidly and at a relatively low sintering temperature. In order to investigate effect of current density on grain growth, ZrB2-SiC bulk specimens are reheated with increasing current density to allow grain growth. Specimen temperatures are monitored directly with an optical pyrometer aiming at the side of each specimen and grain size characterized with scanning electron microscopy. Experiment results show when specimen temperature is kept same, grain size of specimens increases with increasing current density.

S13: International Symposium on Advanced Ceramics and Composites for Sustainable Nuclear Energy and Fusion Energy

Radiation Effects in Ceramics and Composites

Room: Tomoka B

Session Chairs: William Weber, University of Tennessee; Sosuke Kondo, Kyoto University

8:30 AM

(ICACC-S13-043-2015) Irradiation-induced microstructural evolution and swelling of 3C-SiC (Invited)

J. Kai*[1]; Y. Lin[1]; C. Ho[2]; C. Ku[3]; 1. National Tsing-Hua University, Taiwan; 2. National Tsing-Hua University, Taiwan; 3. National Synchrotron Radiation Research Center, Taiwan

Cubic silicon carbide (3C-SiC) is a promising structural and cladding material, and is used in fusion reactors and advanced fission reactors due to its attractive mechanical and thermal properties. Even though several studies have reported the irradiation-induced microstructural evolution and swelling of SiC, the contribution of defects to the swelling of irradiated 3C-SiC is less understood. In this study, an ion-irradiated single crystal 3C–SiC under fluences of up to 20 dpa at 400-1350°C was examined using synchrotron based X-ray diffraction and high resolution transmission electron microscopy. Interstitial clusters, dislocation loops, Frank loops, stacking fault loops, and voids in 3C-SiC were investigated. The high resolution TEM results show that small loops gradually form inside a cluster along {111} with increasing temperature, and develop into Frank loops with an added atomic layer along {111} at 1000°C. Interplanar spacing information of single crystal SiC was obtained from synchrotron XRD radial scan measurements. Irradiation-induced volume swelling at 400-1350°C was measured, and the anisotropic (a=b<c) swelling behavior of SiC was confirmed. In addition, humps on the right side of SiC(002) were observed, which suggested that C+/Si+-Si<100> and/or C+/Si+-C<100> dumbbells gave rise to diffuse scattering.

9:00 AM

(ICACC-S13-044-2015) TEM characterization of advanced SiC fibers irradiated to high dose at relatively low temperature

K. Ozawa*[1]; T. Taguchi[2]; H. Kurotaki[1]; T. Nozawa[1]; H. Tanigawa[1]; 1. Japan Atomic Energy Agency, Japan; 2. Japan Atomic Energy Agency, Japan

A silicon carbide (SiC) matrix composite is a promising candidate for nuclear fusion energy applications. So far, irradiation behavior of high purity and near stoichiometric SiC fiber after irradiation have been assumed to be same as that of β-SiC monolith. However, the assumption recently and unfortunately appeared not to be correct in the case of high dose irradiation at lower temperature. In Kondo's work, the fiber degradation might be associated with the migration of carbon atoms from carbon packets along with grain boundaries to interstitial positions, but the detail knowledge is still limited. This study mainly aims to investigate microstructural changes of the fiber after high dose and relatively low temperatures. Unidirectional CVI SiC/SiC minicomposites reinforced with Hi-Nicalon Type-S and Tyranno-SA3 was irradiated to 30-100 dpa at 600°C at DuET and TIARA facility. After the preparation by FIB and ion-mill processing, the specimen is observed by a conventional FE-TEM (JEM2100F) with EELS analysis. After irradiation at 600°C to 100 dpa, shrinkage of Hi-Nicalon Type-S was confirmed but the degree was smaller than the case for Kondo's work. Degradation mechanism will be discussed in this presentation together with detail results including TEM observation and EELS analysis.

9:20 AM

(ICACC-S13-045-2015) A Quantitative Analysis to Determine the Irradiation Temperature Range and Distribution from Passive SiC Temperature Monitors

A. A. Campbell*[1]; Y. Katoh[1]; L. L. Snead[1]; 1. Oak Ridge National Laboratory, USA

Irradiation temperature is a critical measurement for scientific understanding of materials behavior, and for reactor safety and licensing. Active instrumentation provides real-time measurement but can be cost and space prohibitive, while passive monitors are easier to implement but the results do not provide any insight to the temperature history. Materials irradiations in the flux trap facility at the High Flux Isotope Reactor at Oak Ridge National Laboratory often rely on passive monitoring using silicon carbide temperature monitors (TM). The common exercise of determining the irradiation temperature involves fitting a set of straight lines to the length change versus temperature data extracted from the thermal expansion measurements of the TM. A problem with such a method is the windows used for the linear fits can be subjective due to the temperature distribution within the TM. A new quantitative method has been developed that uses non-linear regression curve fitting to determine the irradiation temperature range from the coefficient of thermal expansion versus temperature of the TM; removing the subjective nature of the conventional method. Deconvolution of the thermal expansion curve provides additional understanding of the temperature profile of the TM. The new analysis methodology and the deconvoluted temperature profile will be presented.

9:40 AM

(ICACC-S13-046-2015) Radiation effects on defect mobility in SiC (Invited)

I. Szlufarska*[1]; D. Morgan[1]; H. Jiang[1]; J. Deng[1]; H. Ko[1]; B. Leng[1]; K. Sridharan[1]; L. He[1]; P. Voyles[1]; 1. University of Wisconsin, USA

Radiation can lead to a number of undesirable changes in SiC that are important for fission and fusion applications. Examples include radiation-induced swelling and creep, which have been attributed to the presence of small defect clusters. Existing models of these phenomena are limited by the lack of understanding of specific defects that form during irradiation. Using a combination of ab initio calculations, advanced structure search methods and accelerated molecular simulations we determined the ground state structures of a number of small interstitial defects in SiC, "invisible" to traditional transmission electron microscopy (TEM). These defects were found to be immobile up to 1200K. Surprisingly, we have also discovered using high resolution STEM that defect clusters can become mobile under electron irradiation. This is the first direct experimental observation of mobility of intrinsic defect clusters in a bulk material. We developed a model for radiation-induced diffusion, which predicts diffusion coefficients in excellent agreement with experimental values. In addition, we have investigated effects of radiation on transport of fission products (Ag) through polycrystalline SiC. By combining diffusion couple experiments and multi-scale modelling approaches we show that grain boundary diffusion and radiation-induced non-equilibrium defects both contribute significantly to accelerating of Ag transport in SiC.

10:30 AM

(ICACC-S13-047-2015) Ionization-Induced Self-Healing of Irradiation Damage in Silicon Carbide

W. J. Weber*[1]; R. Sachan[2]; O. H. Pakarinen[2]; M. L. Crespillo[1]; H. Xue[1]; Y. Zhang[2]; 1. University of Tennessee, USA; 2. Oak Ridge National Laboratory, USA

The interaction of energetic ions and primary knock-on atoms (PKAs) with solids results in energy loss to both atomic nuclei and electrons. At energies typical of PKAs in fusion or accelerator-based neutron environments and ions used to mimic fast neutron damage, electronic energy loss becomes dominate, creating local ionization along the PKA/ion path that can affect damage production from nuclear energy loss. We have employed experimental approaches and atomistic simulations to study the separate and combined effects of nuclear and electronic energy loss on radiation damage in SiC. The results demonstrate that electronic energy loss from PKAs and ions can induce self-healing in SiC at unexpectedly low values of electronic energy deposition, with a threshold value of 1.4 keV/nm at room temperature. This self-healing process becomes more efficient with increasing irradiation temperature and could extend the performance lifetime of SiC in fission and fusion reactor environments. The threshold PKA energies to activate these processes at room temperature are 750 keV and 850 keV for Si and C PKAs, respectively. These results have significant implications regarding the use of high-energy (MeV) ion beams and accelerator-based neutron sources for predicting the response of SiC and other materials to fast neutrons. This work was supported by the U.S. DOE, BES, MSED.

10:50 AM

(ICACC-S13-048-2015) Numerical Study on the Influence of Radiation Damage on Microstructural Evolution of a Binary Two–phase System

E. Hernandez*[1]; V. Tikare[2]; L. Wang[1]; 1. University of Michigan, USA; 2. Sandia National Laboratories, USA

Radiation induced point defects can lead to microstructural changes, which could affect the performance of a given material. This is of special interest for reactor structural materials, which need to perform reliably during reactor operations. Some of the microstructural changes of concern are grain size and distribution, and phase precipitation. One of the main mechanisms affecting this kinetic behavior is the enhanced diffusivity of the atomic components due to the presence and mobility of oversaturated point defects. We developed a hybrid model that is able to simulate how point defect fields influence microstructural changes in a binary system. Our numerical hybrid model couples deterministic–statistical methods to model the evolution of continuum and discrete order parameters. We show that differential diffusion of radiation–induced defects is sufficient to cause microstructural changes. Furthermore, we compare how radiation damage influences the precipitate growth rate due to enhanced diffusion to the defect sinks, i.e. grain/phase boundary. 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.

11:10 AM

(ICACC-S13-049-2015) Quantitative High-Resolution Depth Profiling of Helium in Nano-engineered SiC with Time-of-Flight Elastic Recoil Detection Analysis

C. Chen*[1]; Y. Zhang[2]; E. Fu[3]; Y. Wang[3]; M. L. Crespillo[1]; C. L. Fontana[2]; J. T. Graham[1]; S. C. Shannon[4]; W. J. Weber[1]; 1. University of Tennessee, USA; 2. Oak Ridge National Laboratory, USA; 3. Los Alamos National Laboratory, USA; 4. North Carolina State University, USA

The enhanced radiation-resistant behavior in nano-engineered SiC (NE-SiC) was reported previously. Its outstanding self-healing feature is attributed to the high density of stacking faults (SFs) that have strong impacts on defect migration and annihilation. In this work, the effects of thermal annealing and heavy ion irradiation on damage evolution in NE-SiC implanted with helium to fluences of 0.1 to 1 × 1016 ions/cm2 is studied by complementary techniques of transmission electron microscopy (TEM) and Time-of-Flight Elastic Recoil Detection Analysis (ToF ERDA). No bubbles of measurable size were resolved with TEM in the as implanted and thermally annealed (2 hours, 700 °C) NE-SiC. To simulate high-dose irradiation damage in a high temperature environment, the He-implanted SiC was subsequently irradiated with 9 MeV Au3+ at 700 °C to doses of 10 to 30 dpa, and helium bubble formation was observed for both helium implantation fluences. Although helium bubble formation was observed by TEM examination, the lack of details on the depth distribution limited the evaluation of the helium migration behavior in the NE-SiC. ToF-ERDA is used to quantify the implanted He concentration profile, the He depth distribution determined from the ERDA spectrum is compared with TEM results.

11:30 AM

(ICACC-S13-050-2015) On the Irradiation Stability of Alpha and Beta Silicon Carbide

L. L. Snead*[1]; Y. Katoh[1]; T. Koyanagi[1]; 1. Oak Ridge National Laboratory, USA

SiC is an irradiation-stable and high-performance ceramic with nuclear application spanning both structural and non-structural components. SiC has found practical application in nuclear systems for more than five decades, with first study and use as the micro-pressure vessel for gas-cooled reactor fuel particles. Later, SiC began development for larger component structural application, including development and understanding of SiC composite structdures. In the early stages of structural SiC development a discussion of the relative stability of the most commonly encountered hexagonal polymorph, α compared to the less common cubic β. From the limited data available, it was suggested that α was intrinsically unstable in comparison to β. Unfortunately, no systematic or confirmatory study of the relative stability of various crystallographic polymorphs of SiC has been carried out. The purpose of this paper is to discuss the relative irradiation stability of α-SiC and β-SiC based on the previous data, contrasting to known stability in related ceramic systems. Moreover, a set of data comparing single crystal α-SiC and β-SiC irradiated in the High Flux Isotope Reactor at ~80°C over a damage range from ~0.001 to several dpa will be presented to contrast with the earlier SiC data and behavior of anisotropic low-temperature swelling behavior in materials such as alumina and beryllium oxide.

FS2: Advanced Ceramic Materials and Processing for Photonics and Energy

Glasses I

Room: Tomoka A

Session Chairs: Daniel Milanese, Politecnico Torino; Valerio Pruneri, ICFO-The Institute of Photonic Sciences

8:30 AM

(ICACC-FS2-008-2015) Engineering Novel Infrared Glass Ceramics for Advanced Optical Solutions (Invited)

K. C. Richardson*[1]; C. Smith[1]; J. Musgraves[2]; P. Wachtel[2]; T. Mayer[3]; A. Swisher[3]; A. Pogrebnyakov[3]; D. Werner[3]; C. Rivero-Baleine[4]; 1. University of Central Florida, USA; 2. IRradiance Glass, Inc., USA; 3. The Pennsylvania State University, USA; 4. Lockheed Martin Corporation, USA

Advanced photonic devices require novel optical materials that serve specified optical function but also possess attributes which can be tailored to accommodate specific optical design, manufacturing or component/device integration constraints. Multi-component chalcogenide glass (ChG) materials have been developed which exhibit

broad spectral transparency with a range of compositionally tunable physical properties that be tuned to vary with composition, material microstructure and form. Specific tradeoffs that highlight the impact of material morphology and optical properties including transmission, loss and refractive index, are presented.

9:00 AM

(ICACC-FS2-009-2015) Ultrathin materials and nano-structuring for multifunctional transparent surfaces (Invited)

D. Janner[1]; M. Marchena[1]; D. S. Ghosh[1]; T. L. Chen[1]; I. Mannelli[1]; M. Rude[1]; V. Mkhitaryan[1]; A. Carrilero[1]; V. Pruneri*[1]; 1. ICFO-The Institute of Photonic Sciences, Spain

Ultrathin materials and nano-structuring are becoming essential for the functionalization of optical surfaces, including glass and crystalline materials. In the talk we will show how ultrathin metals can be exploited to create competitive transparent electrodes while graphene and phase change materials to modulate the optical response. Ultrathin metals can also be used to create nanostructured surfaces through mass scalable dewetting and etching techniques. We will also provide examples of applications enabled by these materials and techniques, including self-cleaning or easy-to-clean display screens, efficient indium-free light emitting diodes and solar cells and super-wetting surfaces for biology.

9:30 AM

(ICACC-FS2-010-2015) Laser performances of diode-pumped Yb:CaF2 optical ceramics obtained with an energy-efficient process (Invited)

M. Mortier*[1]; P. Aballea[1]; A. Suganuma[1]; P. Gredin[2]; F. Druon[3]; J. Hostalrich[3]; P. Georges[3]; 1. PSL Research University, France; 2. Université Pierre et Marie Curie, France; 3. Université Paris-Sud, France

In the last years, Yb:CaF2 crystal has been subjected to a growing interest for its potential as a near-infrared high average power amplifier allowing the use of efficient laser-diode pumping around 980 nm. Calcium fluoride gathers high physical properties (thermal conductivity, laser damage threshold) and attractive optical properties (broad absorption and emission bands) because of the specific organization of rare earths as hexameric clusters in the fluorite structure. These properties are promising for high power short pulses with high repetition rates laser operations or applications in widely tunable laser systems. We will report the preparation and laser properties exhibited by Yb:CaF2 laser ceramics synthesized from raw nanopowders obtained from a soft chemistry route[2]. The preparation of the green body uses a newly developed pressureless method[3]. The densification of the green body includes a single step of sintering in air involving no additional pressure assistance, and requiring moderated temperature (typically below 800°C). This entire process is energy extensive. The laser properties (tunability, gain and slope efficiency) of the obtained ceramics were then measured after polishing but without any surface treatment.

10:20 AM

(ICACC-FS2-011-2015) Light manipulation through surface waves in dielectric multilayers (Invited)

E. Descrovi*[1]; 1. politecnico di torino, Italy

An overview of recent results on light manipulation through surface modes on multilayers is provided. Main highlight is put on the confinement, diffraction and guidance of (Bloch Surface Waves) BSWs on photonic nanostructures and the near-field coupling of fluorescence into BSW modes. One-dimensional photonic crystals (1DPC) sustaining either TE or TM BSWs offer new opportunities for light management at the nanoscale. BSWs can be considered as the dielectric equivalent of Surface Plasmon for metals. Compared to SPPs, BSWs present some advantages, such as low losses, long propagation lengths, polarization and spectral tunability. BSW can be coupled on dielectric 1DPC with the help of either a coupling prism (e.g. in the Kretschmann configuration), an oil-immersion objective or a grating. When guidance is concerned, BSW can be confined on ridge waveguides having nanometric thickness, thanks to a dielectric loading mechanism analogous to the plasmonic case. The results presented in this work demonstrate the effectiveness of using BSW on 1DPCs as surface modes for delivering radiative energy to/from localized volumes in a controlled way. Differently from surface plasmons, BSW are less affected by absorption losses and can be designed for operation over a large range of wavelengths.

10:50 AM

(ICACC-FS2-012-2015) Low temperature deposition of photoluminescent Si nanocrystals in a silica matrix (Invited)

N. Quitoriano*[1]; D. Soubane[2]; T. Ozaki[2]; 1. McGill University, Canada; 2. Institut national de la recherche scientifique, Canada

The speed of computer chips has largely stagnated because interconnection delay has become the bottleneck. To address this, many researchers are considering photons to communicate signals on chip. Of course, Si has an indirect band gap and therefore is hard to get electron-hole recombination to result in a photon. However, Si nano crystals because their larger uncertainty in momentum, can luminesce more efficiently than bulk. Si nanocrystals, by themselves, will luminesce for a time; however, oxidation will limit the lifetime of these devices. To increase the device lifetime, researchers have taken to embed Si nanocrystals in silica. They form this structure be creating a Si-rich silica and annealing the material at > 1000 oC. In this paper, we report a relatively low temperature method, 550 oC, to form luminescent Si nanocrystals in silica. These nanocrystals are formed when we deposit Si, using pulsed laser deposition, with a low oxygen partial pressure and heat the substrate to 550 oC. We find that the temperature of the substrate as well as the oxygen partial pressure play important roles in the nanocrystal formation and size, respectively. We report the xray and photoluminescence results from these samples. This lower temperature process could enable this technology to be more relevant, since lower temperature substrates and lower thermal budget devices could take advantage of this.

11:20 AM

(ICACC-FS2-013-2015) Yb/Er-doped optical fibers for pulsed laser and optical amplifier applications

D. Milanese*[1]; D. Pugliese[1]; J. Lousteau[2]; N. G. Boetti[1]; M. Ferraris[1]; L. Scaltrito[1]; I. Forno[1]; M. Actis Grande[1]; A. A. Ishaaya[3]; 1. Politecnico Torino, Italy; 2. Istituto Superiore Mario Boella, Italy; 3. Ben Gurion University, Israel

Compact laser sources require active materials able to provide high gain per unit length: phosphate glasses match these requirements thanks to the high solubility they offer for rare earth ions together with high emission cross sections and chemical stability. The scope of this study is the design, fabrication and characterization of Yb/Er double cladding optical fibers suitable for the development of compact lasers and optical amplifiers. The core and cladding glass compositions were fabricated and characterized in terms of thermal, mechanical and optical properties. Optical damage threshold for pump photons was also measured in order to validate the ability of the glass to withstand high intensity sources. Preforms were fabricated by rod-in-tube technique, with the cladding tubes being obtained by rotational casting. Various types of optical fiber configurations were drawn and characterized. They showed good quality of interfaces between its components and an attenuation loss of 2 dB/m was measured by cut-back method. Optical amplification was demonstrated both by core and cladding pumping thus demonstrating its suitability to fabricate compact optical devices.

FS5: Single Crystalline Materials for Electrical, Optical and Medical Applications

Optical Materials II

Room: Tomoka C
Session Chairs: Luisa Bausa, Universidad Autonoma de Madrid; Patrice Camy, University of Caen

8:30 AM

(ICACC-FS5-034-2015) Optical sources at the nanoscale by the interaction between localized surface plasmons and nonlinear solid state gain media (Invited)

L. E. Bausa*[1]; E. Yraola[1]; L. Sanchez-Garcia[1]; P. Molina[1]; M. O. Ramirez[1]; C. de las Heras[1]; J. J. Carvajal[2]; M. Aguiló[2]; F. Díaz[2]; 1. Universidad Autonoma de Madrid, Spain; 2. Universitat Rovira i Virgili, Spain

Two types of optical radiation sources with improved performances at the nanoscale will be presented. i) Sources based on the interaction between plasmonic nanoparticles and gain systems constituted by rare-earth-based solid state lasers and ii) sources based on nonlinear media in which frequency conversion mechanisms are enhanced due to the intensification of the radiation–matter interaction processes by localized surface plasmon resonances. The plasmonic structures are constituted by different arrays of Ag nanoparticles, which are directly formed on the polar surfaces of the ferroelectric crystals by means of a low-cost polarization mediated photochemical process. The implications of the plasmonic coupling on the laser parameters of the solid-state gain medium are evaluated to show the enhancement of the emitted light by the rare-earth solid state laser as well as a dramatic reduction of the pump power at the laser threshold. With respect to the nonlinear frequency conversion processes a remarkable intensification of the SHG in factor ranging from 20 to 50 is demonstrated. The results constitute a promising approach for gain-enhanced nanoplasmonic metamaterials, as well as for rare earth based nanolasers operating at the subwavelength scale.

9:00 AM

(ICACC-FS5-035-2015) Crystal growth,linear and nonlinear optical properties of BaTeMo2O9 (Invited)

X. Tao*[1]; J. Zhang[1]; 1. Shandong University, China

Noncentrosymmetric (NCS) compounds are of current interest due to their multi-functional properties such as ferroelectricity, piezoelectricity, dielectric behavior, and second-order nonlinear optical (NLO) phenomena. In particular, their excellent nonlinear optical properties exhibit promising applications in the fields of frequency shifting, optical modulating, telecommunications and signal processing. Recently, a class of new NCS materials have been synthesized with d0 transition metal cations (Mo6+ or W6+) and lone-pair cations (Se4+ or Te4+). Both kinds of ions are susceptible to the second-order Jahn–Teller effect which is believed to cause the unique properties of the materials1. Monoclinic BaTeMo2O9 (β-BaTeMo2O9) and orthorhombic BaTeMo2O9 (β-BaTeMo2O9)2 are such two typical materials. Our group reported on the top-seeded solution growth of centimeter-sized single crystals and their functional properties.3,4 It has been demonstrated that β-BaTeMo2O9 possesses an effective NLO coefficient of 10.3 pm/V, being three times larger than that of KTP.4 Here we will report the crystal growth, the phase relationship, linear and nonlinear optical properties, stimulated Raman scattering and self -Raman frequency doubling properties of these two crystals.

9:30 AM

(ICACC-FS5-036-2015) Large-size Nonlinear Optical LBO Crystal Growth (Invited)

Z. Hu*[1]; 1. Technical Institute of Physics and Chemistry,CAS, China

As a nonlinear optical crystal, lithium triborate (LiB3O5, LBO) crystal is widely used in solid-state laser technology. It used to be grown by the Top-Seeded Solution Growth methodand Li2O-B2O3-MoO3 is currently considered the most effective flux system. The LBO crystal grown in conventional methods weighs about 200g and the optical aperture is generally less than 10mm.With the development of high-energy, high-power laser technology, it is required that the LBO crystal has a higher quality and larger size. Our group made a breakthrough in large-size LBO crystal growth, which largely meets the requirements above. This paper briefly introduced our research advances in LBO flux system, large borate growth equipment and new growth methods. The first, we designed a large flux crystal growth equipment to grow LBO crystals. The second, we adopted a new solute transport technique as well as a new flux system. The third, in order to process the large crystals we grew into larger diameter devices, we proposed a new method for the LBO crystal growth: near phase-matching angle direction growth. The largest LBO single crystal reported in the world with the size of 285×160×110 mm3 and the weight of 4798g was successfully grown in 180 days. LBO device with the size of 150×150×10mm3 can be obtained. In the near future, large size LBO crystal will play an active role in the progress of large-aperture, high-energy, high-power laser techniques.

10:20 AM

(ICACC-FS5-037-2015) Coilable Single Crystals Fibers of Doped-YAG for High Power Laser 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 both guiding laser light and matching the efficiencies found in bulk crystals, which is making them ideal candidates for high-power laser and fiber laser applications. This work focuses on the growth of a flexible fiber with a core of dopant (Er, Nd, Yb, etc…) that will exhibit good wave guiding properties. Direct growth or a combination of growth and cladding experiments are described. Scattering loss measurements at visible wavelengths along with dopant profile characterization are also presented. Amplification experiments results on Nd:YAG fibers are also presented.

10:50 AM

(ICACC-FS5-038-2015) Complex layered SSL sources produced by a multipurpose, adaptable and fast ceramic process (Invited)

L. Esposito*[1]; J. Hostaša[1]; A. Piancastelli[1]; M. Vannini[2]; G. Toci[2]; 1. CNR, Italy; 2. CNR, Italy

Ceramic-based materials have shown to be a competitive alternative to single crystals as sources for solid state lasers especially in case of high power applications. The ceramic process is highly flexible in terms of feasible geometries and shapes, as well as dopant distribution control. This provides a real advantage over the crystalline equivalent. This study focuses on the production process of ceramic laser sources with complex shapes and structured doping. Innovative solutions have been obtained with the tape casting technique in combination with thermal compression of ceramic tapes with a tailored modulation of the doping level. To make this process as adaptable as possible, commercial micrometric ceramic powders have been used. These results are compared with those obtained with nanometric powders and other processing techniques. The study focusses on YAG (Y3Al5O12) based components doped with Yb3+ as lasing ion. The microstructure and the Yb diffusion profile across the doped/undoped interfaces have been characterized by FEG SEM and ESEM. Laser performance has been characterized in a longitudinally diode pumped laser cavity. The laser efficiency under high thermal load conditions has been compared to that obtained from samples with uniform doping, under the same conditions. Thermal effects (thermal lensing, thermal depolarization) were characterized under laser operation.

11:20 AM

(ICACC-FS5-039-2015) Transparent YAG ceramics – the effect of doping ions

J. Hostaša*[1]; L. Esposito[1]; W. Pabst[2]; 1. CNR ISTEC, Institute of Science and Technology for Ceramics, Via Granarolo 64, 48018, Italy; 2. Institute of Chemical Technology, Prague, Technická 5, 166 28, Czech Republic

Transparent YAG ceramics doped with active ions have become a valuable alternative to single crystals in solid state lasers in the last 10 years. The dopant ion substitutes Y^{3+} in the crystal, and despite low concentration it influences the sintering process. It has been shown for example that, differently to Yb, Nd fastens sintering, and this is related to the ionic radius. This work describes the influence of doping ions on the microstructure evolution of transparent YAG ceramics and on the material properties. Variously doped YAG ceramics have been prepared by solid state reaction under high vacuum and characterized in terms of microstructure and thermal and mechanical properties. A model relation approximating the optical transmittance is provided. Transmittance is then presented not only as a material characteristic, but also as an indicator of microstructure development. The sintering and densification is discussed in relation to the transmittance and to material properties, in all cases considering the effect of the doping ions. It is interesting to show the sensitivity of various properties on the microstructural homogeneity and the small differences in porosity lying between nearly dense, translucent and transparent material. The influence of the active ions on the sintering evolution and consequently final properties highlighted in the present work can be exploited for the optimization of the processing conditions.

S1: Mechanical Behavior and Performance of Ceramics & Composites

Reliability and Small Scale Testing

Room: Coquina Salon D

Session Chairs: Jonathan Salem, NASA Glenn Research Center; Dietmar Koch, Institute of Structures and Design

1:30 PM

(ICACC-S1-058-2015) FEAMAC-CARES: CARES (Ceramics Analysis and Reliability Evaluation of Structures) and MAC/GMC (Micromechanics Analysis Code/ Generalized Method of Cells) Software Coupling Development Effort for CMC Stochastic-Strength-Based Damage Simulation (Invited)

N. N. Nemeth*[1]; O. Walton[1]; B. Bednarcyk[1]; E. Pineda[1]; S. Arnold[1]; 1. NASA Glenn Research Center, USA

Reported here is a coupling of two NASA developed codes: CARES (Ceramics Analysis and Reliability Evaluation of Structures) with the MAC/GMC (Micromechanics Analysis Code/ Generalized Method of Cells) composite material analysis code. The resulting code is called FEAMAC/CARES and is constructed as an Abaqus finite element analysis UMAT (user defined material). Here we describe the FEAMAC/CARES code and an example problem (taken from the open literature) of a laminated CMC in off-axis loading is shown. FEAMAC/CARES performs stochastic-strength-based damage simulation response of a CMC under multiaxial loading using elastic stiffness reduction of the failed elements.

1:55 PM

(ICACC-S1-059-2015) Internal pressure test and finite element analysis of a C/C-SiC rocket nozzle (Invited)

F. Breede[1]; N. Jain[1]; S. Hofmann[1]; D. Koch*[1]; 1. Institute of Structures and Design, Germany

Nozzle extensions made of ceramic matrix composites (CMC) have the potential to improve the performance of liquid fueled rocket engines. In the past gas permeability has been identified as a critical aspect in CMC rocket nozzles. C/C-SiC nozzle structures can reduce gas permeability, due to its inherent fairly dense matrix. This work shows the results of an internal pressure test to evaluate the mechanical integrity as well as the helium leak rates of a radiation cooled C/C-SiC nozzle. The experimental strain results of the internal pressure test are compared with a FEA-simulation in which the complex multi-angle fiber architecture and its varying layer thickness were implemented as UD-stackings by virtual separation of each cross winding laminate. Then a Finite Element (FE) approach based on inverse laminate theory could be used. Input data are derived from tensile and shear testing of even cross-wound plates. The procedure of generating the FE model of the C/C-SiC nozzle structure using the commercial FE-code ANSYS Workbench and Composite Pre- and Postprocessing (ACP) is described. Compression load and internal pressure were tested and simulated and a good agreement of strain gauge measurement and FEA results were obtained. This analysis was accompanied by hot firing tests in the P6.1 test bench in Lampoldshausen, DLR which were performed for the first time with a radiation cooled C/C-SiC nozzle.

2:20 PM

(ICACC-S1-060-2015) Post-Impact Damage Modeling of Ceramic Matrix Composites

P. M. Rao*[1]; R. S. Kumar[1]; 1. United Technologies Research Center, USA

Ceramic Matrix Composites (CMCs) are being actively considered for insertion into commercial aircraft propulsion system components such as turbine blades and exhaust systems. In-service impact damage from events such as tool drop and hail may result in both near-surface and sub-surface damage manifesting as inter-laminar delaminations, thereby adversely affecting retained properties. Therefore, the primary objective of this study is to develop robust and validated computational methods to estimate the post-impact residual strength of CMCs. The observed damage is represented in a parameterized fashion within the developed computational framework. Subsequently, a two-step solution scheme comprising of a linear eigenvalue buckling analysis followed by a non-linear static post-buckling analysis is implemented to compute the post-impact residual strength. The parametric computational framework provides sufficient fidelity to assess the interplay between various damage parameters. Favorable comparisons with published literature and in-house experimental data serve to validate the modeling methodology.

2:40 PM

(ICACC-S1-061-2015) Fracture Analysis of Strengthened Glass for Strength and Fatigue Applications

V. Subramanian*[1]; G. Hu[2]; I. Ahmed[1]; 1. Corning Incorporated, USA; 2. Corning Incorporated, USA

Fracture analyses of flaws, comprising both analytical and numerical approaches, in strengthened glass are presented for the purpose of estimating retained strength and fatigue susceptibility of these glasses. Analytical approaches for estimating stress intensity factors for cracked geometries with residual stress distributions have been known for some time now. It is shown that in some situations, the concept of superposition, which forms the crux of the analytical approach breaks down when the crack faces experience partial crack closure. The results can be significantly different when compared to numerical approaches that consider crack face contact and assume no superposition of residual stress profile effect and external loading. Because there is no warning of such a breakdown, it is suggested that analytical approaches be used with caution especially for edge cracks whose crack tips may be in the tensile region and whose outer edge may be subject to compression. Efforts are underway to validate these results using experiments and the experimental results will be presented if available.

3:20 PM

(ICACC-S1-062-2015) Interlaminar Mode I and Mode II Fracture Toughness in Ceramic matrix composites

M. Bailakanavar*[1]; P. Woelke[1]; N. Abboud[1]; G. Ojard[2]; T. Barnett[3];
1. Weidlinger Associates Inc., USA; 2. United Technologies Research Center, USA; 3. Southern Research Institute, USA

Characterization of Mode-I and Mode-II interlaminar fracture toughness at room and elevated temperature is vital for the life cycle prediction of structural components. The potential concepts included: Mode I DCB test with bonded doublers & machined dovetail doublers/Mode II ENF test and Mixed-mode four point bending test .The Mode-I DCB test with bonded doublers at room temperature addresses the issue of arm flexibility without having to apply any compliance correction. The Mode I DCB with machined dovetail doublers is a simple, reliable and effective test concept developed specifically for elevated temperature testing. The three-point bending based Mode-II ENF test is applicable to both room and elevated temperature. The consistency of the results makes it a viable candidate for evaluating Mode II fracture toughness. Finally the four point bend test is developed and investigated to quantify mixed-mode fracture toughness at both room and elevated temperatures. The test method also serves as a supplement test to validate Mode I and Mode II fracture toughness's determined by the DCB test and the ENF test respectively. Numerical analyses were performed to optimize specimen geometries and proof of concept was successfully demonstrated for each test procedure. Some challenges related to crack tip tracking, notch fabrication and unstable crack growth, were observed.

3:40 PM

(ICACC-S1-063-2015) Deformation of fine-grained CrAlN hard coatings (Invited)

W. J. Clegg*[1]; S. Liu[1]; J. M. Wheeler[2]; X. T. Zeng[3]; J. Michler[2]; 1. University of Cambridge, United Kingdom; 2. EMPA, Switzerland; 3. Singapore Institute of Manufacturing Technology, Singapore

CrAlN hard coatings with a grains approximately 10 nm in size and surrounded by a grain boundary silicon nitride phase show a greatly improved wear resistance compared with conventional CrAlN coatings. This is generally attributed to the improvements in hardness. However, the properties of these materials are generally only simulated and there is no understanding of how these structures deform. This paper uses micropillar compression to make direct measurements of the yield stress of these coatings. These measurements of the uniaxial yield stress show that the hardness is predicted without the need to invoke increases in the elastic modulus due to the compression under the indenter. It is also shown that the grain-size is sufficiently small that the grains deform at the theoretical yield stress, so that the overall deformation occurs by the individual deformation of the grains, rather than by the formation of slip bands as is more often seen. Measurements of the strain-rate sensitivity and the variation of the flow stress with temperature show that deformation is determined by the CrAlN, rather than the grain boundary phase and suggests that boundary effects should not influence the flow behaviour. However, measurements of the toughness of the coating using a micro-double cantilever beam sample show that the decease in the grain size is associated with an increase in the toughness of the coating material.

4:05 PM

(ICACC-S1-064-2015) Large strain plasticity of silica microspheres under electron irradiation

D. D. Stauffer*[1]; S. Bhowmick[1]; R. C. Major[1]; S. Asif[1]; O. Warren[1];
1. Hysitron, Inc., USA

The stress-strain behavior of silica glass is highly dependent on the strain rate and energy of electron irradiation. When tested ex situ these commercially available, highly uniform 1μm, silica spheres tend to fracture. However, when irradiated at 20keV and 30pA in an SEM the spheres can be plastically deformed to strains of more than 50% at room temperature without any evidence of fracture or cracking. In situ experimentation allows for tip/sample alignment, variation of beam voltage, and imaging to determine the resulting deformation, where the electron optics are used both for irradiative and imaging purposes. A stage mounted nanomechanical testing instrument is used to collect the mechanical data during loading inside an SEM. The effect of blanking the beam is immediate. A reduction in the accelerating beam voltage corresponds to a reduction in the overall residual plastic strain under load. Simple modeling, using CASINO, shows that this reduction in the irradiation voltage results in a corresponding decrease in both sample penetration and ejected secondary electrons. The mechanical affects can then be explained via Auger processes, which act to change the density of states and reduce the overall strength of the 0-Si-O bonds.

4:25 PM

(ICACC-S1-065-2015) The Influence of Large Deflections on the Weibull Strength of Silicon Nanowires

R. Kirkpatrick[2]; J. Collins*[1]; C. L. Muhlstein[1]; 1. Georgia Tech, USA; 2. Penn State, USA

Silicon nanowires synthesized with vapor-liquid-solid (VLS) deposition techniques are routinely 10s of micrometers in length with diameters on the order of 10s of nanometers. As a result, they are extremely flexible when loaded in bending and have strengths that are an appreciable fraction of the theoretical strength. In this work we show how weakest link (Weibull) analyses can be extended to high strength, flexible, ceramic nanowires that were loaded in fixed-fixed bending using an atomic force microscope. The large deflections (relative to the nanowire diameter) at failure were associated with nonlinear elastic behavior that was followed by brittle fracture (average strength ~14 GPa). The nanowire flexure strengths ranged from 5 to 20 GPa, and their dependence on diameter (ranging from ~40 to 80 nm) and growth orientation ([110], [111], and [112]) was evaluated. Numerical analyses were also used to evaluate the implications of boundary conditions and large deflections for weakest link statistical theories. A key finding was that as the flexibility of the nanowire increases, the tensile stresses associated with stretching of the nanowire lowers the probability of that a high strength will be observed.

4:45 PM

(ICACC-S1-066-2015) Accuracy and Limitations of Raman-Based Strain Measurements in Ceramic Nanowires

M. Yashinski[2]; H. Gutierrez[3]; C. L. Muhlstein*[1]; 1. Georgia Tech, USA;
2. Penn State, USA; 3. University of Louisville, USA

The relationship between first order Raman scattering and tensile strain can be used for non-contact strain measurement and mapping in a wide range of ceramics. Moreover, because Raman-based strain measurements are directly related to deformation of the interatomic bonds in the material of interest, they are particularly useful when evaluating small specimens such as freestanding ceramic nanowires. In this work individual [111] oriented GaP nanowires (50 to 300 nm diameter) were synthesized with chemical vapor deposition and were deformed in uniaxial tension to failure. The strongest of the nanowires had tensile strengths approaching 5 GPa, so the Raman-shifts exhibited clear splitting of the transverse optical mode. This allowed for deeper insights into the phonon deformation potentials (PDPs), and was used to develop a general methodology to quantify the accuracy of Raman-based strain measurements. In the case of GaP, PDPs measured directly from nanowires provided elastic moduli and fracture strains that were consistent with the orientation and structure of the nanowires, but were significantly different than the generally accepted values found in bulk specimens. The implication of this research is that the relationships between stress, strain, and Raman peak shift derived from bulk specimens cannot be used in small specimens when peak splitting is expected.

5:05 PM

(ICACC-S1-067-2015) Effect of scale on the hardness of multiphase ceramics

L. J. Vandeperre[1]; A. Madamombe*[1]; 1. Imperial College London, United Kingdom

Hardness measurements can be made at a wide range of applied loads and with current commercial instruments the possible load range covers 10 orders of magnitude (30 nN to 294 N). It is well known that the hardness values obtained from tests at different loads can be very different with higher loads often resulting in lower measured hardness values. In monolithic materials, there is a growing consensus that small indentations, where cracking can be avoided entirely, relate more to the plastic properties of ceramics whereas larger indentations yield a more complex mixed resistance to cracking and plasticity and the choice of load therefore is dominated by the type of information desired. In multiphase ceramics a further consideration is whether the size of the indent is sufficiently large to cover a representative sample of the microstructure. To clarify the effect of multi-phase microstructures on hardness, hardness measurements across a range of loads were made in silicon carbide, boron carbide and silicon carbide – boron carbide composites. The scale of the microstructures was varied using prolonged sintering to induce coarsening. The different mechanisms of deformation are characterised with specifically care being taken to characterise the onset of cracking and trends in hardness versus microstructure are established with a view of determining the composite effect on the hardness and its meaning.

5:25 PM

(ICACC-S1-068-2015) Measuring Nanoscale Mechanical Properties of Brittle Materials at Elevated Temperatures

S. Syed Amanulla*[1]; 1. Hysitron, USA

Nanoindentation-based techniques are routinely utilized to quantitatively measure the mechanical properties of thin films and small microstructures. Traditionally, these techniques have not been well suited for nanoscale creep characterization over long time durations or at elevated temperatures due to substantial measurement inaccuracies that arise from thermal drift. Here we present a new approach with specially designed heating stage combined with dynamic nanoindentation technique capable of performing nanoscale mechanical properties, mainly hardness, modulus, fracture toughnes and creep measurements free from thermal drift effects. The probe force modulation is superimposed over a static load to provide a continuous measurement of contact stiffness, from which the time dependent mechanical response at nanoscale contact can be studied. By measuring the contact stiffness between the probe and the material rather than a raw displacement sensor signal, nanoscale creep measurements can be reliably performed at high temperatures and over long time durations (hours). High temperature nanoscale mechanical response of silicate glass, fracture and creep properties of thermal barrier coatings will be presented utilizing this technique.

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

Environmental Barrier Coatings II

Room: Coquina Salon G

Session Chairs: Soumendra Basu, Boston University; Bradley Richards, University of Virginia

1:30 PM

(ICACC-S2-032-2015) Failure mechanisms associated with the silica scale in BSAS coated C/SiC composites (Invited)

Y. Wang*[1]; 1. Northwestern Polytechnical University, China

The SiCN-barium strontium aluminosilicate (BSAS) coated C/SiC composites were corroded in 50%H2O-50%O2 environments at 1250oC. It was found that the coated composites suddenly lost their strength as the corrosion time was up to 250 hours. A continuous silica scale was formed between the SiC bonding coat and SiCN-BSAS coating during the water-vapor corrosion. When the formed silica scale grew over a certain thickness, some cracks formed and propagated along the interface between the silica scale and SiC bonding coat, resulting in the spallation of SiCN-BSAS coatings. The C/SiC composites were thus corroded in water vapor quickly. Analysis indicates that the silica scale results in growth stress, which increases with the growth of the silica scale. When the growth stress is over the bonding stress between silica and SiC, the cracks will be formed and propagate along their interface, resulting the failure of the composites.

2:00 PM

(ICACC-S2-033-2015) Formation of preferential orientation on dense Al_2O_3 coating prepared by aerosol deposition method

M. Hasegawa*[1]; K. Akiyama[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

Environmental barrier coatings (EBCs) applied for SiC fiber reinforced SiC ceramic matrix composites (CMCs) are a candidate coatings to protect the hot-section components of next-generation gas turbine blades. Recently, advanced EBCs which effectively reflects thermal energy and prevent oxidation of the substrate CMCs have been proposed from us. During the high temperature service, cracks will form at the EBCs due to the shrinkage by sintering of coating. Thus, EBCs are required to have a dense coating from the beginning. Aerosol deposition (AD) method is known to fabricate a dense ceramic coating at room temperature by impacting fine ceramics particles on the substrate. We pay attention to this method as the coating process for the advanced EBCs. In this study, formation behavior of texture on Al_2O_3 coating by AD method was researched. Al_2O_3 particles were deposited on the $Y_2Ti_2O_7$ and Mo substrate. After coating, the materials were heat treated from 1173 K to 1673 K up to 100 hours. With the increase in heat treatment temperature and time, the size of the crystal grain of Al_2O_3 increased. Weak fiber texture was observed at as-coated material. (0001) plane was tilted about 10 degree from the coating plane. With the increase in heat treatment temperature and time, texture changed to (0001) fiber texture and the volume fraction of (0001) orientation increased.

2:20 PM

(ICACC-S2-034-2015) Oxygen permeation within α-alumina in advanced EBCs: An atomistic theoretical approach

T. Ogawa*[1]; A. Kuwabara[1]; C. Fisher[1]; H. Moriwake[1]; S. Kitaoka[1]; 1. Japan Fine Ceramics Center, Japan

A novel environmental barrier coating for SiC/SiC matrix composites, which is composed of $Al_2O_3/Y_2Ti_2O_7$ multilayers, has been designed and developed to reflect thermal energy effectively and protect the underling matrix against oxidation. The latter ability is attributed to slow mass transfer in the alumina layers, but grain boundary (GB) diffusion induced by a steep gradient in the oxygen potential pressure, P_{O2}, can cause degradation of the layer structures due to high diffusivity of O and Al atoms along the GBs. It therefore is necessary to understand and control or limit such diffusion. Recent oxygen permeation experiments using alumina wafers revealed that the dominant diffusing species switch over depending on P_{O2}. In this study, we investigate the switching behavior using atomistic approaches such as first-principles quantum-mechanical simulations. Electronic structures of representative grain boundaries of alumina reveal that the band gap can be narrowed by 60% relative to the bulk. When the narrowing effect is taken into account, the concentration of O and Al vacancies as a function of P_{O2} changes dramatically, reproducing the switchover in the dominant defect observed by the experiment. By combining an atomistic description of vacancy formation and a diffusion model for oxygen permeation, we have also analyzed the relationships between the band gap and permeability.

2:40 PM

(ICACC-S2-035-2015) Pulse phase thermography NDE for detection of partial delamination behavior in mullite/Si/RB-SiC model EBC system

Y. Arai*[1]; R. Inoue[1]; T. Kuribara[1]; Y. Kagawa[1]; 1. The University of Tokyo, Japan

Detection of local interfacial delamination between environmental barrier coating and substrate has been carried out using pulse phase thermography. Mullite/Si/(RB-SiC) model EBC system is used for the test. After heat exposure temperatures above 1400°C, mad crack pattern appeared on the surface of the EBC layer. Observation of transverse section of the system reveals that observed mud crack propagated through-the-thickness direction of the EBC layer and deflected near interface between EBC layer and Si bond coat layer. The delaminated crack pattern is "L" or "T" shape and the deflected crack typically stops within several hundred micrometers. Temperature change after pulse light irradiation from the EBC surface shows difference of temperature-time relation. The temperature change above delaminated area is different from that of bonded area. At the same time after pulse irradiation, temperature of EBC surface above the delaminated area is higher than that of bonded area. Potential of pulse phase thermography will be discussed based on set of experimental results.

Multifunctional, Corrosion and Wear

Room: Coquina Salon G

Session Chair: Kevin Plucknett, Dalhousie University

3:20 PM

(ICACC-S2-036-2015) Porosity Control in Ceramics Coated Layers by Friction Effect Modulations on Tilted Thermal Nanoparticles Spraying (Invited)

S. Kirihara*[1]; 1. Osaka University, Japan

Thermal Nanoparticles spraying were newly developed to create fine metals or ceramics layers rapidly on alloy components. The nanometer sized alumina particles of 200 nm in average diameter were dispersed into liquid resins at 40 % in volume contents, and the obtained high viscosity slurry was blown as micro mists of 50 μm in drop size into an argon arc plasma spray. In this study, incidence angels of the plasma spraying were adjusted from 30 to 90 degree systematically to investigate about the influences of the friction effects between the particles and substrate on nanometer order porosity distributions in the coated layer. Microstructures were observed by using scanning electron microscopy. X-diffraction spectroscopy was used to analyze the residual carbon elements produced by imperfect combustions of the liquid resin. Effective dielectric constants of the ceramics layers were measured successfully to calculate the porosities of air defects volume contents by using time domain spectroscopy of electromagnetic waves in a terahertz frequency range. The porosity control by the friction effect modulations on the tilted thermal nanoparticles spraying technique will be discussed.

3:50 PM

(ICACC-S2-037-2015) Aqueous corrosion behavior of Ti(C,N)-Ni3Al cermets

M. Holmes[1]; G. Kipouros[1]; Z. Farhat[1]; K. P. Plucknett*[1]; 1. Dalhousie University, Canada

The aqueous corrosion behavior of a range of titanium carbonitride-nickel aluminide (Ti(C,N)-Ni3Al) cermets has been assessed using a variety of electrochemical approaches. The cermets were produced using a simple vacuum melt infiltration route, using the Ni3Al alloy IC-50 (with additions of Zr and B). The Ni3Al binder content was varied from 20 to 40 vol. % for selected compositions, while the C:N ratio of the Ti(C,N) ranged from 100:0 to 30:70. It is demonstrated that a galvanic attack occurs between the two phases, referentially attacking the Ni3Al intermetallic, and ultimately leading to removal of the ceramic phase. Post-corrosion assessment of the cermets was undertaken using both scanning electron microscopy and inductively coupled plasma optical emission spectroscopy, and this will also be discussed.

4:10 PM

(ICACC-S2-038-2015) Sol-gel based Nano-composites for Self cleaning applications

A. S. Khanna*[1]; 1. IIT Bombay, India

Nanotechnology is perhaps one of the most charismatic phenomenon of the recent times, whose applications are widespread, ranging from several day to day applications to the most important industrial applications. In the present work, use of nano-technology was made to create self cleaning coatings for solar panels. Eco-friendly water borne coatings were prepared using sol-gel route using epoxy based silanes. These were then made hydrophobic by grafting with flurosilanes. In order to make the coatings superhydrophobic, which can slide at very low angles, further modification was carried out using nano-silica. Detailed procedure of making such coatings, fully characterized by SEM/EDAX, FTIR, TEM, AES and finally by AFM, is presented in the paper. A suitable mechanism, based on continuum theory has also been proposed which confirms that for achieving optimum properties for nano-composites, optimum concentration of nano-particles and their uniform distribution is very important. Use of these hydrophobic coatings was then demonstrated on various substrates: metal, glass, wood, fabric, concrete and paper. The coating maintained its hydrophobic character on all substrates with a sliding angle varying from 5-15o. These coatings are now being tested for solar panels so that they can be used to remove the dust and other deposits by self cleaning effect.

4:30 PM

(ICACC-S2-039-2015) Formulation of hexagonal boron nitride suspensions for lubrication applications

S. Murali*[1]; R. Haber[1]; 1. Rutgers, The State University of New Jersey, USA

Hexagonal boron nitride powders make excellent lubricant materials due to their high thermal conductivity, low coefficient of friction, and oxidation resistance at high temperatures. They have been widely used as a solid lubricant additive owing to better high temperature resistance compared to graphite and molybdenum disulfide. However, there are limited reports on formulations of liquid-based lubricants using hexagonal boron nitride. In this work, we report on the formulation of hexagonal boron nitride suspensions using three different methods of surface modification. The rheology and stability of the suspensions as well as coating quality is discussed. Effect of microstructure on suspension rheology is discussed and coating quality of the most promising suspension formulations is compared to commercially available liquid-based lubricant coatings.

4:50 PM

(ICACC-S2-040-2015) Preparation and microstructure of Cr2AlC coating by cathodic arc deposition

Y. Qian*[1]; 1. Institute of Metal Reasearch, Chinese Academy of Sciences, China

As one of the MAX phases, ternary layered carbide Cr2AlC exhibits unique merits of both metals and ceramics, especially excellent high temperature corrosion resistance, has a great potential for applications as high temperature structural material and high temperature protective coating. Cathodic arc deposition technique is a practical way to produce coating because of its high efficiency. In the present paper, a dense Cr-Al-C coating was prepared by cathodic arc deposition at ambient temperature from a sintered Cr2AlC compound target, and then followed by subsequent annealing process. The experimental results indicated that the as-deposited coating was amorphous. Compared with the stoicheiometry of ideal Cr2AlC, C-deficiency was detected, caused by strong re-sputtering effect. Besides, nano-layering structure of the as-deposited coating appeared, resulted from substrate rotation during the preparation. After annealing treatment at 620oC in Ar for 20 h, the amorphous Cr-Al-C coating transformed into crystallization. Finally, a coating with Cr2AlC as the major phase combining with the co-existence of AlCr2 and Cr7C3 was obtained. As a result, the synthesis temperature of Cr2AlC was greatly decreased from high sintering temperature above 1050oC for the sintered bulk to 620oC for the deposited coating. And the C-deficiency resulted in the presence of the AlCr2 in the annealed coating.

S3: 12th International Symposium on Solid Oxide Fuel Cells (SOFC): Materials, Science and Technology

Degradation, Modeling and Simulation / Novel Processing and Design

Room: Crystal

Session Chairs: Ulrich Vogt, Empa; Mihails Kusnezoff, Fraunhofer IKTS

1:30 PM

(ICACC-S3-052-2015) Steam Electrolysis with Electrode and Electrolyte Supported Solid Oxide Cells: Stability Testing Focussing on the 5000+ Hours Time Scale (Invited)

J. Schefold*[1]; A. Brisse[1]; 1. European Institue for Energy Research, Germany

Steam electrolysis with solid oxide cells (SOCs) reaches high electrical-to-chemical energy-conversion efficiency for hydrogen production. Faradaic efficiency is close to 100 %, and cell voltages typically amount to about 1.0 V with H2 electrode supported cells and 1.2 to 1.3 V with electrolyte supported cells. This implies high conversion efficiency, even above 100 % provided that thermal energy is supplied for evaporation. EIFER is involved in long-term SOC testing with cells and cell stacks from different suppliers in a power range from about 20 Wel to several kWel. The focus of recent work is on testing beyond 5000 h, including a benchmark test exceeding 10000 h with an electrolyte supported cell. The cells under consideration are both SOFCs, and SOCs where the electrolysis application was already considered in the development. Typically, a voltage degradation below 1 %/1000 h is aimed at, required for practical application. Lowest degradation rates (< 0.6 %/1000 h) were obtained with an electrolyte supported cell, which increasingly compensates for the initially higher cell voltage after long-term operation. Current densities of 0.7 to 1 Acm-2 are higher than those used for SOFC testing. Impedance spectroscopy is routinely applied as in-situ tool for degradation analysis. An overview on the recent cell-testing results will be given.

2:00 PM

(ICACC-S3-053-2015) NiO behavior observation in Ni-GDC anode during redox cycle

K. Sato*[1]; T. Hatae[1]; S. Amaha[1]; 1. Tokyo Gas Co.,Ltd., Japan

Improvement of both durability and reliability of Solid Oxide Fuel Cells (SOFCs) under various operation conditions is important issue. The improvement of redox resistance in shutdown is especially important among them. The degradation of the conventional anode such as Ni-YSZ by redox cycles has been studied by some researchers. Its mechanism was reported as follows. When Ni is oxidized into NiO, Ni particles divide finely, expand, and connect with the next one. Then the connected NiO particles are sintered and agglomerated by reduction (so-called re-organization). The Ni particles expand much larger after the redox cycles, which cause both mechanical destruction and performance degradation of the cell. We succeeded in observation of behavior of NiO particles of NiO-YSZ anode material during a redox cycle by both measurement of AC impedance and dimensional change. The increase in grain boundary resistance in addition to bulk resistance of NiO was observed. On the other hand, it is known that the volume of GDC which is a general SOFC anode material in oxidation is smaller than that in reduction, which behavior is opposite to the Ni. Therefore smaller dimensional change in the redox of Ni-GDC anode is expected than that of Ni-YSZ anode. In the present study, we will report the behavior of NiO particles in the Ni-GDC anode by measuring the changes both conductivity and dimension in the redox cycle.

2:20 PM

(ICACC-S3-054-2015) Application of Computational Thermodynamics in Solid Oxide Fuel Cell

Y. Zhong*[1]; M. Yang[2]; M. Chen[3]; 1. Florida International University, USA; 2. The Pennsylvania State University, USA; 3. Technical University of Denmark, Denmark

High sintering and operation temperatures promote unwanted interface reactions in Solid Oxide Fuel Cell (SOFC), especially at the cathode-air-electrolyte triple phase boundary (TPB). The phase stability at TPB has been identified as the dominant mechanism for the long-term degradation, which is a critical parameter for SOFC. It is greatly needed to use the CALPHAD approach to investigate the phase equilibria between the cathode (perovskite) and the electrolyte (doped zirconia). The combined approach with Computational Thermodynamics and experiments has been used to investigate the phase stabilities at TPB. Sr- substituted LaMnO3 perovskite (LSM) and yttria-stabilized zirconia (YSZ) mixture was investigated by thermodynamic calculations to understand the factors affecting the stabilities of La2Zr2O7 (LZO) and SrZrO3 (SZO), the two zirconates, at different conditions. Experimental investigations were done on the thermodynamic stabilities of the two zirconates in N2 and air to simulate the phase equilibria at different conditions. The experimental data proved that thermodynamic calculations were reliable and they can be used to provide guidance on the control of the phase stability at TPB.

2:40 PM

(ICACC-S3-055-2015) Long-term Degradation Due to Cation Ordering in Rare Earth Doped Ceria

S. Grieshammer[1]; B. Grope[1]; J. Koettgen*[1]; M. Martin[1]; 1. RWTH Aachen University, Germany

We investigate the dopant distribution and its influence on the oxygen ion conductivity of rare earth doped ceria. The association energies of dopant pairs, oxygen vacancy pairs and between dopant ions and oxygen vacancies are calculated by means of density functional theory using a GGA+U functional including finite size corrections. The distribution of oxygen vacancies and dopant ions

(Y, Gd) in thermodynamic equilibrium is simulated using a Monte Carlo algorithm according to Metropolis et al. and a pair interaction model based on the association energies. The resulting cation coordination numbers show remarkable agreement with experimental data if all defect interactions are considered. The oxygen-ion conductivity is calculated in Kinetic Monte Carlo simulations using the equilibrated lattices as starting configurations. The migration energy for each occurring ion configuration can be calculated combing explicit nudged elastic band calculations within DFT and a pair interaction model. Random and equilibrated yttrium distributions lead to different oxygen ion conductivities. Lattices, which are equilibrated at intermediate operation temperatures, show a decreased ionic conductivity due to ordering of the dopant cations. Cation diffusion is very slow and therefore the ordering process might take several years at typical operation temperatures of SOFCs. However, this coincides with their operation time.

3:20 PM

(ICACC-S3-056-2015) Improving performance and long-term stability of solid oxide cells by integration of AA-CVD thin films (Invited)

M. V. Schlupp*[1]; M. M. Wehrle[1]; R. Delmelle[1]; A. Borgschulte[1]; A. Remhof[1]; U. F. Vogt[1]; A. Zuettel[2]; 1. Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland; 2. EPFL, Switzerland

Aerosol-assisted chemical vapor deposition (AA-CVD) is a thin film deposition technique which combines the advantages of chemical vapor deposition with those of a simple, cost-effective ultrasonic spray pyrolysis setup and allows on a precise control of chemical composition, thickness and surface morphology of deposited thin film. This technique offers great potential for solid oxide cell applications: Yttrium-stabilized zirconia (YSZ) thin films of few hundred nanometers thickness prepared by AA-CVD have successfully been applied as electrolytes in micro-solid oxide fuel cells on Si substrates, and dense gadolinium-doped ceria thin films prepared by this technique constitute effective diffusion barrier layers at the electrolyte/oxygen electrode interface. Furthermore, nano-crystalline and thermally stable Pt microstructures as well as Ni-YSZ cermets are accessible by AA-CVD. Integration of such thin films with conventionally prepared solid oxide cells offers a good opportunity to improve their performance and long-term stability.

3:50 PM

(ICACC-S3-057-2015) Application of Full Metal Fuel Cells (FMFCs) with Solid Oxide Thin Films in smartphone chargers

S. Kuehn*[1]; A. Weber[1]; K. M. Paciejewska[1]; A. Stoeck[1]; L. Winkler[1]; S. Mnich[1]; 1. eZelleron, Germany

One Drawback in the commercialization of Solid Oxide Fuel Cells (SOFCs), especially concerning mobile applications, is their long start-up time of typically several hours and the low thermo-cycling stability. A fuel cells ability to start-up in a few seconds and to resist more than one thousand full thermo-cycles demands high requirements to the fuel cells ability to withstand thermo-mechanical stress. Thermo-gradients of several hundred degrees Celsius and heat-up-ramps of more than 6.000 K/min can be demonstrated by omitting brittle materials like glasses or thick ceramic films. Metallic substrates, interconnects, cathode current collectors and metallic sealing's combined with thin ceramic films (<10 μm, sub-micro- or nano-crystalline texture) lead to a high thermo-mechanical shock resistance. A full metal fuel cell (FMFC) was developed and combined with thin ceramic functional layers. Low-cost high-throughput manufacturing steps like powder injection molding and aqueous electrophoretic deposition were used to create the complex microstructure matched to the high requirements of a quick-start-able fuel cell with very high-power densities. Challenges in the application of this FMFC in smartphone charging devices are presented.

4:10 PM

(ICACC-S3-058-2015) Development of Flat-tubular Solid Oxide Fuel Cells and Stacks

T. Suzuki*[1]; H. Sumi[1]; T. Yamaguchi[1]; K. Hamamoto[1]; H. Shimada[1]; Y. Fujishiro[1]; J. D. Carter[2]; S. Barnett[3]; 1. National Institute of Advanced Industrial Science and Technology, Japan; 2. Argonne National Laboratory, USA; 3. Northwestern University, USA

In this study, 1 mm thick micro flat-tubular Solid oxide fuel cells (SOFCs) and their stacks have been fabricated using cost effective extrusion technique and dip-coating technique, aiming for small scale power devices. The cell has showed the power density at 0.75 V of 0.19 and 0.385 W cm-2, respectively, at 600 and 650 oC operating temperatures. Using the cell with the electrode area of 3.75 cm2, five and ten series stacks are built, and then, a hot module was assembled by placing the stack in an insulator with small gas heaters for fuel and air. The hot module was tested under quick start-up condition and confirmed the power generation within 20 min. The module was successfully operated using hydrogen and methane + air mixed fuel, generated 8-14 W at 600-700 oC operating temperatures.

4:30 PM

(ICACC-S3-059-2015) Ni-free Hybrid Metal-Ceramic Supported SOFC

R. Costa*[1]; R. Poss[2]; A. Chesnaud[3]; F. Willot[4]; G. Syvertsen[5]; M. Viviani[6]; A. Sanson[7]; L. Dessemond[8]; R. Semerad[9]; A. Ansar[10]; 1. German Aerospace Center, Germany; 2. Alantum Europe GmbH, Germany; 3. ARMINES, France; 4. ARMINES, France; 5. Ceramic Powder Technology AS, Norway; 6. CNR, Italy; 7. CNR, Italy; 8. Grenoble INP, France; 9. Ceraco Ceramic Coating GmbH, Germany; 10. Saan Energi AB, Sweden

An hybrid cell architecture is presented, aiming at combining benefits of existing Anode Supported (high power density, lifetime) and Metal Supported cell (robustness) architectures, while limiting carbon coking, sulphur poisoning and redox stability issues - mainly linked with the use of pure nickel as structural component ie. Ni/YSZ cermet - by using perovskite material. The composite substrate is made of porous Alumina forming alloy (NiCrAl) acting as long life, redox-stable structural component, combined with an electron conducting oxide ceramic: $La_{0,1}Sr_{0,9}TiO_{3-\alpha}$ (LST). The chosen materials have been proven to be thermo-chemically stable over the whole manufacturing route, and were successfully implemented into a full cell using plasma spraying for producing the electrolyte. Electrochemical tests have shown limited performance at 750°C but very high stability with nearly no detectable degradation in tested conditions, confirming their compatibility. The thick electrolyte (100μm) together with limited electronic conductivity in the current collector and the catalytic activity of the perovskite have been identified as performance's limiting factors. Further developments lead to the introduction of thin bi-layer electrolyte (<3μm) by PVD. The actual cell architecture is presented and results are critically reviewed at the level of material science, ceramic processing and electrochemistry. Further improvement routes are discussed.

4:50 PM

(ICACC-S3-060-2015) Manufacturing of Metal Foam Supported SOFCs with Graded Ceramic Layer Structure and Thin-film Electrolyte

F. Han*[1]; R. Semerad[2]; G. Constantin[3]; L. Dessemond[3]; R. Costa[1]; 1. German Aerospace Center, Germany; 2. Ceraco Ceramic Coating GmbH, Germany; 3. Université Grenoble Alpes, France

Manufacturing of thin and gas tight electrolyte is still a challenging issue for metal supported solid oxide fuel cells (SOFCs). In this work, we present a porosity graded multi-layer structure supporting thin-film electrolyte. The substrate is made of NiCrAl metal foam impregnated with La-substituted $SrTiO_3$ (LST) ceramic. Furthermore, a composite anode functional layer with LST and gadolinium doped ceria (GDC) was deposited onto the substrate. The surface of the anode functional layer is later engineered with a suspension of nano-particles with 40 nm average particle size of yttria-stabilized zirconia (YSZ). This results in a mesoporous layer with smooth surface able to support a thin film GDC layer. Finally, a gas-tight GDC electrolyte was deposited by EB-PVD method. The thickness of the thin-film YSZ layer and the gas-tight GDC layer was approximately 1 µm and 2 µm, respectively. Button half cells with size up to 25 cm^2 were produced showing an air leakage rate down to $7.0*10^{-4}$ $(hPa*dm^3)/(s*cm^2)$, satisfying the gas-tightness quality control threshold of the state of the art metal supported SOFCs at DLR. Full cells with LSCF cathode were then produced and electrochemically tested. Results will be presented and discussed in this paper.

5:10 PM

(ICACC-S3-061-2015) Effect of specific surface area and particle size distribution of gadolinium doped ceria slurry on densification during sintering process

K. M. Paciejewska*[1]; S. Kühn[1]; A. Stoeck[1]; S. Mnich[1]; 1. eZelleron GmbH, Germany

This study addresses the preparation of chemical reaction blocking layer (CRBL) for SOFC microtubes by dip coating in GDC suspensions and subsequent sintering. Experiments with three different commercial GDC powders revealed that optimum layer properties (maximum densification, absence of defects, smooth surface) are determined by colloidal stability and particle size distribution (PSD) of the slurry. Colloidal stability is much harder to achieve for powders with a large surface (nanopowders) than powders with BET values in the range of ~10 m2/g – 50 m2/g. But narrow PSD is essential even for well stabilised systems to get a dense layer after sintering. Two methods were applied for this purpose: centrifugation of the priory dispersed GDC slurries and grinding. After centrifugation as a refinement approach, the particles could be sintered together even at 1300°C and a layer with density close to 99% could be reached. In contrast, simple ultrasonic dispersion or grinding diminished the distribution width insufficiently and gave porous layer even at 1600°C. Furthermore, experiments at the sintering process showed that particles with the narrowest original PSD can be sintered at lower temperature than others with a broader PSD.

5:30 PM

(ICACC-S3-062-2015) The Effect of Precusor Gel Desiccation, Ceria Oxide Pre-Infiltration, and Solution Composition on the Size of Lanthanum Strontium Ferrite-Lanthanum Strontium Cobaltite Infiltrate Nano-Particles

T. Burye*[1]; J. D. Nicholas[1]; 1. Michigan State University, USA

The objective of this study was to determine if the size of infiltrate particles with varying lanthanum strontium iron cobaltite compositions could be reduced through nitrate gel desiccation and/or the pre-infiltration of a nitrate decomposition catalyst. Since nano-particle size is also coupled to the polarization resistance, (RP), the effects of these two techniques on RP were also evaluated. Cells were infiltrated using citric acid containing La0.6Sr0.4CoxFe1-xO3 (X=0 to 1) (LSF-LSC) precursor nitrate solutions. The cells were then fired and electrochemically tested. Cells with identical scaffolds were infiltrated and then desiccated prior to firing and electrochemically testing. Lastly, identical scaffolds containing nano-sized cerium gadolinium oxide (GDC) were infiltrated, fired and electrochemically tested. Infiltrated nano-particle sizes were determined using scanning electron microscopy. In all cases RP decreased as X increased. Desiccation lowered RP in all cases but not as much as GDC pre-infiltration, which lowered RP to 0.1 Ωcm2 at 550°C for X=1. In all cases RP decreased as the particle size decreased. Nano-particle sizes were reduced from 48-27 nm. These RP reductions agree with the predicted RP changes resulting from the observed 48-27 nm particle size reductions.

S5: Next Generation Bioceramics and Biocomposites

Bioceramics III

Room: Coquina Salon F

Session Chairs: Akiyoshi Osaka, Okayama University; Jacqueline Johnson, UTSI

1:30 PM

(ICACC-S5-019-2015) Structure and Properties Study of Calcium Phosphate Bioceramics

Y. Gao*[1]; R. law[1]; N. Karpukhina[2]; R. Hill[2]; 1. imperial college london, United Kingdom; 2. Queen Mary University of London, United Kingdom

Calcium apatite is the basis for a multiplicity of inorganic solids important in geology and materials science. As we know, hydroxyapatite (HA; Ca5(PO4)3OH) is the main mineral component of human dental enamel and bone, and can react readily with fluoride or absorb it from solutions to form fluoride-substituted hydroxyapatite (HFA) Ca10(PO4)6F2x(OH)2-2x (0<x<1). However, the different proportions of fluoride-substituted hydroxyapatite have different solubility and thermal stability. It is difficult to distinguish these different types of apatites using X-ray diffraction; this is because the patterns are very similar, as these apatites are isostructural and the crystals are too small to be detected photographically or by X-ray diffraction. High-resolution solid state nuclear magnetic resonance (NMR) is a sensitive local probe of atomic and molecular structure, which can be used to determine oxygen/fluorine ordering in the structure of calcium apatite. The quantitative and qualitative structural information of calcium apatites can be obtained by 1H, 19F and 31P NMR spectra.

1:50 PM

(ICACC-S5-020-2015) Computed radiography with glass ceramic imaging plates (Invited)

R. L. Leonard[1]; S. Gray[2]; R. Lubinsky[3]; R. Weber[2]; J. A. Johnson*[1]; S. Schweizer[4]; 1. UTSI, USA; 2. Materials Development, Inc., USA; 3. SUNY, Stony Brook, USA; 4. South Westphalia University of Applied Sciences, Germany

Glass-ceramic imaging plates have advantages over current commercial plates used in computed radiography. The imaging plates are synthesized as glasses, then heat-treated in order to develop $BaCl_2$ nanocrystals within the glass matrix, creating a novel glass ceramic with unique optical properties. Depending on the size and number of the embedded nanocrystals, the plates can be optically transparent in the visible spectral range and offer the potential of high spatial resolution. High spatial resolution is desirable in applications such as mammography and dental radiography. Characterization methods include differential scanning calorimetry (DSC), photoluminescence (PL), photostimulated luminescence (PSL), x-ray diffraction (XRD), Mössbauer spectroscopy, and transmission/scanning electron microscopy. Recent developments pertaining to dental radiography and portal imaging will be presented.

2:10 PM

(ICACC-S5-021-2015) Experimental approach to study the thermal induced state of stress in a medical ceramic bilayer

V. Mercurio*[1]; M. Paganelli[1]; 1. TA Instruments, Italy

An experimental study is presented to provide a simple basic analysis of the causes and key thermo-mechanical parameters of residual stress development in ceramics medical implant. For simplicity, a bilayer planar geometry is considered, that is constituted by of a veneering porcelain and tetragonal zirconia (Y-TZP). A novel non-contact optical based instrument was adopted to measure the thermal expansion as well as the deflection upon heating of the bilayer fabricated from these two materials. This non-contact technique enables the thermal behavior below and above the glass transition temperature (Tg) of the porcelain to be determined and the coupling attitude of the materials to be evaluated. The approach is then used to investigate the influence of cooling rate during initial fabrication of the porcelain-zirconia bilayer upon the subsequent heating and cooling. Breaking off the acquisition before the dilatometric softening in order to avail any plastic deformation of the sample and following the cooling process also, the optical dilatometer allowed in fact to study the thermal expansion dependence on the prior thermal history. The observations of the bilayer deflection enable the crucial role of the neo-formation interface between the layers to be investigated and its effects upon cooling to be analyzed.

2:30 PM

(ICACC-S5-022-2015) New biomimetic strategies for regeneration of load-bearing bones (Invited)

S. Sprio*[1]; M. Dapporto[1]; S. Panseri[1]; A. Tampieri[1]; 1. National Research Council of Italy, Italy

The regeneration of load-bearing bone parts is a clinical need of great relevance, also due to the progressive ageing of the world population. In this respect, it is highly desirable to develop bioactive devices enabling early sustain of critical bone defects and extensive bone formation and penetration, so to soon recover the original biomechanical performances. In this respect calcium phosphates are elective biomaterials for bone regeneration; however they are characterized by insufficient mechanical strength to manage the biomechanical loads. In this respect, new bioactive composites can be designed to associate the good osteogenic character of CaPs to the high mechanical strength of titanium dioxide providing a suitable increase of fracture strength and toughness. On the other hand, injectable apatitic bone cements (CPCs) provide bone-like composition and do not induce any drawbacks related to the use of acrylic cements. Strong limitation to the use of CPCs is the insufficient porosity limiting new bone penetration as well as the weak mechanical strength. In this respect, the addition of bio-erodible polymers to cement precursors enables fast and increased penetration of the new bone and suitable osteointegration. These new devices can function as injectable regenerative scaffolds that can be used in a number of clinical cases where the implantation of 3D devices is hard to perform.

2:50 PM

(ICACC-S5-023-2015) Nano-sized calcium phosphate particles with varied morphology prepared in a micro-flow reactor

E. Fujii[3]; K. Kawabata[3]; Y. Shirosaki[2]; Y. Nakamura[1]; S. Hayakawa[4]; A. Osaka*[1]; 1. Okayama University, Japan; 2. Kyushu Institute of Technology, Japan; 3. Industrial Technology Center of Okayama Prefecture, Japan; 4. Okayama University, Japan

Morphology control of calcium phosphate (CP) crystallites is one of the hot topics since their shape, size, or specific crystallographic facets exposed to the moiety are significant factors for adsorption of physiological substances like proteins, DNA's, amino acids, and so forth. Moreover, CP's crystallize in a few forms other than hydroxyapatite (HAp), all of which can be converted to HAp under proper conditions. The resultant HAp crystallite morphology may follow that of the original particles, that is, those are topotaxically correlated to each other. The present study proposes a small-size continuous flow type reactor for controlling the morphology of those CP crystallites due to the reaction temperature and pH under a fixed supply rate for the calcium and phosphate ion source solutions. At pH 6, brushite (CaHPO4.2H2O) was the primary phase, in the range 0° to 40 °C, with a little amount of octacalciumphosphate (OCP), and OCP became the primary one at 60 °C with trace OCP. The CP particles whose X-ray diffractions were assignable to HAp papered only at 80°C or higher. The particles were all thin plate-like at pH 6 and 40°C, while they were needle-like at pH 9 and 40 °C.

3:30 PM

(ICACC-S5-024-2015) Effect of Na+/Mg2+ dopant ions on β→α phase transition of TCP bioceramics

M. Frasnelli*[1]; R. S. Pillai[1]; D. Cabiddu[1]; V. M. Sglavo[1]; 1. University of Study of Trento, Italy

The thermal behavior of tricalcium phosphate – TCP to be used as potential biomaterial was investigated in the present work. In particular, the reconstructive β→α phase transition which is associated to evident volume change was analyzed in detail, it being involved in many processing procedures. The aim of the present work is to determine the useful conditions to avoid, after cooling, the stabilization of the weakly bioactive α-TCP phase and to evaluate the influence of doping ions such as Mg2+ and Na+. Moreover, an annealing treatment, to reconvert metastable α to β, was proposed and kinetically evaluated. Na/Mg-doped TCP powders were synthesized by solid state reaction. Bulk samples produced by uniaxial pressing the synthetized powders were analyzed by calorimetry and dilatometric analysis. The influence of doping ions on β→α kinetic was evaluated by fast cooling the samples after annealing at 1300-1600° C. Crystalline phases evolution was studied by XRD. The obtained data point out that β→α transition temperature depends on dopant content (Mg2+ better than Na+), this affecting the sintering behavior of TCP: the presence of dopants allows better densification above 1400°C. Regarding transition's kinetics, in addition, the presence of Mg/Na ions decreases the β→α rate conversion upon heating, while it promotes α→β reconversion after moderate cooling and, especially, after an annealing treatment.

3:50 PM

(ICACC-S5-025-2015) Simultaneous Testing of Calcite, Vaterite and Aragonite in Lac-SBF at 37 C (Invited)

C. Tas*[1]; W. M. Kriven[1]; A. S. Madden[2]; 1. University of Illinois, USA; 2. University of Oklahoma, USA

Conventional SBF (simulated/synthetic body fluid) solutions are buffered at pH 7.4 and 37°C by using 50 mM Tris ((HOCH2)3CNH2). Tris is not present in human blood or metabolism and its high concentration makes it the third major component of SBF solutions. All three crystalline polymorphs of calcium carbonate (calcite, aragonite and vaterite) have never been tested simultaneously in an SBF solution. This study presents the SBF-testing of the particles of these polymorphs at 37°C in a Na-L-lactate (22 mM)-buffered Lac-SBF solution. While the calcite rhombohedra remained completely inert in the solution, vaterite spherulites and aragonite needles accrued apatitic CaP (calcium phosphate) deposits on their surfaces. Mg-doped (1050 ppm) synthetic aragonite particles did not transform into calcite for 96 h in the Lac-SBF solution while increasing their BET surface area by about 560% via the apatitic CaP deposits. Given the well-established use of calcite powders in CaP cement formulations, synthetic aragonite particles may be a potential replacement for calcite due to their rapid response to blood plasma-like solutions in between 24 and 48 h at 37°C.

4:10 PM

(ICACC-S5-026-2015) Processing techniques and Characterizations of metastable biomimetic nanocrystalline apatites: Towards a new generation of calcium phosphate coatings and ceramics (Invited)

D. Grossin*[1]; E. Kergourlay[1]; F. Brouillet[1]; C. Drouet[1]; G. Bertrand[1]; C. Rey[1]; 1. Université de Toulouse, France

Biomimetic nanocrystalline apatites analogous to bone mineral can be prepared by different ways. These non-stoichiometric compounds possess a high reactivity related to the presence of a metastable hydrated layer on the surface of the nanocrystals. The processing of such unstable phases by conventional techniques at high temperature strongly alters their physico-chemical and biological properties. Therefore, several low temperature routes have been investigated taking advantage of the structural characteristics of these compounds. Spark plasma sintering (SPS), Matrix Assisted Pulsed Laser Evaporation (MAPLE), Cold-spray and others processes have been developped. These techniques produce coatings or ceramics retaining most of the characteristics of the nanocrystals. The mechanism is thought to implicate the high mobility of ions within the hydrated layer. This communication will summarize the most recent advances in preparations and characterizations of a new generation of resorbable highly-reactive biomaterials.

4:30 PM

(ICACC-S5-027-2015) Effect of grain boundary segregation on the hydrothermal degradation of Y-TZP

F. Zhang*[1]; K. Vanmeensel[1]; M. Inokoshi[2]; B. Van Meerbeekb[2]; I. Naert[2]; J. Vleugels[1]; 1. KULeuven, Belgium; 2. KU Leuven - University of Leuven, Belgium

Objective: To assess the influence of rare-earth oxide additions on the hydrothermal degradation and grain-boundary segregation of Y-TZP ceramics. **Methods:** Different rare-earth oxides with different cation radius were chosen to dope 3Y-TZP ceramics. The grain-boundary segregation of the doped cation and the grain growth of zirconia was studied by STEM-EDS and SEM, respectively. Ceramics were subjected to accelerated hydrothermal degradation at 134°C, and the hydrothermally induced phase transformation was assessed by X-ray diffraction and micro-Raman spectroscopy to evaluate the degradation kinetics. **Results:** The degradation resistance of 3Y-TZP ceramics can be significantly improved by doping the ZrO_2 grain boundary with a small amount of trivalent cations. Nd_2O_3-doped 3Y-TZP for example was more hydrothermally stable than Sc_2O_3-doped 3Y-TZP, and Nd^{3+} was found to have segregated at the ZrO_2 grain boundary, whereas Sc^{3+} was not. Furthermore, a doping element with larger ionic radius resulted in a higher degradation resistance because of the finer microstructure. The addition of 0.2-0.6 mol% rare-earth oxides to a 3Y-TZP allowed to combine an excellent fracture toughness, fracture strength and hydrothermal degradation resistance. **Conclusion:** The hydrothermal degradation behaviour of rare-earth oxide doped 3Y-TZP ceramics is dominated by the grain size and the atomic structure of the grain boundaries.

4:50 PM

(ICACC-S5-028-2015) Fabrication and Characterization of Nano Bioglass -Ceramic Scaffold for Bone Tissue Engineering

A. K. Sampath*[1]; H. Tripathi[1]; S. P. Singh[1]; R. Pyare[1]; V. Sri Sravya[1]; M. Vyshali Nanda[1]; 1. Indian Institute of Technology(BHU), India

Fabrication of multifunctional scaffolds having good mechanical strength, tailored porosity, bioactivity and drug delivery ability is of great importance for bone tissue engineering. Bioactive glass (BG) with a system of SiO2–Na2O–CaO–P2O5-Ag2O-SrO was prepared by sol–gel method with different proportions of sucrose addition to develop porosity. The thermal behavior of the sample was analyzed using DTA and TGA. The sample was sintered at different temperatures to get optimum densification and the formed crystalline phases were identified using XRD. The morphology and structure of the prepared scaffolds were characterized by SEM and FTIR. Bioactivity of this glass was measured by the immersion of the sample in SBF for different time periods. The formation of hydroxy carbonate apatite layer was identified by FTIR, SEM and XRD which showed the presence of HCA as the main phase in the bioglass sample. The human blood compatibility of the sample was evaluated by hemolysis. The Young's modulus and compressive strength of bioglasses have been measured. Cell attachment, spreading and proliferation on the sample was determined using Human osteosarcoma MG-63 cells. The bioactivity, porosity, mechanical properties and biocompatibility of the glass samples make it a good potential prospect in the area of tissue engineering.

5:10 PM

(ICACC-S5-029-2015) Mesoporous bioactive glass particles and their potential for bone regeneration (Invited)

C. Vitale-Brovarone*[1]; 1. Politecnico di Torino, Italy

Mesoporous bioactive glass are amazing material with unique surface texture and enhanced bioactivity, due to their very high surface area. They are promising and attractive biomaterials for many different applications, including bone regeneration and drug delivery. Spherical mesoporous bioactive glass particles, of a few microns in size, have be efficiently obtained through the spray-drying technique. An injectable radiopaque cement for vertebroplasty applications can be obtained by combining a calcium sulfate hemihydrate matrix, spherical mesoporous bioactive glass particles and a radiopaque glass-ceramic phase. Vertebroplasty is a percutaneous procedure in which a cement is injected in a fractured vertebra to consolidate it and to relieve the pain. Vertebral compression fractures are one of the most frequent osteoporosis-related diseases, especially in post–menopausal women and so, an injectable cement with enhanced bioactivity, holds a great potential in this field.

S7: 9th International Symposium on Nanostructured Materials: Innovative Synthesis and Processing of Nanostructured, Nanocomposite and Hybrid Functional Materials for Energy, Health and Sustainability

Solution Synthesis, Functionalization and Assembly of Metal Oxide Nano-materials III

Room: Coquina Salon B

Session Chair: Mohamed Siaj, UQAM

1:30 PM

(ICACC-S7-040-2015) Nanostructured metal oxides by wet chemical synthesis with applications for energy and health (Invited)

A. Hardy*[1]; M. K. Van Bael[1]; 1. Hasselt University and imec division imomec, Belgium

Metal oxides are characterized by dielectric, ferroelectric, multiferroic, magnetic, conducting, semiconducting, optical etc. properties. Thus, many applications such as oxide electronics, energy generation and storage, health care etc have adopted metal oxide materials as device components. Nanosized oxides either can have improved functionality or totally new, interesting properties. Wet chemical synthesis routes have as advantages: low cost, short synthesis times and compositional flexibility. Here, recent results are reviewed concerning metal oxide nanoparticles and thin films from sol-gel, hydro/solvothermal, precipitation and thermal decomposition syntheses. To understand the precursor and its reaction into the oxide, both dictating the final properties, we applied XRD, SEM, AFM, FTIR, Raman, UV/Vis and NMR spectroscopy, high resolution TEM, as well as electrochemical and physical characterization. This will be exemplified by studies of (doped) mono-metal oxides (e.g. ZnO, TiO2) and multi-metal oxides (high-k oxides, multiferroics, ferroelectrics, electrodes and electrolytes for LIB etc.) with possible applications in solar cells, data storage devices, lithium ion batteries, biomedical imaging etc. These in-depth studies are vital to finetune compositions and process conditions to provide optimal materials for their final applications.

2:00 PM

(ICACC-S7-041-2015) Synthesis Strategies for the Low-Temperature Processing of Functional Oxide Thin Films by Advanced Solution Methods (Invited)

I. Bretos*[1]; R. Jiménez[1]; J. Ricote[1]; M. Calzada[1]; 1. ICMM-CSIC, Spain

Fabrication of high-performance, metal oxide layers has traditionally demanded high annealing temperatures that limit their integration in emerging technologies for large-scale, flexible electronics on plastic. Amorphous oxide semiconductors have recently shown processing temperatures compatible with polymeric substrates (<400°C), but this remains elusive for metal oxides whose functionality relies on long-range crystalline order (e.g., polar oxides). During the last decade, significant efforts have been devoted in our group to address this challenge. The result is the development of an efficient series of synthesis strategies for the low-temperature processing of crystalline oxide layers. All of them consist in different low-cost, highly versatile solution approaches such as those based on Photochemical Solution Deposition, either implemented with the use of high-photosensitivity metal complexes or combined with other low-temperature methods. Here, the main features of these strategies will be shown for the ferroelectric $PbZr_xTi_{1-x}O_3$ and multiferroic $BiFeO_3$ perovskites. Emphasis will be placed on our last innovative approach; the synthesis of low-temperature liquid precursors by heterogeneous photocatalysis. The multifunctional properties of these films foresee their potential application in transduction and sensing to photovoltaics and electronic skin.

2:30 PM

(ICACC-S7-042-2015) Modeling molecular precursors conversion to advanced materials (Invited)

G. Tabacchi*[1]; 1. University of Insubria, Italy

Molecule-to-material conversion in bottom-up fabrication routes is usually a multi-step process involving several complex and environment-dependent chemical phenomena. Lack of molecular-detail knowledge of these largely unexplored events still prevents a rational control of the composition and organization of the resulting nanosystems. Modeling may play a key role in bridging this gap by providing microscopic level insight on molecular precursors and high temperature conversion processes, which could be particularly crucial for Chemical Vapor Deposition routes to supported functional nanomaterials. Herein, we show how theoretical studies, especially when combined with experiment, can shed light on fundamental steps of such processes, like precursor adsorption/activation, decomposition and bonding to the growth surface. Open issues and challenges in the field will be also highlighted by presenting recent results and current research work, focusing in particular on the deposition of first row transition metal oxides. Possible directions for future developments will also be discussed.

Metal Oxide Nanostructures for Chemical and Biological Sensors

Room: Coquina Salon B

Session Chairs: An Hardy, Rutgers University; Gloria Tabacchi, University of Insubria

3:20 PM

(ICACC-S7-043-2015) Simultaneous Detection of Glucose, Cholesterol and Urea with Integrated ZnO Nanorods Field-Effect Transistor Array Biosensors (Invited)

R. Ahmad[1]; D. Jung[1]; Y. Hahn*[1]; 1. Dept of Earth and Envron Sci, Korea (the Republic of)

There is an urgent requirement for development of integrated/hybrid biosensor devices capable of simultaneous detection of clinically important multi-analytes coupled with high sensitivity, excellent selectivity, fast response and cost benefits. Here, for the first time, we report a novel approach for simultaneous detection of glucose, cholesterol and urea with integrated ZnO nanorods field-effect transistors (FETs) array biosensors. Key to our sensor design is an integrated approach capable of simultaneous and highly selective detection of biomolecules without any interference in each sensor response. Furthermore, the FETs-based biosensor successfully used for the determination of glucose, cholesterol and urea concentrations in whole mice blood samples. Interestingly, the concentrations determined by the biosensor for glucose, cholesterol and urea were well matched with those of the pre-analytically determined results. Thus, the ZnO nanorods FETs array biosensor has a great potential to become a useful tool not only for biomedical research but also for patients suffering from glucose, cholesterol, and urea related disorders or diseases. The development of an integrated, low-cost biosensor will yield real-time detection under critical patient conditions, early identification of disease and disorder, and have an enormous impact on the future generations.

3:50 PM

(ICACC-S7-044-2015) Catalyst loaded micro-reactors: A new nano/micro-architecture for highly selective metal oxide gas sensors

J. Yoon*[1]; Y. Hong[2]; Y. Kang[1]; J. Lee[1]; 1. Korea University, Korea (the Republic of); 2. Konkuk University, Korea (the Republic of)

Metal oxide semiconductors are good material platforms for environmental monitoring. However, selective detection of a specific gas still remains a challenge. In this contribution, we suggest that catalyst-loaded micro-reactors (yolk-shell structures), which consist of movable core and multi-shells with uniformly loaded catalyst, are new nano/micro architectures to achieve selective and sensitive detection of a gas. The Pd- and Ag-loaded SnO2 micro-reactors were prepared by ultrasonic spray pyrolysis and their gas sensing characteristics were investigated. The Pd-loaded SnO2 micro-reactors exhibited high selectivity and response to methylbenzenes and Ag-loaded SnO2 micro-reactors showed ultra-high selectivity and response to hydrogen sulfide, respectively. These unprecedentedly high selectivity and gas response, which can be hardly achieved by simple loading of noble metal catalysts on oxide nanostructures, were attributed to the synergetic combination between micro-reactor with semi-permeable thin shells and noble metal catalyst.

4:10 PM

(ICACC-S7-045-2015) One-step In-Situ Core Shell Graphene-Nanoparticles Growth by Chemical Vapor Deposition for Biosensing applications (Invited)

M. Siaj*[1]; 1. UQAM, Canada

A one-step in situ route to free standing core-shell metal or carbide nanoparticles on graphene will be presented. The core-shell nanoparticles-graphene (NP-Gr) growth was realized by a simple chemical vapor deposition process. The NPs-graphene resulting devices are examined as electrode material for electrochemical biosensing applications. We report here a facile strategy for the covalent functionalization of NPs-graphene by electrochemical reduction of carboxyphenyl diazonium salt prepared in situ in acidic aqueous solution. We will show that the number of grafted carboxyphenyl groups on NPs-graphene surface can be controlled by the number of cyclic voltammetry (CV) scans. The fabrication and characterization of an immunosensor based on immobilization of ovalbumin antibody on the NPs-graphene surface will be presented. The percentage change of charge-transfer resistance (Rct) after binding shows a linear response with the ovalbumin concentrations, with a detection limit of 0.9 pgmL−1. Our results indicate good sensitivity of the developed functionalized CVD NPs-graphene platform, which opens the way for use of CVD NPs-monolayer graphene electrodes in a wide range of electrochemical biosensing devices.

4:30 PM

(ICACC-S7-046-2015) Wet chemical synthesis of WO_3 quantum dots and gas sensing enhancement by surface oxygen vacancies

M. Epifani*[1]; E. Comini[2]; R. Diaz[3]; T. Andreu[4]; A. Genç[5]; J. Arbiol[5]; P. Siciliano[1]; G. Faglia[2]; J. R. Morante[4]; 1. CNR-IMM, Italy; 2. SENSOR Lab, Brescia University and CNR-INO, Italy; 3. IMDEA Energy Institute, Spain; 4. Institut de Recerca en Energia de Catalunya (IREC), Spain; 5. Institut de Ciència de Materials de Barcelona, ICMAB-CSIC, Italy

We report for the first time the synthesis of monoclinic WO_3 quantum dots. A solvothermal processing at 250 °C in oleic acid of W chloroalkoxide based solutions was employed. It was shown that the bulk monoclinic crystallographic phase is the stable one even for the nanosized regime (mean size 4 nm). The nanocrystals were characterized by X-ray diffraction, High resolution transmission electron microscopy, X-ray Photoelectron spectroscopy, UV-Vis, Fourier transform infrared and Raman spectroscopy. It was concluded that they were constituted by a core of monoclinic WO_3, surface covered by unstable W(V) species, slowly oxidized upon standing at room conditions. The WO_3 nanocrystals could be easily processed to prepare gas-sensing devices, without any phase transition up to at least 500 °C. The devices displayed remarkable response to both oxidizing (nitrogen dioxide) and reducing (ethanol) gases in concentrations ranging from 1 to 5 ppm and from 100 to 500 ppm, at low operating temperatures of 100 and 200 °C, respectively. The analysis of the electrical data showed that the nanocrystals were characterized by reduced surfaces, which enhanced both nitrogen dioxide adsorption and oxygen ionosorption, the latter resulting in enhanced ethanol decomposition kinetics.

4:50 PM

(ICACC-S7-047-2015) Electrophoretic deposition of ZnO film and effect of UV light on Surface wettability

A. K. Singh*[1]; U. T. Nakate[2]; 1. Armament Research and Developement Establishment, India; 2. Defence Institute of Advanced Technology, India

We report Electrophoretic deposition (EPD) of ZnO film on steel substrate using microwave synthesized ZnO nanoparticles(NPs). Synthesized ZnO NPs and film were characterized using XRD, SEM, EDS, UV-Vis spectroscopy, respectively, for their structural and morphological, elemental and optical behaviour. On UV light irradiation ultra-hydrophobic ZnO film switches to superhydrophilic. The contact angle of the as deposited ZnO film was found to be 145 deg and decreased to 7 deg with UV light exposure. The mechanism of UV effect on wettability has been analyzed. Roughness of the ZnO film was calculated and was found to be 2.184. The ZnO film changes from ultra-hydrophobic to superhydrophilic on exposure to UV light. The reversible super-hydrophobic-super-hydrophilic transition of the of ZnO films under the alternation of UV irradiation and dark storage was also analysed. This process has been repeated several times, and good reversibility of the surface wettability was observed. From the above results, it can be concluded that the reversible switching between super-hydrophilicity and super-hydrophobicity is governed by surface chemical composition and the surface roughness. The reversible conversions of the surface wettability proceed only by the adsorption and desorption of surfacehydroxyl groups at the outermost layer of oxide films.

5:10 PM

(ICACC-S7-048-2015) Highly Sensitive Graphene Electrochemical Sensor for Detecting Colourants in Food

K. Huang*[1]; J. Ting[1]; 1. National Cheng Kung University, Tainan, Taiwan, Taiwan

The use of graphene in electronchemical sensor for detecting colourants is reported. Graphene was first obtained using a chemical vapor deposition technique. The resulting graphene has a controllable number of layers, which is critical for use in electrochemical sensors. The obtained graphene was characterized using atomic force microscopy, scanning electron microscopy, transmission electron microscopy and Ranman spectroscopy. Selected graphene was then fabricated into graphene field effect transistor (G-FET). Cyclic voltammetry and differential pulse voltammetry test were carried out to examine the sensing performance. The performance was correlated to the characteristics of the graphene and improvement of the sensitivity was then achieved.

S8: 9th International Symposium on Advanced Processing and Manufacturing Technologies for Structural and Multifunctional Materials and Systems (APMT9)

Advanced Composite Manufacturing

Room: Coquina Salon A
Session Chairs: Shaoming Dong, Shanghai Institute of Ceramics, Chinese Academy of Sciences; Vojislav Mitić, Serbian Academy of Sciences

1:30 PM

(ICACC-S8-054-2015) Mechanical properties and plasma sputtering resistances of textured h-BN ceramic composites (Invited)

Y. Zhou*[1]; X. Duan[1]; D. Jia[1]; N. Jing[1]; Z. Tan[1]; Z. Yang[1]; S. Wang[1]; 1. Harbin Institute of Technology, China

Textured hexagonal boron nitride ceramic composites were fabricated by hot-press sintering with different sintered pressures, and mullite was used as the sintered additive. The mechanical properties along different directions of the sintered samples were measured, which showed the textured h-BN ceramic composites were obviously anisotropy. Furthermore, the fracture mechanisms were also explained according to the fractographs. The plasma sputtering experiments were tested under the Xe plasma flow generated by Hall thruster, and the sputtering yields were calculated by the mass change. The sputtering yields parallel and perpendicular the h-BN layers are almost same, but significantly depend on the relative density and the sintered pressures. The phase compositions of textured h-BN ceramic composites kept stable during the plasma sputtering. There are two main material damage mechanisms during the plasma sputtering. One is the B-N bonds were broken, the other is the whole grains separated from the surface.

2:00 PM

(ICACC-S8-055-2015) Multi-scale enhanced C/SiC composites with one dimension nano structure (Invited)

S. Dong*[1]; J. Hu[1]; Y. Kan[1]; 1. Shanghai Institute of Ceramics, Chinese Academy of Sciences, China

Carbon fiber reinforced SiC ceramic matrix composites (C/SiC) show low density, high strength at room and high temperature, good oxidation and ablation resistance, which make them attracting materials potentially applied in aerospace, nuclear energy and transportation. However, the ceramics matrix in C/SiC composites often exhibits brittle fracture behavior at microscale. Transverse cracks propagate easily through fiber bundles perpendicular to the direction of stress or interlaminar matrix. To strengthen the weak area in the composites, one dimension nano structures (Carbon nano tubes and SiC nano wires) are introduced into the C/SiC composites acting as the second reinforcements in present study. Hybrid reinforcements are prepared via growing one dimension nano structures in situ on carbon fiber by chemical vapor deposition method. Effect of growing parameters on microstructure and distribution of the nano structures are investigated. Composites with multi scale structure are fabricated using the hybrid reinforcements. The influences of interface and processing method on the mechanical properties are discussed. The strengthen mechanism, relationship between

toughness and strength are analyzed. Designed material performance can be realized by tailoring the microstructure of carbon fiber reinforced silicon carbide composites.

2:30 PM

(ICACC-S8-056-2015) Development of Particle Dispersion Novel Silicon Carbide Composites

T. Hinoki*[1]; K. Shimoda[2]; 1. Kyoto University, Japan; 2. National Institute for Materials Science, Japan

Silicon carbide (SiC) is one of very attractive engineering ceramics in particular for high temperature use due to high temperature strength, oxidation resistance, chemical stability and so on. Silicon carbide composites basically require weak fiber/matrix interphase like carbon (C) or boron nitride (BN). The interphase material and its thickness are keys to determine material properties. However precise control of the interphase is the critical issue in particular for large scale production and affect material cost significantly. The objective of this work is to develop novel SiC composites without fiber/matrix interphase by applying particle dispersion SiC matrix. Silicon carbide composites were fabricated by CVI method and LPS method. Silicon carbide with C matrix was formed by mixture of SiC source gas and C source gas in CVI composites. Silicon carbide with BN matrix was formed by mixture of SiC powder and BN powder in LPS composites. Mechanical properties were characterized by tensile test and flexural test. Microstructures were characterized by FE-SEM. Both SiC composites with C and with BN in matrix showed ductile fracture behavior without fiber/matrix interphase. The tensile strength of 2D-CVI composites with C was approximately 260 MPa. The flexural strength of UD-LPS composites with BN was approximately 500 MPa.

2:50 PM

(ICACC-S8-057-2015) Optimization of porous SiC/SiC composites fabricated by liquid phase sintering

S. Maeta*[1]; T. Hinoki[1]; 1. Kyoto University, Japan

Porous silicon carbide composites reinforced with silicon carbide fibers (porous SiC/SiC composites) are novel materials which simply consist of SiC fibers and porous SiC matrix. Porous SiC/SiC composites can be used at high temperature in air atmosphere because of no fiber/matrix interface layer like carbon. In previous study, considering industrial application, a low-cost and simple, reproducible manufacturing process for the porous SiC/SiC composites was developed using green sheet. In this research, experimental conditions, for example temperature or holding time, were controlled from view point of matrix control in order to optimize porous SiC composites. Porous SiC materials fabricated by each condition are compared and selected. Optimized porous SiC composited were developed.

3:30 PM

(ICACC-S8-058-2015) One-step mechanical processing to prepare LSM/ScSZ composite particles for SOFC cathode

A. Kondo*[1]; E. Nakamura[1]; T. Kozawa[1]; M. Naito[1]; 1. Osaka University, Japan

Novel one-step mechanical processing was proposed to prepare LSM/ScSZ composite particles for SOFC (Solid oxide fuel cell) cathode. Using an attrition type milling apparatus, LSM (strontium doped lanthanum manganite) nano particles were mechanically synthesized from the starting raw powders and the synthesized LSM particles were directly bonded with ScSZ (scandia stabilized zirconia) fine particles during the same processing. As a result, LSM/ScSZ composite particles were obtained by only 10min mechanical processing using three kinds of raw powder materials of LSM and ScSZ fine particles without extra heat. The resultant powders were used for fabrication of the cells to evaluate electrochemical properties. At the volume ratio (LSM:ScSZ = 50:50), the polarization resistance of the cathode made by the composite particles was lower than that made by using commercially available LSM nanosized powder. By TEM-EDX analysis, very fine composite structures consisted of several 100 nm size LSM and ScSZ grains were observed in the cathode layer. It suggests that the proposed method is very simple and energy-saving way to prepare high quality composite particles used for SOFC cathodes.

3:50 PM

(ICACC-S8-059-2015) Si3N4/SiC self-healing ceramic nanocomposites

K. Krnel*[1]; L. Gruden[1]; T. Kosmac[1]; 1. Jozef Stefan Institute, Slovenia

Self-healing ceramics are a group of self-healing materials, whose main characteristic is their ability to repair itself in its typical working environment. Si3N4/SiC composite was chosen as our material of interest due to its desired material properties, which would make such a material applicable in many engineering solutions. The key to designing ceramics with self-healing properties is the presence of silicon carbide, which is responsible for crack healing effect during the high temperature oxidation process. High temperature oxidation is most efficient when the SiC is present in a form of a nanoparticles which are evenly distributed through material and due to their small size enable the oxidation process to start at lower temperatures. The silicon nitride ceramics with dispersed SiC nanoparticles was prepared by mixing the Si3N4 powder with polycarbosilane polymeric ceramic precursor, which forms SiC after pyrolysis. The powders were successfully densified using spark plasma sintering machine (SPS), while the size of the SiC particles remained in the nano scale due to high heating rates and fast densification process. Synthesized materials exhibit better oxidation properties (and possible self-healing ability) compared to conventionally prepared Si3N4/SiC composites. We will report on the synthesis, material properties, microstructure and self-healing properties of the Si3N4/SiC ceramic composite.

4:10 PM

(ICACC-S8-060-2015) Fractal aspects of the Coble's model corrections

V. Mitić*[2]; V. Paunovic[1]; V. Pavlovic[2]; L. Kocic[1]; 1. University of Nis, Serbia; 2. Serbian Academy of Sciences, Serbia

The structure of rare earth doped BaTiO3 materials can be controlled by using different sintering parameters. Sintering process is a complex of different synergetic effects during the ceramics materials consolidation. The microstructural level properties control is very important as a stage in advanced materials prognosis. Coble's two-sphere model is used as initial one for developing a new two-ellipsoid model. Ellipsoidal geometry can better approximate sintering particles than spherical. The relations connecting geometric parameters of the ellipsoidal model with consolidation parameters-sintering time and temperature are established. In this paper, the grains contact models based on spherical, ellipsoidal and polyhedral geometries are presented. Intergranular impedance analysis of grains clusters and fractal method was also introduced. Fractal method traces a new approach for analysis the structure of ceramics and describing and prognosis and modeling the grains shape and relations between BaTiO3-ceramics structure and dielectric properties. These fractal effects and fractal materials nature have been used for better understanding interrelation between structural and electrical parameters.

4:30 PM

(ICACC-S8-061-2015) Ti doped alumina dispersion strengthening copper prepared using internal oxidation at ambient atmosphere

S. Han*[1]; S. Lim[2]; B. Han[3]; K. Kim[4]; 1. Korea Institute of Materials Science, Korea (the Republic of); 2. Kangwon National University, Korea (the Republic of); 3. Daegu Kyungbook Institute of Science and Technology, Korea (the Republic of); 4. Pusan National University, Korea (the Republic of)

In the present work, the alumina and Ti doped alumina dispersed copper matrix composite were fabricated by internal oxidation at ambient atmosphere as a simulation experiment prior to conventional consolidation process. The small amount of aluminum solutionized copper and aluminum and titanium solutionized copper were oxidized at 980oC at ambient atmosphere. The fine (~30nm) and homogeneously distributed sphere type alumina were obtained during the oxidation of copper with Al and Ti, because that Ti atom was doped to alumina with introducing extra stable interface between oxide and copper matrix. The average particle size and inter-distance between particles in the matrix were decreased, and it leads simultaneous increasing strength and conductivity, although which is it's trade-off property. The microstructure of Ti doped alumina dispersed copper composite was investigated by HRTEM and why alumina in the copper matrix was spherodized were predicted by first principle calculation.

4:50 PM

(ICACC-S8-062-2015) Simple Synthesis Technique for Production of Boron Nitride Nanotubes

J. Hurst*[1]; 1. NASA Glenn Research Center, USA

Boron nitride nanotubes (BNNT) are promising materials which offers many of the advantages of carbon nanotubes, e.g. high strength and light weight, while also providing the additional advantage of much greater thermo-oxidative stability. This material is also of interest for radiation protection as well as many thermal management applications due its unique high thermal conductivity and low electrical conductivity. Progress in developing products utilizing BNNT is hampered as BNNT has proven difficult to produce in sufficient quantities. A variety of synthesis techniques have been attempted, however many have proven to be difficult to scale-up due to poor BNNT reproducibly and/or expense. A simple, inexpensive, and reproducible way to synthesize boron nitride nanotubes (BNNT) in a method which is easily scalable to large quantities in a batch method or continuous processing method is discussed.

5:10 PM

(ICACC-S8-063-2015) Enhanced Spinodal Phase Separation of SnO_2-TiO_2 Ceramics by Iron Doping and their Electrical Properties (Invited)

T. Sekino*[1]; T. Kusunose[2]; S. Tanaka[3]; 1. Osaka University, Japan; 2. Kagawa University, Japan; 3. Tohoku University, Japan

SnO_2-TiO_2 binary ceramic is well known to exhibit a solid solution over 1430°C and to form a spinodal phase separation with lamellar structure by annealing within its immiscibility region. This self-organized composite structure has a large heterogeneous interface area in its bulk form, and thus it is regarded to act as "functional interface" in ceramic materials. We have challenged multidisciplinary controls of spinodal phase separation-originated microstructures and materials electrical properties . It was found that doping of Fe^{3+} to SnO_2-TiO_2 accelerated spinodal phase separation; the Fe-doped system exhibited the lamellar just after the sintering over 1360°C. This phenomenon was considered due to the increase of miscibility region of the system by the Fe^{3+} incorporation. The lamellar was formed by the Ti diffusion to the SnO_2 grains at low-temperature and then mutual-diffusion of the Ti and Sn started to complete the lamellar formation at higher temperature. Electrical resistivity of the composite depended on these phase development, and decreased with the lamellar formation. Detailed microstructural development and electrical properties including semiconductive characteristics of the Fe-doped oxides as well as self-organized ceramic composites will be discussed.

S9: Porous Ceramics: Novel Developments and Applications

Applications of Porous Ceramics I

Room: Coquina Salon H
Session Chair: Alberto Ortona, SUPSI

1:30 PM

(ICACC-S9-033-2015) Treatment of Produced Water Using Silicon Carbide Membrane Filters (Invited)

A. K. Bakshi*[1]; 1. Saint-Gobain, USA

Large quantities of effluent water are produced from oil and gas wells during exploration and production stages. The produced water from oil and gas wells contain significant amount of hazardous material and are typically disposed of in abandoned oil wells or re-injected into operating wells. Due to growing environmental concerns and water scarcity, more attention is given to reuse this water. However, scale forming ions, bacteria and residual oil must be removed prior to re-injecting the produced water into the well. Otherwise, they reduce oil output by plugging the channels in the deposit. Current methods to remove these contaminants often use large amount of chemicals and settling tanks to condition or clean the water. These methods are often expensive and use large footprints which are scarce in the vicinity of the wells. Silicon carbide membrane filters have shown good results in filtering produced water. They use small footprint and effectively remove bacteria, suspended solids and residual oil in simple steps. SiC filters have shown high flux compared to polymeric and other ceramic filters. They exhibit good abrasion and corrosion resistance, are easily cleaned with any chemical and do not exhibit fouling tendencies. In this article, different filter designs and process parameters are discussed which increase separation efficiency and flux of SiC filters.

1:50 PM

(ICACC-S9-034-2015) 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/mK 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.

2:10 PM

(ICACC-S9-035-2015) Titanium oxide-based ceramic catalysts: processing and applications

E. Medvedovski*[1]; 1. Endurance Technologies Inc., Canada

Titanium oxide-based ceramics can be successfully used as a catalyst for the selective catalytic reduction of nitrogen oxides (deNOx processes) in the coal and biomass combustion processes and some other processes of power generation to minimize environmental issues. The catalysts with the honeycomb shape provide the highest efficiency in terms of the NOx conversion due to high contacting surface, uniform gaseous flow and lower pressure drop. TiO2 of the anatase form in a combination of small amounts of V2O5, WO3 and some other oxides should be used due to the highest catalytic activity and contact surface area and durability in the presence of poisoning S-contained gases; however, in this case, the thermal treatment of the products should be conducted at rather low temperatures (below 700oC). Some features of the preparation of the porous TiO2-based (anatase) ceramics and of the formation of the monolithic honeycomb-shape products from these ceramics will be discussed.

2:40 PM

(ICACC-S9-036-2015) The development of porous ceramics for waste heat reduction

Y. Tanaka*[1]; S. Sasaki[1]; A. Matsuyama[1]; T. Ebi[1]; 1. Mino ceramic Co., Ltd., Japan

Ceramic thermal insulators are suitable for use as heat rejection bodies that inhibit heat transfer in many industrial applications such as industrial furnaces, chemical plants and energy storage at elevated temperatures. Improvement of the energy efficiency in these industrial applications and the prevention of heat leakage directly lead to energy saving, and has thus encouraged the development of advanced ceramic thermal insulators. In this study, for the purpose of energy-saving manufacturing process of ceramics, we introduce the high strength and high thermal insulation ceramic porous body can be expected to reduce unused heat in ceramics for firing furnace.

Applications of Porous Ceramics II

Room: Coquina Salon H

Session Chair: James Zimmermann, Corning

3:20 PM

(ICACC-S9-037-2015) Ceramics Flat-sheet Membrane for Waste Water Treatment (Invited)

A. Nakagawa*[1]; H. NOGUCHI[1]; 1. MEIDENSHA CORPORATION, Japan

Currently, membrane treatment technology using polymer materials have been widely used in field of waste water treatment. However, polymer membranes have some problems, such as product life cycle and resistance to oil and chemicals, so they cannot perform well in harsh environments such as industrial waste water treatment. On the other hand, ceramics materials have improved physical strength and resistance to oil and chemicals. These features of ceramics can solve the limitations of polymer membranes. Therefore, we have developed our Ceramic Flat-sheet Membrane (CFM) and succeeded in building the fully automated production facility which can provide both high quality and large product volumes for MEIDEN CFM element. This element is 1000 x 250 x 6mm size with 0.1µm pore on its surface. As you can see, MEIDEN CFM has high value especially for industrial waste water treatment where polymers have limited effectiveness. With appropriate control & operation methods to maintain these CFM operational features, high quality treated water can be produced, and stable water treatment operation can be obtained for a long time. We are now looking at the opportunity for Produced water treatment in Oil & Gas industry. In this time we would like to introduce our test results of OSPW treatment with MEIDEN CFM as one of the CFM application case studies and are glad to discuss further about various expected fields for MEIDEN CFM with you.

3:40 PM

(ICACC-S9-038-2015) CMC tubes with internal engineered cellular ceramics for high temperatures heat exchange applications

A. Ortona[1]; D. Yoon[2]; T. Fend*[3]; S. Gianella[4]; 1. SUPSI, Switzerland; 2. Yeungnam University, Korea (the Republic of); 3. German Aerospace Center, Germany; 4. EngiCer, Switzerland

Lightweight ceramics and fiber reinforced ceramic composites, such as non-oxide Ceramic Matrix Composites (CMCs) represent very promising solutions for high temperature applications in strategic industrial sectors, such as transport and energy. In fact, these materials are one of topical priorities of the European Technology Platform EuMAT and a strategic issue of the EC Research Roadmap on Materials. Huge market opportunities are expected for CMC provided to overcome the three major identified gaps: high cost, difficulty of processing and materials reliability. New and more efficient manufacturing technologies can pave the way to improve material quality, reduce processing time, converge towards near-net shape fabrication, trim energy spent and abate production costs. The FP7 project HELM is addressing these challenges by employing innovative high-frequency electromagnetic, microwaves (MW), heating technologies for integrating and, in the long term, replacing standard thermal processing routes for several processes among which stands Liquid Silicon Infiltration (LSI). The process is being applied in several SiSIC applications such as brake discs, antiballistic protections, as well as porous ceramics.

4:10 PM

(ICACC-S9-039-2015) Engineered ceramic laminates with improved mechanical reliability achieved by tailoring the porosity

N. Bellettati[1]; V. M. Sglavo*[1]; 1. University of Trento, Italy

Engineered porous laminates composed of alumina/zirconia were designed and produced. Samples were obtained by stacking together and cosintering green layers with a specific pore formers content prepared by tape casting water-based suspensions. Laminates with a good adhesion between layers and a homogeneous distribution of the phases were achieved. Engineered laminates showed a stress profile due to the presence of different amount of pore formers in each layer, which affected the elastic modulus of the layers generating residual stresses during the cooling phase of sintering process. Ring-on-ring biaxial flexural tests were performed on samples, also on pre-cracked ones, to verify mechanical behavior. Engineered laminates showed a T-curve behavior with a stable crack propagation, responsible for an improved mechanical reliability and also higher fracture strength with an evident insensitivity to surface defects dimensions.

4:30 PM

(ICACC-S9-040-2015) Highly porous waste-derived glass-ceramics for structural and functional applications

E. Bernardo*[1]; I. Ponsot[1]; M. Marangoni[1]; 1. University of Padova, Italy

Direct sintering of wastes, combined with recycled glasses, is a valid low-cost option for the obtainment of glass-ceramics, from wastes with limited hazardousness. Further improvements rely on the development of a homogenoues cellular structure, especially when the foaming, at moderate temperature (generally <1000°C), is operated by the same wastes, such as residues with remarkable content of iron oxides. Highly porous waste-derived glasses and glass-ceramics were found to possess a high specific strength, appreciated for the manufacturing of lightweight panels, but also interesting functional properties. Besides thermal and acoustic insulation, due to the remarkable porosity, selected cellular glass-ceramics, derived slags from Cu and Pb metallurgy, were found to exhibit a ferrimagnetic behavior. This specific feature, due to the formation of magnetite inclusions, could favor the application in electromagnetic shields (e.g. panels shielding from low frequency magnetic fields produced by power lines).

4:50 PM

(ICACC-S9-041-2015) Porous glassceramic material for building and engineering applications

J. Aderiye*[1]; 1. Federal Polytechnic Ado-Ekiti, Nigeria

Very lightweight insulating glass ceramic material is made for use in building and engineering applications. Explanations are made on the preparation of the batch material, mixing, melting and refining at 600° C temperature. Various reasons are given for the material high porosity and the batch melting reactions. Gases and other chemical oxides produced are also technically explained. The type and quality of waste glass used as basic raw material is a dependant of characteristic properties of the glassceramic material being formed at 600° C temperature. There is a correlation between the use of insulating glassceramic product; the material characteristic properties and the 600° C forming temperature. Four variable factors (raw material, melting, refining and quality of the finished product) is technically examined, explained and analysed with the required data in the research work.

S10: Virtual Materials (Computational) Design and Ceramic Genome

Ceramic Genome and Modeling of Structure and Property III

Room: Coquina Salon C
Session Chair: Yanwen Zhang

1:30 PM

(ICACC-S10-016-2015) Thermodynamic modeling and simulations for Lithium-ion batteries and their materials (Invited)

H. J. Seifert*[1]; M. Lepple[1]; D. M. Cupid[1]; C. Ziebert[1]; M. Rohde[1]; A. Melcher[1]; 1. Karlsruhe Institute of Technology, Germany

Binary and ternary compounds in Li-Mn-O and Li-Cu-O systems are electrode materials for lithium-ion batteries which are based on intercalation and conversion mechanisms, respectively. Thermodynamic models and descriptions of the ternary systems can be used to calculate the reversible open circuit voltages of electrochemical (half) cells based on electrode materials such as $LiMn_2O_4$, Li_2MnO_3, CuO and Cu_2O. Our experimentally determined thermochemical and thermodynamic data were used as key input data for CALPHAD-type system optimizations. We used ab-initio results and different types of experimental data simultaneously for model parameter determination. Based on such data and on crystallographic information, consistent and compatible analytical descriptions of the Gibbs free energies for all active (ceramic) phases in the materials systems were developed. The thermodynamics and phase diagrams of the ternary systems and coulometric titration curves for various electrochemical cells were calculated and compared with experimental information. The thermodynamic dataset and more thermophysical data were used for a combined electrochemical-thermal modeling and simulation. The temperature behavior and heat effects during the cycling of Lithium-ion batteries were simulated by using proper software packages like Matlab / Simulink and Comsol Multiphysics (Battery Module), respectively.

2:00 PM

(ICACC-S10-017-2015) An ab initio Electronic Structure and Bonding Study of Elemental Boron, Boron Rich Crystals, and Amorphous Hydrogenated Boron Carbide (Invited)

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

Elemental Boron, Boron rich crystals, and amorphous hydrogenated boron carbide (a-BxC:Hy) are complex materials that each contain hallmark icosahedral structures. There is particular interest in a-BxC:Hy because when grown as a thin film via plasma enhanced chemical vapor deposition it has a number of potential practical applications. Additionally, it serves well as a model system for the study of complex amorphous molecular materials. In an ongoing effort to model and understand the structure of a-BxC:Hy this work will discuss efforts to compute and compare the unique three center – two electron (3c-2e) bonding patterns that are seen in Boron rich materials including a-BxC:Hy. Refined models of a-BxC:Hy have been created through a customized version of the LAMMPS molecular dynamics package and the ab initio VASP package taking into account structural rules determined by an NMR spectroscopy study. Based on the models, the distribution of 3c-2e bonds are compared to and categorized against the types of 3c-2e bonds seen in elemental Boron and Boron rich materials such as α-B12, β-B106, γ-B28, and B11C-CBC (crystalline Boron carbide).

2:30 PM

(ICACC-S10-018-2015) Atomic Structure and Bonding of Metal Atoms Adsorbed on Titania Surfaces (Invited)

K. Matsunaga*[1]; 1. Nagoya University, Japan

Metal atoms on TiO_2 are important for their practical applications to catalytic systems. Especially, noble metals atoms such as Au and Pt on TiO_2 are expected to have excellent catalytic activity. It is thought that the catalytic activity is dependent on interactions between metal and oxide support. In order to understand an origin of the catalytic activity, therefore, it is essential to characterize atomic structures and bonding of metal atoms on oxide surfaces. In this study, electronic and atomic structures of metal-atom adsorption on TiO_2 were investigated by density functional theory calculations. For platinum atoms on $TiO_2(110)$, Pt adsorption sites were investigated, and it was found that the presence of oxygen vacancies on the TiO_2 surface is responsible for the energetically favorable adsorption site of Pt. Especially, Pt adsorption at the vacancy of basal oxygen atom was most stable, which was also confirmed with experimental scanning transmission electron microscopy observation. It is worth mentioning that the basal oxygen vacancy is different from the bridging oxygen vacancy that is considered as a major vacancy species on $TiO_2(110)$. Comparison with Au and other metals will also be discussed.

Integrated Materials Computational Engineering

Room: Coquina Salon C
Session Chairs: Gerard Vignoles, University Bordeaux; Romana Piat, Karlsruhe Institute of Technology

3:20 PM

(ICACC-S10-019-2015) Image-based modeling of stitched C/C composites (Invited)

G. L. Vignoles*[1]; 1. University Bordeaux, France

Carbon/carbon composites are used in extreme environments due to their excellent strength/weight ratio, high ablation resistance and low heat expansion. They are often prepared by Chemical Vapor Infiltration (CVI) of a pyrocarbon matrix in a complex arrangement of carbon fibers. Indeed, the fibrous reinforcement is commonly stitched in the direction perpendicular to the stacked cloth layers, in order to prevent delaminating. Modeling may dramatically help increasing the performances of these materials,. This presentation will summarize several numerical developments aimed at providing design tools, paying special attention to image-based modeling. 3D blocks obtained by computerized micro-tomography are a very good starting point for simulations, since they are able to capture enough details on the material organization. However, in the case of stitched woven C/C composites, it is quite difficult to separate the architecture in bundles and needling zones; so, direct imaging is used instead, in the frame of a “handbook homogenization” technique. We will present the application of this class of methods to the simulation of matrix infiltration by CVI, and to the prediction of elastic and heat expansion properties. The numerical procedures will be described briefly, then the validations with respect to experimental data.

3:50 PM

(ICACC-S10-020-2015) Phase field modeling of rapid solidification in thermal spray coatings

T. Pinomaa*[1]; N. Ofori-Opoku[2]; A. Laukkanen[1]; N. Provatas[2]; 1. VTT Technical Research Centre of Finland, Finland; 2. McGill University, Canada

This work demonstrates an accurate mesoscopic model for solidification in thermal spray, where particles –typically metal or ceramic powder– are heated and propelled towards a substrate, leading to a thick and lamellar coating. Upon impact, melted droplets solidify rapidly – 1-100 MK/s. This leads to microstructures with metastable phases, high residual stresses, and heterogeneous distribution of grains and solutes; these features need to be incorporated in an integrated computational materials engineering (ICME) tool for thermal spray. We use a 2D phase field method to simulate the rapid solidification of metallic droplets. We assume that dendrites nucleate at the bottom center of each molten droplet. In our phase field simulations, we vary the interface parameters, as these are difficult to estimate reliably. Phase field simulations are used to predict a heterogeneous distribution of dendrites, their sizes, morphologies, solute distribution, and the solidification-induced residual stresses. Such microstructure is then used to simulate the material properties such as strength and toughness in the coating layer using high-fidelity finite-element methods. Our work presents a model that can be used to generate virtual microstructures of thermal spray coatings, and additionally, the model can be employed to model other powder consolidation and sintering processes, such as selective laser sintering.

4:10 PM

(ICACC-S10-021-2015) Micro-Computed Tomography Image Based Modeling of MMCs

Y. Sinchuk[1]; S. Dietrich[2]; M. Merzkirch*[2]; K. Weidenmann[2]; R. Piat[1]; 1. Karlsruhe Institute of Technology, Germany; 2. Karlsruhe Institute of Technology, Germany

Properties of an interpenetrating metal–ceramic composite with freeze-cast preforms are investigated. For the estimation of elastic properties of the composite numerical homogenization approaches for 2D and 3D finite element models are implemented. The FE models are created based on micro-computed tomography (μCT) images. The results of the numerical 2D and 3D modeling coincide and are in good agreement with available experimental measurements of elastic properties.

4:30 PM

(ICACC-S10-022-2015) Multiscale modeling assisted tailoring of thermal spray coatings

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

Surfaces of severely-wearing components can be protected with thick composite coatings, which can be produced with the thermal spraying technique. The thermal spraying process –also the resulting composite structure, and the coating's response to environment–, are poorly understood due to their complexity and multiscalar nature of the resulting nano-microstructures. This makes it difficult to tailor optimal thermal spray coatings for a specific application. To tailor thermal spray coatings in a consistent way, we propose a computer-assisted "process-structure-properties-performance" (PSPP) approach adopting principles of integrated computational materials engineering, to systematically consider the thermal spray coatings from process parameters to the micromechanisms that dominate the coating performance. This methodology employs phase field simulation to model the solidification process, and mesoscale finite-element method based multiscale material modeling of the resulting final microstructure in order to describe its properties and performance with respect to wear resistance. Performance criteria driven microstructure tailoring case study is presented for metallic thermal spray coatings under abrasive wear conditions to demonstrate linkages and exploitation pathways between thermal spray process parameters, coating nano-microstructure and its performance.

4:50 PM

(ICACC-S10-023-2015) Structure and Mechanical Properties of Novel Carbon Enriched SiC based Ceramics

A. Adnan*[1]; 1. University of Texas, USA

Thermodynamic viability and mechanical properties of a new type SiC-based "C enriched" ceramics where certain Si atoms are substituted by C atoms have been studied using MD simulation. Five different systems with different fraction of "C" enrichments, namely 10%, 20%, 30%, 40% and 50% have been investigated. After equilibrating all types of enriched systems as well as the control SiC system, we studied their equilibrium densities, free energy profiles and internal morphologies as a function of "C" enrichment amount. The energy profiles suggest that all "C" systems should be thermodynamically viable because total configuration energies for all systems were minimized and remained stable over a long period of time. The densities of different "C" enriched system drop from 3.25 gm/cm3 to 3.05 gm/cm3 for "C" enrichment upto 20%. For higher than 20% "C" enrichments, densities then increase monotonically. We explore the microstructures by measuring the average coordination number and radial distribution functions of different systems. Both these studies confirm that the newly designed materials have local microstructure change. We then evaluated tensile and shear response of these newly developed materials and found the mechanical properties depend on amount of carbon enrichment.

5:10 PM

(ICACC-S10-024-2015) Sharp Interfacial Energy Driven Phase Ripening in the Presence of Wetting Boundaries

E. Hernandez*[1]; V. Tikare[2]; L. Noirot[3]; 1. University of Michigan, USA; 2. Sandia National Laboratories, USA; 3. Commissariat á l'Énergie Atomique Cadarache, France

We developed a hybrid deterministic–statistical model that is able to simulate microstructural evolution. The model accounts for interfacial energy by calculating the sharp interface (discrete) curvature. An Ising model–like approach was used to calculate the sharp interface curvature. By calculating the curvature this way, we obtain an intuitive approach to account for interfacial energy from sharp interfaces. The deterministic–statistical model couples phenomenological equations to the Potts Monte Carlo model to study compositional and microstructural evolution. This intuitive approach of directly calculating the curvature retains the proper kinetics when isotropic boundary conditions are employed. Our results were compared to a previous hybrid model developed by Homer et al. and found to correlate to Ostwald ripening. Furthermore, we explore the kinetics of abnormal grain growth by incorporating wetting grain boundaries, which were simulated by an adapted Potts Monte Carlo algorithm. The presented models were applied to a binary–two phase system with isotropic and wetting grain boundaries. 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.

S11: Advanced Materials and Innovative Processing Ideas for the Production Root Technology

Coating Process for Low Friction and Energy Solution I

Room: Coquina Salon E
Session Chairs: Tim Hosenfeldt, Schaeffler Technologies GmbH & Co. KG; Hiroshi Tamagaki, Kobe Steel, Ltd.

1:30 PM

(ICACC-S11-008-2015) Extraordinary Friction and Wear Behavior of One-atom-thick Graphene (Invited)

A. Erdemir*[1]; D. Berman[1]; A. V. Sumant[1]; 1. Argonne National Laboratory, USA

Graphene is made of one-atom-thick carbon and offers a wide range of unusual electrical, thermal, optical, and mechanical properties. Due to its super-smooth, strong, and chemically inert nature, it holds high promise for providing unusual tribological properties as well. In our laboratory, we have indeed confirmed that even a one-atom-thick graphene layer can last thousands of sliding cycles and dramatically reduce friction between sliding steel surfaces at macro-scales under severe contact conditions. In the presence of a few layers of graphene, the wear life is extended to tens of thousands of sliding cycles and the rubbing surfaces are completely protected against wear. With respect to environmental effects, our research have shown that graphene works the best in hydrogen but it also provide impressive low friction and wear in humid or inert test environments. These findings are in contrast to the high environmental sensitivity of other popular solid lubricants like graphite and molybdenum disulfide. Overall, these results suggest a very unique friction and wear mechanism that distinguishes graphene from the rest of the other know solid lubricant materials and coatings. In this talk, we will present our research findings on unusual friction and wear behavior of graphene and in light of surface and structure analytical studies, provide mechanistic explanation for their extraordinary friction and wear performance despite being only one or a few atoms thick.

2:00 PM

(ICACC-S11-009-2015) Impact of lubricant chemistry on friction and wear behavior of thin-film ceramic coatings (Invited)

C. Lorenzo Martin*[1]; O. Ajayi[1]; A. Erdemir[1]; G. R. Fenske[1]; 1. Argonne National Laboratory, USA

Lubricants are usually formulated with different chemical additives to impart some desirable properties, such as friction and wear reduction. These additives are optimized to react with ferrous materials to form tribochemical surface films. Although a variety of hard thin-film coatings are increasingly being used in tribological components, there are still major uncertainties on the effects of thin film coatings on reactions of lubricant additives on coated surfaces in lubricated sliding contact. In this study, we evaluated the friction and wear behavior of several commercially available thin-film ceramic coatings when lubricated with fully formulated and unformulated synthetic lubricants. With fully formulated lubricants variety of behaviors were observed for different coatings, which can be explained in terms of the differences in tribochemical film formation and properties on the coatings surfaces.

2:30 PM

(ICACC-S11-010-2015) Deposition technologies of carbon-based coating; unbalanced magnetron sputtering and MF-AC PECVD (Invited)

H. Tamagaki*[1]; K. Akari[1]; H. Junji[1]; 1. Kobe Steel, Ltd., Japan

Diamond-like carbon (DLC) coatings are drawing attentions as coating materials for important applications like automotive components because of their properties with both low friction coefficient and high hardness. As discussed elsewhere, there are many processes for DLC deposition, including arc evaporation, sputtering and PECVD process by various methods for generating plasma. In the presentation, the deposition technologies for DLC coatings are presented focusing on two processes that we developed. One is an unbalanced magnetron sputtering (UBMS) process that features flexibilities to control film properties of DLC, such as hardness and hydrogen content in the film. The other is a MF-AC PECVD process featuring an unique method to generate the plasma for deposition, which applies mid-frequency AC voltage between the substrates divided into two groups connected two output of AC power supply. Also discussed are the properties of DLC films obtained from these processes.

Coating Process for Low Friction and Energy Solution II

Room: Coquina Salon E
Session Chairs: Ali Erdemir, Argonne National Laboratory; M. Ürgen

3:20 PM

(ICACC-S11-011-2015) Surface Technology as Key Technology for Future Mobility (Invited)

T. Hosenfeldt*[1]; Y. Musayev[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 drives 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 modern surface technology. Innovative vacuum coating technology has the ability to reduce the friction losses of vehicle components by mandatory lightweight design, improved fuel efficiency and reduced CO2-emissions. Close collaboration between research and production, industry and academia is required to achieve this challenging goal. In the future, the role of coatings as a design element will strongly increase in further technical applications. The Schaeffler Group delivers around 100 million high-quality PVD- and PACVD-coated components every year and, along with its comprehensive coating tool box, enables outstanding applications, preserves resources and meets increasing customer requirements.

3:50 PM

(ICACC-S11-012-2015) Innovative process technologies for enhanced product performance (Invited)

R. Tietema*[1]; D. Doerwald[1]; R. Jacobs[1]; J. Landsbergen[1]; 1. IHI Hauzer Techno Coating B.V., Netherlands

Vacuum coating equipment technology is on a large scale applied to produce thin films with low friction and high wear resistance. Requirements to maintain a strong market position encompasses a continuous development of new coating systems to follow immediately new requirements. Besides performance, also coating cost plays a major role for market acceptance. This requires large volume systems, operating with high up-time and reproducibility and possibly shortest process time. The automotive market requires higher and still increasing wear resistance as well as reduced friction. In other market segments PVD/PECVD coatings will play an important role in the replacement of galvanic plating coatings, as hazardous materials like hexavalent chromium will be completely banned in the near future. Technologies and applications will be addressed in this presentation.

4:20 PM

(ICACC-S11-013-2015) Aluminizing-Alloying of Metal Surfaces with Cathodic Arc Plasma Treatment (Invited)

M. Ürgen*[1]; 1. Istanbul Technical University Department of Metallurgical and Materials Engineering, Turkey

Cathodic arc plasma generated by the initiation and propagation of an arc on the metallic targets in a vacuum environment results in almost totally ionized metal vapors. The character of the plasma allows us to treat substrates in different manners. Application of a negative potential (bias potential) to the substrate results in bombarding of the substrate surface with the metal ions, energy of which depends on the magnitude of potential. We benefit from ion bombardment effects for heating and sputter cleaning of the substrates (high bias voltages) prior to initiation of the deposition process and also for densifying the coating structure (low bias voltages). Another possibility is to heat the substrates by electrons with supplying positive voltages to the substrates. Both of these approaches are used for coating production with cathodic arc PVD. In this presentation, the possibility of the production of well adherent and dense diffusion layers, with a tunable composition, on metallic substrates by the application of positive and negative bias voltages to the substrates will be introduced. The motivation behind this approach is the very fast and controlled heating possibilities of the substrates both by positive and negative bias applications. Examples of applications will be mainly concentrated on aluminizing of Ni alloys, titanium, copper and iron alloys.

4:50 PM

(ICACC-S11-014-2015) near-nanocomposite cermet coatings for corrosion, friction, and wear

A. Sherman*[2]; E. Vogli[1]; G. Santini[1]; 1. Mesocoat Inc, USA; 2. Abakan Inc, USA

Nanocomposite cermet coatings have been developed to provide unique combinations of friction, wear, and fracture properties. By combining near-nano and nanoscale ceramics with metallic binders in an engineered powder, a thermal spray feedstock is created which has high deposition efficiency, good machinability, as well as excellent mechanical and wear performance. These nanocomposite coatings have been increasingly accepted in a variety of industries, offering improved component life and coating economics compared to traditional carbide and cermet thermal spray coatings.

5:10 PM

(ICACC-S11-015-2015) Hard Coatings in a Challenging Tribological Application (Invited)

O. L. Eryilmaz*[1]; G. Ramirez[1]; A. Erdemir[1]; 1. Argonne National Laboratory, USA

Tribology field plays a key role in many moving mechanical systems to understand and improve their energy efficiency. Since tribology is a surface phenomenon, applying thin coatings onto bulk material and chancing the tribological performance of these systems is a well-known approach in the field. There are two main thrusts on improving energy efficiency of moving mechanical systems: lowering friction, and improving wear performance (since improved component and tool life indirectly contributes to energy savings). Accordingly, improving friction and wear performance of these systems can be considered as an enabling technology as in high power-density engines for example. However, "Harder coatings perform better" is a commonly mistaken approach in many cases. Combination of all mechanical, thermal, structural, chemical properties, and composition of the coatings play a key role on tribological performance of a coating in a given application. The environment (dry, lubricated), sliding speed, direction, load, temperature also play very important roles. So, almost every application should be evaluated in a case by case approach. This paper focuses on a specific example give some insights how it can potentially reduce frictional losses and/or improve component durability as elaborated below.

5:40 PM

(ICACC-S11-016-2015) Friction and wear properties of the ZrN/Cu nano composite films fabricated by multicomponent single alloying targets for automobile industry

J. Sun[1]; S. Shin*[1]; K. Moon[1]; 1. Korea Institute of Industrial Technology, Korea (the Republic of)

DLC(Diamond like carbon) is a representative coating material that has been widely used in automobile engine moving parts to enhance its wear and friction properties. However, problems in DLC coating have been reported such as thermal stability and compatibility with engine oil additives because the engine conditions for future automobiles are becoming more severe. Recently, nitride nanocomposite films such as nc-MoN/Cu and nc-ZrN/Cu films have been introduced with high hardness and low friction properties which are expected to be substituted for DLC coating. In this study, nc-ZrN/Cu films were coated on the automobile engine moving parts by DC magnetron sputtering process with multicomponent single alloying targets, and the friction and wear properties of the films were investigated. Friction properties were tested with high frequency reciprocating test machine at 100 oC for 6 hrs with 200 N of load conditions. The nc-ZrN/Cu films showed as much as 30% of friction reduction compared with DLC coating and wear of the nanocomposite films was not observed. Moreover, the nc-ZrN/Cu films were coated in the mass production equipment to verify the possibilities of the mass production. Thickness of the films of the tappet, piston ring and piston ring were 3 μm, 3 μm and 10 μm, respectively.

S13: International Symposium on Advanced Ceramics and Composites for Sustainable Nuclear Energy and Fusion Energy

Design Properties and Interactions for Nuclear Ceramics

Room: Tomoka B

Session Chairs: Stephen Gonczy, Gateway Materials Technology; Mark Mitchell, EON Consulting

1:30 PM

(ICACC-S13-051-2015) Development of a Standard for the use of composites in a High Temperature Reactor (Invited)

M. N. Mitchell*[1]; Y. Katoh[2]; S. T. Gonczy[3]; 1. EON Consulting, South Africa; 2. Oak Ridge National Laboratory, USA; 3. Gateway Materials Technology, USA

Several High Temperature Reactors have been designed, built and operated successfully using conventional materials. This application invariable pushed the materials to the edge of their envelope. Over the last 20 years it has become clear that unlocking the use of advanced materials – such as Ceramic Matrix Composites and Carbon-Carbon composites will enable significant improvements in the performance of High Temperature Reactors. We will provide an overview of some of the work completed to enable the use of these materials in various reactor development programmes as well as explaining the current work that is being completed in the ASME Boiler and Pressure Vessel Code committees to establish codes and standards for this application.

2:00 PM

(ICACC-S13-052-2015) Hoop Tensile Strength of Composite Tubes for LWRS Applcations Using Internal Pressurization: Draft ASTM Test Method (Invited)

M. G. Jenkins*[1]; J. Salem[2]; J. E. Gallego[1]; 1. Bothell Engineering and Science Technologies, USA; 2. NASA Glenn Research Center, USA

The US DOE plans to replace conventional zirconium-alloy fuel rod tubes in light water reactors (LWR) with those consisting of SiC/SiC CMCs to enhance fuel performance and accident tolerance. SiC/SiC CMCs show tolerance to the irradiation and chemical environments of LWRs. Failure modes in LWR fuel cladding include loss of gas tightness and 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. A draft ASTM test method is being developed and will be submitted for full consensus balloting that uses internal pressurization to introduce hoop stresses in composite tubular test specimens. This test method is 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. The draft ASTM test method contains test specimen dimensions, testing geometries, test conditions and results interpretation based on this theory and subsequent empirical tests applied to various materials and geometries. This test method for material development, material characterization, material screening, model validation, and quality assurance.

2:20 PM

(ICACC-S13-053-2015) Composition, Structure, Manufacture, and Properties of SiC-SiC CMCS for Nuclear Applications: ASME BPVC Section III

M. G. Jenkins*[1]; S. T. Gonczy[2]; Y. Katoh[3]; 1. Bothell Engineering and Science Technologies, USA; 2. Gateway Materials Technology, Inc, USA; 3. Oak Ridge National Laboratory, USA

The US DOE plans for future nuclear reactors call for the use of SiC/SiC CMCs to enhance fuel performance and improve accident tolerance. In particular, SiC/SiC CMCs show tolerance to the irradiation and chemical environments of current and future nuclear reactors. Because SiC/SiC CMCs are nonconventional materials, part of the 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. Therefore, the NRC regulates nuclear reactors and new reactor design as well as the reactor materials. The NRC not only employs, 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, with some details, regarding the composition, structure, manufacture, and properties of SiC/SiC CMCs for nuclear applications as currently being developed in ASME BPVC Section III.

2:40 PM

(ICACC-S13-054-2015) An ASTM C28 Standard Guide for the High Temperature Oxidation Exposure Testing of Nonoxide 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, automotive, industrial power, and environmental systems.These ceramics are commonly much more stable and oxidation resistant than the metals they are replacing, but may not be 100% inert at very high temperatures. Oxidation testing is commonly done to assess the life of the component and to characterize the oxidation reaction chemistry and kinetics of the ceramic across a range of temperatures and atmosphere conditions. Changes in specimen mass and dimensions are measured and the composition, phase, and microstructure of the reaction product and ceramic substrate. Oxidation testing is also used to evaluate exposure effects on the retained functional properties of the ceramic material. The ASTM C28 committee has drafted and is balloting a new guide for the high temperature oxidation exposure testing of nonoxide 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.

3:20 PM

(ICACC-S13-055-2015) The ASTM C28 Test Standard for the Torsional Shear Strength of Adhesive Bonds for Advanced Ceramics

S. T. Gonczy*[1]; Y. Katoh[2]; M. Ferraris[3]; 1. Gateway Materials Technology, USA; 2. Oak Ridge National Laboratory, USA; 3. Politecnico di Torino, Italy

High temperature adhesive bonding (sintered bonds, fused glass-ceramic, brazes, etc) of ceramic parts (monolithic and composite) to form complex components is a critical engineering technology in the application of ceramics in high temperature, harsh service environments, such as nuclear power, aerospace, and heat transfer. The shear bond strength is a primary engineering property that needs to be determined across the entire temperature range. The ASTM C1469 shear strength test (asymmetrical 4 point bend) has size, relative strength, alignment, and temperature limitations. The research at Politechnic di Torino and Oak Ridge National Laboratory on torsional shear tests of adhesive face bonds in ceramics shows advantages in specimen size, simpler stress states, and gage section failure. That work has been used to draft and ballot a new ASTM C28 standard test method for the torsional shear strength of adhesive bonds in ceramics. The new test standard is addressing the full range of test factors – the fundamental variables in adhesive variables, different specimen geometries, size effects, flaw sources, edge and notch stress concentrations, torsion fixtures and grips, specimen alignment, bond uniformity, adhesive failure modes, data analysis, failure analysis, and reporting requirements.

3:40 PM

(ICACC-S13-056-2015) Joining SiC for Nuclear Applications: Modeling Miniature Torsion Tests with Experimental Validation

C. H. Henager*[1]; B. Nguyen[1]; R. Kurtz[1]; T. Roosendaal[1]; B. Borlaug[1]; M. Ferraris[2]; A. Ventrella[2]; Y. Katoh[3]; 1. PNNL, USA; 2. Politecnico di Torino, Italy; 3. ORNL, USA

The use of SiC and SiC-composites in fission or fusion environments appears to require joining methods for assembling larger components and systems. The international fusion materials community designed miniature torsion specimens for joint shear strength testing and irradiation testing in HFIR. In this study, miniature torsion joints were fabricated using displacement reactions between Si and TiC to produce Ti_3SiC_2/SiC joints with CVD-SiC as the base material and were tested in shear prior to and after HFIR irradiation testing at 1073 K. However, these miniature torsion specimens fail out-of-plane for strong ceramic joints, which causes difficulties in determining the joint shear strength and for comparing unirradiated and irradiated joints. A finite element damage model has been developed that indicates shear fracture is likely to occur out-of-plane and in the base CVD-SiC material when a certain modulus and strength ratio between the joint material and the joined material exists. Below a certain modulus and strength ratio, however, shear failures occur in plane within the joint region and accurate shear strength values

can be obtained. The implications for torsion shear joint data based on this sample design are discussed.

4:00 PM

(ICACC-S13-057-2015) Notch effects on silicon carbide matrix composites by various failure modes

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

A silicon carbide matrix (SiC/SiC) composite is a candidate material for nuclear fission and fusion applications. Generally, composites' failure initiate from inherent internal/surface flaws and hence these flaws as potential failure origins need to be adequately considered in qualification of the material for the practical application. Focusing on the surface flaw issue, identifying notch sensitivity is essential to judge cracking tolerance of composite materials. To date, many extensive work evaluated notch sensitivity of various types of composites and it has almost been concluded that SiC/SiC composites with moderate fiber/matrix interface are notch insensitive by fast fracture monotonically loading mechanical tests. This study aims to further evaluate the notch effects on tensile properties of SiC/SiC composites by various failure modes such as cyclic tensile loading/unloading. For that purpose, various damage monitoring methods such as acoustic emission, digital image correlation, replica film, etc. are supplementarily adopted to evaluate the detailed failure behavior of the composites.

4:20 PM

(ICACC-S13-058-2015) Thermal Conductivity of Silicon Carbide Ceramics

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

The tristructural-isotropic (TRISO) particles in graphite matrix form the integral part of the typical fuel design for future nuclear power plants of the Very High Temperature gas-cooled Reactors(VHTR). In case of fuel design for Light Water pressurized Reactors (LWR) fully ceramic microencapsulated fuels (FCM) which consist of TRISO fuel particles embedded in a silicon carbide (SiC) matrix are recently introduced, as a similar fuel concept of VHTR. The SiC matrix offers potential advantages compared to graphite matrix: (1) improved irradiation stability, (2) incorporation of another effective barrier to fission product release, (3) environmental stability under operating and transient conditions as well as long-term storage, and (4) proliferation resistance. One of the most important properties required as a matrix material of FCM is the high thermal conductivity. This presentation deals with the recent developments of high thermal conductivity SiC ceramics. First, the effect of initial α-phase content on the thermal conductivity of LPS-SiC ceramics is investigated using rare-earth oxide additives. Second, the recent achievement of highly thermally conductive SiC ceramics with a thermal conductivity of 234 W/mK is presented. Finally, the factors influencing the thermal conductivity of SiC ceramics are clarified and the potential approaches to realize high thermal conductivity are suggested.

4:40 PM

(ICACC-S13-059-2015) Laser Flash Thermal Diffusivity Measurements on Composite Tubes

J. Zhang*[1]; H. E. Khalifa[1]; C. P. Deck[1]; C. A. Back[1]; 1. General Atomics, USA

Silicon carbide fiber reinforced, silicon carbide matrix (SiC-SiC) composites tubes are promising nuclear fuel cladding components. This work presents the development of a reliable thermal conductivity / diffusivity measurement for cylindrical cladding geometries that can be used as a tool in assessing cladding architectures. Laser flash analysis (LFA) method is a very popular and reliable method for thermal diffusivity measurement. However, the typical LFA method is designed to measure flat samples. The work presented here focuses on LFA thermal diffusivity measurement method development for the tube samples. Modelling and laboratory measurements have been performed to examine the dependence of the thermal diffusivity measurement on radius and thickness. Lead and stainless steel were used to establish a geometrical factor and results for these and silicon carbide composites will be presented. Results show the method developed is suitable for composite tube sample thermal diffusivity measurements. *This work is supported by General Atomics internal funding.

5:00 PM

(ICACC-S13-060-2015) Irradiation Creep of Silicon Carbide in Medium-to-High Dose Regime

Y. Katoh*[1]; T. Koyanagi[1]; L. L. Snead[1]; T. Hinoki[2]; 1. Oak Ridge National Laboratory, USA; 2. Kyoto University, Japan

Irradiation creep is an important irradiation-induced phenomenon for nuclear materials. However, the irradiation creep of SiC, as well as all ceramics and ceramic composites, is only now becoming understood and studied. Recently, the authors reported on the creep behavior of SiC ceramics in the initial transient and early post-transient regimes. In the course of previous works it was found that a linear stress dependency of creep strain in both regimes and a linear swelling-creep coupling existed for high purity CVD SiC in initial transient regime, due likely to the stress-induced re-orientation of ultra-fine multi-dimensional defect clusters. That work is extended to even higher dose in an experimentally identical fashion into medium to high dose regimes, in the dose range up to 30 dpa. The materials studied included grades of polycrystalline beta-phase CVD SiC and a monocrystalline 4H-SiC. Thin strip samples of these materials were irradiated in the High Flux Isotope Reactor in a temperature range ~300 to ~1200°C in the bend stress relaxation (BSR) irradiation creep capsules. The initial bending stress levels ranged from ~100 to ~300 MPa. The stress relaxation behavior and irradiation creep compliances will be analyzed and discussed.

FS2: Advanced Ceramic Materials and Processing for Photonics and Energy

Glasses II / Synthesis

Room: Tomoka A

Session Chairs: Nate Quitoriano, McGill University; Gunnar Westin, Uppsala University

1:30 PM

(ICACC-FS2-014-2015) Enhanced electrical and structural properties of Antimony doped Cuprous oxide and their application to visible-light photonic device

S. Baek*[1]; H. Cho[2]; 1. Sungkyunkwan University, Korea (the Republic of); 2. Sungkyunkwan University, Korea (the Republic of)

Cuprous oxide (Cu2O) is nonstoichiometric p-type material and their electrical property is related to the copper vacancy and oxygen interstitial. Interestingly, the Cu2O has high absorption and earth-abundant property, and thereby it can be used in several photonic devices, such as absorber layer in solar cell and photocathode in water splitting system. Among various deposition techniques, electrodeposition is particularly attractive deposition process of Cu2O, because of its simplicity, scalability, and economy. However, the Cu2O films formed by electrodeposition show high resistivity and low carrier concentration, and wet based process generally causes poor electrical and optical properties of Cu2O in photonic devices. In this study, we deposited antimony (Sb) doped Cu2O layers with solution process, which show enhanced electrical and structural properties, compared with undoped Cu2O layer. Surprisingly, doped Cu2O shows high transmittance > 70 % and semiconducting properties. These improvements are attributed to different nucleation and growth mechanism by doped Sb. Also, the doped Cu2O film is appreciable to photonic devices on short wavelength visible region, due to considerable crystallinity and improved conductivity. The Sb doped Cu2O exhibits columnar structure with vertically arrayed well-defined grain boundaries.

1:50 PM

(ICACC-FS2-015-2015) Development of Polycrystalline Ceramic Core-Clad Fibers for Optical Applications

H. Kim*[1]; G. E. Fair[1]; R. G. Corns[1]; H. Lee[1]; S. A. Potticary[1]; M. O'Malley[1]; N. G. Usechak[1]; R. Hay[1]; 1. Air Force Research Laboratory, USA

Since Ikesue's lasing demonstration with polycrystalline YAG (Yttrium Aluminum Garnet), enormous efforts have been taken to develop polycrystalline ceramic gain media for high energy laser applications due to lower production cost and higher dopant concentration of polycrystalline ceramics relative to single crystals. In addition, novel gain media with fiber form have attracted attention because they offer compactness, vibration-resistance and reduced cooling. State-of-the-art silica glass fiber is used as a laser host but its performance is limited by its lower thermal conductivity, higher thermo-optic coefficients, and higher losses beyond mid-IR range compared to crystalline ceramics. Consequently, in order to take advantage of both fiber architecture and polycrystalline ceramic form, we are endeavoring to develop polycrystalline ceramic core-clad fibers for optical applications. In this talk, focus will be given to process improvements for fabrication of polycrystalline ceramic fibers in terms of defect population and scattering loss. Additionally, a limited discussion on cladding methods and corresponding microstructures will be presented.

2:10 PM

(ICACC-FS2-016-2015) Complex oxides through alkoxide based solution synthesis (Invited)

G. Westin*[1]; 1. Uppsala University, Sweden

The ever increasing demands for complex nano-materials put great demands on the development of the synthesis techniques, but for practical applications in the areas of sustainable energy conversion and storage, catalysis and magneto-electric applications the processes also have to provide the materials at high rate and low cost. Solution based processing routes allowing for designed multi-phase, multi-elemental nano-materials in one or few steps, are probably the best suited for achieving this. Here synthesis routes to complex oxides and nano-composites using homo- or hetero-metallic alkoxides are described. Multi-component oxides were prepared at very low temperatures in the forms of polycrystalline and epitaxial thin- and ultra-thin films on flat and nano-structured surfaces such as wires and porous nano-structures of nano-particles. Systems of varying complexities will be discussed such as doped and non-doped Fe2O3 and ZnO, spinels and perovskites. The influence of the alkoxide precursor and thermal treatment will be discussed in relation to the structure, processing temperature and quality of the target oxides, as well as the option to make thermodynamically unstable extended doping-levels when using reactive alkoxides in a controlled way.

2:40 PM

(ICACC-FS2-017-2015) Dynamics of quantum dot uptake into mesoporous TiO2 thick films through electrophoretic deposition

L. Jin*[1]; H. Zhao[2]; D. Ma[1]; A. Vomiero[2]; F. Rosei[1]; 1. Institut National de la Recherche Scientifique, Canada; 2. CNR-INO SENSOR Lab, Italy

An intense effort is boosting the development quantum dot (QD)-based solar cells due to their unique optical properties, tunable bandgap, high extinction coefficient and stability. This interest has been reinforced by near infrared (NIR) QDs with photoconversion efficiency (PCE) boosted above 8.5%. Electrophoretic deposition (EPD) has been demonstrated for preparation of high efficiency photo-anodes for QD solar cells, in which QDs are grafted to a mesoporous TiO2 thick film, but a complete analysis of EPD process is missing. Here, for the first time, we systematically investigated the dynamics of NIR QDs loaded into TiO2 mesoporous film via EPD. PbS/CdS core/shell QDs were applied as a model system with Rutherford backscattering for Pb depth profiling. By using Fick's law of diffusion, we explained the observed trends as a fast (and depth-independent) QD uptake induced by the presence of the electric field, followed by a diffusion-induced QD migration from outside the film. In addition, we demonstrated the increased stability of the core/shell structure compared to PbS QDs in terms of structure and optical properties, which makes these materials strong candidates for the development of highly efficient and stable light absorbers in PV devices.

3:20 PM

(ICACC-FS2-018-2015) Composing Metal Oxide Nanocrystals for Improved Gas-Sensors: from Surface Modification to Inter-Oxide Cross-Talk (Invited)

M. Epifani*[1]; 1. CNR-IMM, Italy

TiO_2-WO_3 nanocomposites are of great interest in photoelectrochemical devices, due to the favorable band alignment of the two components, and many efforts have been devoted to the synthesis of such materials. On the other hand, there are only very few related studies in gas-sensing field. In fact, metal oxide heterojunctions have been long-time known as an interesting alternative approach to modify the sensing performances of single oxides, by properly coupling the electronic/chemical features of each component. TiO_2-WO_3 nanocrystals were prepared by colloidal synthesis, exploiting the different chemical reactivity of the Ti and W precursors to obtain a range of structures ranging from monolayer WO_x deposition onto TiO_2 to heterojunctions. The complex structural evolution of the nanocomposites will be discussed in detail, depending on the W concentration. The resulting sensing devices displayed large responses to various test gases, such as acetone and ethanol. Addition of the smallest W concentration boosted the sensor response to values comparable to those of pure WO_3, ranging over 2-3 orders of magnitude of conductance variation. With the help of basic electrical measurements, it will be showed that classical doping effects are not likely and that more complex phenomena should be invoked, like cross-talk between the different nanograins.

3:50 PM

(ICACC-FS2-019-2015) Analysis of nano structures of In-Ga-Zn-O thin films deposited by sputtering at room temperature

N. Sorida*[1]; K. Dairiki[1]; M. Takahashi[1]; M. Yano[1]; E. Takahashi[1]; T. Hirohashi[1]; Y. Komatsu[1]; M. Sumikawa[1]; S. Yamazaki[1]; 1. Semiconductor Energy Laboratory Co.,Ltd., Japan

We deposited In-Ga-Zn-O (IGZO) thin films at room temperature (RT) with two sputtering deposition conditions (A: high power low pressure, B: low power high pressure). Field effect transistors (FETs) using the films A and B as active layers had small and large characteristic variations, respectively. Nano structures of the films A and B were analyzed. In nano beam electron diffraction using a 1 nmϕ electron beam performed on the film A, spotty diffraction patterns were obtained. In a TEM image, randomly oriented nanometer-size crystals were observed. We call this film "nanocrystalline-IGZO (nc-IGZO) film". A nanometer-size crystal existed also in the film B. However, voids were observed and the crystal size was changed depending on the amount of electron-beam irradiation; thus, the film B was unstable. We call the film B "amorphous like IGZO (a-like IGZO) film". In contrast, the nc-IGZO had a high crystal stability because of its high electron beam resistance. In our experiments, the nanometer-size crystals existed in the stable and unstable RT deposited IGZO, and a completely amorphous film was not obtained. Those results show that an IGZO film with a high crystal stability is preferably used for an active layer to form an FET with small variations and stable characteristics.

4:10 PM

(ICACC-FS2-020-2015) Nano energy conversion phosphors

A. V. Mudring*[1]; A. V. Mudring[2]; 1. Iowa State University, USA; 2. Ames Laboratory, USA

Rare earth elements are amongst the most critical materials – non only is the world market supply limited but also they are crucial for a number of energy related technologies. However, due to their special photophysical propoerties rare earth materials are of great interest as photonic materials.Substituting most of the precious rare earth ions and simultaneously retaining the efficiency of the energy conversion phosphor at the nanoscale is a major and quite challenging goal. In that context alkaline earth fluorides appear to be the cheapest, benign and readily available materials. We succeeded in synthesizing highly efficient quantum cutting phosphors based on alkaline earth host lattices with low rare earth ion concentrations nanoparticles doped with trivalent lanthanide ions. As doping trivalent ions into a host with divalent cations requires charge compensation, this effect was thoroughly studied by powder X-ray and electron diffraction, luminescence spectroscopy and 23Na, 139La and 19F solid state NMR spectroscopy to gain a better understanding of these materials. In the end, the rare earth content (cation content) of nanoparticles with a size of less than 10 nm could be reduced by 94 % compared to typical GdF3:Eu VUV quantum cutting material while simultaneously retaining the quantum cutting efficiency close to the theoretical limit (199 %). With such performance values, these materials appear quite promising for solar energy conversion.

4:30 PM

(ICACC-FS2-021-2015) Thermal Processing and Properties of Conductive Refractory Composites for High-Temperature Electrical Applications

G. A. Yakaboylu*[1]; R. Chockalingam[1]; S. Chockalingam[1]; B. Armour[1]; M. Palmisiano[2]; K. Sabolsky[1]; E. M. Sabolsky[1]; 1. West Virginia University, USA; 2. ANH Refractories Company Technology Center, USA

Electrical interconnects that are capable of operating at high temperature (750-1500°C) and high pressure (up to 1000 psi) have been required by many advanced energy devices and electronics that operate in harsh-environments. The materials widely used in thermocouples, thermistors, pressure sensors, thermopiles, and strain gauges are not appropriate for long-term use under these critical conditions. This study specifically investigated the use of intermetallic composites embedded in refractory oxides. The compositions studied were various silicides (such as $MoSi_2$, WSi_2, and $ZrSi_2$) incorporated within a matrix composed of mixtures of Al_2O_3, ZrO_2, Y_2O_3, and Cr_2O_3 materials. The electrical conductivity measurements were performed between 1000-1500°C. Besides, x-ray diffraction (XRD) was completed to better understand phase stability at various oxygen partial pressures, and scanning electron microscopy (SEM) was performed to investigate microstructural development of the silicide/oxide composites. Finally, coefficient of thermal expansion (CTE) and four-point bending tests were completed particularly on composites showing the highest conductivity values.

4:50 PM

(ICACC-FS2-022-2015) Copper Clad Ultra-Thin Flexible Ceramic Substrate for High Power Electronics

J. A. Olenick*[1]; 1. ENrG Incorporated, USA

ENrG has established itself as the global source for ultrathin flexible ceramics known as Thin E-Strate®. Industry product trends require innovative high performance materials for SWaP - smaller, lighter weight and better performance. There are no other self-supported ceramic membranes on the market this thin at 20 or 40 microns, with the ability to flex, take high temperatures and handle extreme transitions in temperature. These unique properties and advantages show promise as an enabling technology platform into a variety of markets and products, such as microbatteries, solar PV and microelectronics packaging. Ultimately these high volume markets want the new materials in larger sheets, like is now available for FR4, or in a roll-to-roll format. This paper will present work done in conjunction with Oak-Mitsui on double-sided copper cladding of the thin ceramic, with subsequent circuit definition and application testing. Material and application performance data will be presented as available across multiple market applications. The two companies' objective is to meet the growing market need for thermal management in electronics, including LEDs, resistive heater circuits, and power electronics.

5:10 PM

(ICACC-FS2-023-2015) Optimization of Barium Chloride Powder Synthesis by Spray-drying for the Fabrication of Transparent Ceramic Scintillators

B. D. Doan*[1]; T. Shoulders[1]; G. Bizarri[2]; E. Bourret-Courchesne[2]; R. M. Gaumé[1]; 1. University of Central Florida, USA; 2. Lawrence Berkeley National Laboratory, USA

The fabrication of transparent ceramics for photonic applications requires access to pure and highly sinterable powders. Here, we investigate the spray-drying of aqueous solutions of barium chloride for the preparation of novel BaCl2 scintillator ceramics. Because of the complex relationship between the spray-drying parameters (such as salt concentration, feed rate, gas flow, nozzle temperature and aspirator flow) and the size and morphology of the synthesized powders, we have designed a comprehensive and systematic study in order to find the best experimental conditions for producing suitable powders. It is found that dry, dense, spherical, dispersed, and narrowly size-distributed particles, suitable for the fabrication of fully dense transparent ceramics of BaCl2, are obtained from spray-drying parameters confined to a limited range of values. Our findings, displayed in the form of processing maps, are supported by kinetics and thermodynamics models.

FS5: Single Crystalline Materials for Electrical, Optical and Medical Applications

Optical Materials III

Room: Tomoka C

Session Chair: Alain Largeteau, ICMCB-CNRS

1:30 PM

(ICACC-FS5-040-2015) Impact of rare-earth ion clustering on the spectroscopic and thermo-mechanical properties of the Yb3+ and Nd3+ doped laser crystals (Invited)

R. Moncorge[1]; P. Camy*[1]; 1. University of Caen, France

Yb:CaF2 has been proved in the last years as an exceptional laser crystal for the generation of ultra-short laser pulses and for the realization of high-peak power laser amplifiers. However, there still exists some controversy concerning the occurrence of only one or several co-participating laser active Yb3+ centers in this apparently simple crystalline material. Therefore, the first part of the presentation will concentrate first on a recent analysis made to elucidate that important question, and to better understand correlative effects observed in the spectroscopic and thermo-mechanical properties of the materials, by using two complementary and original experimental approaches (low temperature site-selective laser excitation spectroscopy related to visible cooperative luminescence and direct imaging at the atomic scale of isolated ions and clusters using a high resolution STEM-HAADF electron microscope) and by correlating the data with simple crystal field calculations. The second part of the presentation will concentrate on the newly rediscovered Nd:CaF2 laser system and more specifically on the effect of co-doping the crystals with other non-optically active "buffer" ions on the spectroscopic, laser and thermo-mechanical properties of the materials.

2:00 PM

(ICACC-FS5-041-2015) Recent progress in growth of rare-earth vanadate single crystals by the Edge-Defined Film-Fed-Growth (EFG) technique (Invited)

V. Kochurikhin*[1]; Y. Furukawa[2]; W. Lee[3]; 1. General Physics Institute, Russian Federation; 2. OXIDE Corp., Japan; 3. TPS Corp., Korea (the Republic of)

Rare-earth vanadate single crystals demonstrate some wonderful properties as large birefringence, high chemical stability and thermal conductivity, wide transparency range. However, the wide application of rare-earth vanadate single crystals is still limited due to serious difficulties with growth of large size crystals using famous techniques like Czochralski. Shaped methods possess some important advantages in comparison with Czochralski technique. In this report the overview of recent progress in EFG growth of rare-earth vanadate single crystals will be given. The production of few crystals simultaneously as well as the growth of core-doped crystals will be discussed. Also, the model for the calculation of the Nd^{3+} dopant diffusion in $GdVO_4$ melt during the growth of core-doped crystals was suggested. The value of the diffusion coefficient of Nd^{3+} ions was calculated using experimental data of core-doped crystal composition. The peculiarities of EFG growth of $TbVO_4$ crystals will be discussed. It was found that $TbVO_4$ crystals demonstrated the efficient magneto-optical properties at 1064 nm (1.5 higher than traditional $Tb_3Ga_5O_{12}$ crystals).

2:30 PM

(ICACC-FS5-042-2015) Effective segregation coefficient of rare - earth ions in fluorite crystals (Invited)

O. M. Bunoiu*[1]; M. Stef[1]; I. Nicoara[1]; 1. West University of Timisoara, Romania

Fluorite crystals are used as a host for applications in laser, opto-electronic devices and detectors. Calcium fluoride (CaF2) crystals doped with various rare-earth (RE) ions have attracted much interest in order to develop new laser materials. BaF2 is a scintillating crystal, having two fast emission components (195 and 220 nm) and a slow emission at 310 nm. Among the RE ions, the Er3+ and Yb3+ ions are more investigated in order to improve the laser efficiency. The homogeneous distribution of the impurity in laser crystals is important because this affects the efficiency of the laser. The spectroscopic and laser properties of the ErF3 and YbF3 doped CaF2 crystals are well studied. Although these crystals are known as good laser host, surprising, the analysis of the Er3+ and Yb3+/Yb2+ ions distribution along the CaF2 and BaF2 crystal has been less investigated. The goal of this work is to determine the effective segregation coefficient using the optical absorption method. ErF3 and YbF3 – doped CaF2 crystals and YbF3 doped BaF2 were grown using the Bridgman method. The optical absorption spectra reveal the characteristic peaks of the Er3+, Yb3+, Yb2+ ions. The effective segregation coefficient of the various ions has been calculated and it was observed that the effective segregation coefficient of the Er3+, Yb3+, Yb2+ ions in the CaF2 and BaF2 hosts depends on the doping concentration and on the host.

New Directions II

Room: Tomoka C
Session Chair: Xutang Tao, Shandong University

3:20 PM

(ICACC-FS5-043-2015) Rare Earth Doped Crystals for Quantum Information Storage (Invited)

P. Goldner*[1]; A. Ferrier[1]; 1. Chimie Paristech, France

Quantum storage, a basic function in quantum information processing, consists in transferring quantum states between different qubits. It is especially useful for converting flying qubits, like single photons, which can carry information over long distances, into stationary ones, like atomic systems, where quantum states can be maintained for extended times. Storage time is limited by the atomic coherence lifetime, but within this delay, stationary quantum states can be transferred back to a propagating photon. To be useful, quantum storage has to fulfil strict requirements like high fidelity and long storage time. Rare earth doped crystals are actively investigated in this field, because their optical and hyperfine transition coherence lifetimes can be long, up to several ms, at liquid helium temperature. These materials have therefore a strong potential for long-term quantum storage in the solid state. Moreover, the large inhomogeneous linewidths of rare earth ion transitions have stimulated the development of storage protocols that are compatible with single photon noise level. In this paper, we will discuss recent results obtained on rare earth doped hosts developed in our group for optical and microwave quantum storage. This could be useful for long-distance quantum cryptography and to extend capabilities of superconducting qubits, one of the most promising quantum processors.

3:50 PM

(ICACC-FS5-044-2015) Influence of oxygen partial pressure on $SrTiO_3$ crystal growth from non-stoichiometric melt (Invited)

C. Guguschev*[1]; D. Kok[1]; Z. Galazka[1]; A. Kwasniewski[1]; U. Juda[1]; D. Klimm[1]; R. Uecker[1]; 1. Leibniz Institute for Crystal Growth, Germany

Strontium titanate ($SrTiO_3$) is one of the most commonly used substrate material for the epitaxy of perovskite thin films. However, advanced applications are limited by high dislocation density (EPD values > 10^6/cm^2) of the currently commercially available Verneuil crystals. Only few crystal growth methods are suitable to meet high quality demands with a sufficient crystal size. It is known that $SrTiO_3$ with the lowest dislocation density can be grown by flux growth (<10^3/cm^2), but faceted crystals are not commercialised yet due to low yields, small crystal sizes (5 – 15 g crystal weight) and relatively low growth rates (< 0.5 mm/h). Nearly cylindrical $SrTiO_3$ crystals of several cm lengths and with diameters larger than 1 inch were pulled from non-stoichiometric melt below 1740°C using top-seeded solution growth (TSSG) method. Despite of the large crystal diameter the quality has been improved compared to commercial crystals. Typical EPD values are the range between 2 - 9x10^4/cm^2. At elevated temperatures an effective heat transport through the crystal is important to avoid growth instabilities. It was found that the growth at a sufficient high oxygen partial pressure can suppress spiral or foot formation due to higher optical transparency of the crystals in the infrared light region compared to crystals grown under slightly reducing conditions.

4:20 PM

(ICACC-FS5-045-2015) Terahertz Time-Domain Spectroscopy Application to Non-destructive Quality Evaluation of Industrial Crystalline Materials (Invited)

S. Nishizawa*[1]; T. Nagashima[2]; M. W. Takeda[3]; K. Shimamura[4]; 1. University of Fukui, Japan; 2. Setsunan University, Japan; 3. Shinshu University, Japan; 4. National Institute of Materials Science, Japan

The coherent terahertz (THz) radiation emitted through femtosecond pulse laser irradiation on a photoconductive antenna has been effectively utilized for the terahertz time-domain spectroscopy (THz-TDS). THz-TDS with the advantage of better SNR below 150 cm-1 than that of the conventional spectrometers makes it possible to measure not only the spectral transmission intensities T (ω) but also the intrinsic phase shifts Δϕ(ω) of the propagating THz radiation through a sample specimen. The Simultaneous measurements of both T (ω) and Δϕ(ω) make exact estimation of both the real ε'(ω) and imaginary ε"(ω) parts of complex dielectric constants ε*(ω). The intrinsic phase shifts Δϕ(ω) estimate analytically the dispersion relations for various elementary excitations coupled with the propagating THz radiations. Thus THz-TDS measurements are effectively applied to the far-infrared spectroscopic analysis of intermolecular dynamics. Here, an overview of the THz-TDS instrument newly developed with the advantages of wide wavenumber coverage and high dynamic range, and some of the latest results of applications focusing on the THz-TDS non-destructive quality evaluation for industrial materials of ferroelectrics (BIT, LGO, LN) and high-permittivity crystals (STO,BTO) and also crystalline polymorphs of active component APIs of OTC pharmaceutical products will be described.

Friday, January 30, 2015

S1: Mechanical Behavior and Performance of Ceramics & Composites

Tribology and Wear

Room: Coquina Salon D
Session Chairs: Kevin Plucknett, Dalhousie University; Oyelayo Ajayi, Argonne National Lab

8:30 AM

(ICACC-S1-069-2015) Synergy of Ceramic Coatings and Lubricant Technologies on Scuffing of Surfaces (Invited)

O. Ajayi*[1]; C. Lorenzo-Martin[1]; D. Singh[1]; G. Fenske[1]; 1. Argonne Nat Lab, USA

Scuffing, described as a sudden catastrophic failure in lubricated components, is one of the most challenging problems in tribology. This paper presents an experimental study of the impact of the synergy between two commonly used approaches for scuffing prevention, namely thin-film ceramic coatings and lubricant formulation. Using a block-on-ring contact configuration and a step load increase test protocol, the scuffing performance of 5 different ceramics coatings were evaluated. Lubricant alone increased scuffing resistance by two to three times, while ceramic coatings alone produced about the same increase. In some cases, combined ceramic coating and lubricant technologies synergistically increased scuffing resistance by more than five times. Results of surface analysis, and information on the mechanisms of scuffing in different contact combinations, are presented. Ceramic coated surfaces scuffed only after wearing through the coating. Tribochemical surface films were observed in some coatings, but not all.

9:00 AM

(ICACC-S1-070-2015) Nanotribological Behavior of Graphene Nanoplatelet Reinforced Alumina Nanocomposites

A. Nieto*[1]; L. Huang[1]; Y. Han[2]; J. M. Schoenung[1]; 1. University of California Davis, USA; 2. Yeungnam University, Korea (the Republic of)

The tribological behavior of graphene nanoplatelet (GNP) reinforced alumina nanocomposites consolidated by spark plasma sintering is investigated. GNPs have been shown to provide toughening to ceramic matrix composites and promising results in improving macroscale wear behavior. High volume fractions (5-15%) of GNP are utilized in order to investigate the effects on wear behavior at multiple length scales. GNPs can serve as a solid state lubricant due to weak interlayer bonding and can thereby reduce the coefficient of friction (CoF). The toughening effect of GNPs can also aid in reduce wear rates reducing crack propagation. Excellent dispersion along with high volume fractions of GNPs is expected to yield improvements in performance even at very small scales. The wear performance of the nanocomposites is investigated using nanoindentation, nanoscratch and atomic force microscopy. The wear mechanisms are elucidated by scanning electron microscopy, high resolution transmission electron microscopy, and focused ion beam techniques.

9:20 AM

(ICACC-S1-071-2015) Oxides as high temperature abrasives

L. Mendez-Garcia*[1]; F. Di-Gioacchino[1]; R. J. Stearn[1]; L. W. Pallett[2]; M. E. Hancock[2]; W. J. Clegg[1]; 1. University of Cambridge, United Kingdom; 2. Rolls-Royce plc, United Kingdom

The aim of this research is to investigate whether Al2O3 abrasives can be used in gas turbines. Pin on disc testing was used to investigate the abrasion behaviour at 1100 °C of a tough Al2O3-ZrO2 eutectic, as well as a single crystal and a polycrystalline Al2O3 abrasive where the abrasives were fixed to the pin by a Ni-based matrix. It was found that the eutectic was ineffective due to reaction with the Ni-based matrix leading to weakening of the particle. This reaction occurred to a much lesser extent in the single crystal which tended to fracture in a manner dependent on its crystal orientation. However, the polycrystalline abrasive fractured less readily. Using EBSD, differences in fracture behaviour of the particles have been correlated with the microscale behaviour of the different microstructures.

9:40 AM

(ICACC-S1-072-2015) Enhanced mechanical and wear properties of ultrafine-grained Si_3N_4 doped with Y_2O_3

C. A. Lee*[1]; H. Lu[2]; H. Lin[3]; P. Sajgalik[4]; D. Lii[5]; C. Chen[1]; J. Huang[1]; 1. National Cheng Kung University, Taiwan; 2. National Chin-Yi University of Technology, Taiwan; 3. Oak Ridge National Laboratory, USA; 4. Slovak Academy of Sciences, Slovakia; 5. Cheng Shiu University, Taiwan

It is known that tribochemical reaction of ultrafine-grained Si_3N_4 is enhanced during sliding wear with high speed, leading to reduced wear rate with decreasing grain size. Two amorphous Si_3N_4 nanopowders doped with (1) 6 wt% Y_2O_3 and (2) 6 wt% Y_2O_3 and 8 wt% Al_2O_3 were used to fabricate monolithic Si_3N_4 ceramics. Due to high amount of SiO_2 which was expected to form on the matrix of nanopowders, nanosized carbon black was added as one of the reagents for the reaction of carbothermal reduction treatment at a calcination temperature of 1400ºC. A relatively low sintering temperature of 1700ºC was chosen for spark plasma sintering, as this meant that the compacts could be densified and their grain size was most likely to stay below 200 nm as calculated by image analyses. Even though the average grain size of Si_3N_4 doped with Y_2O_3 is greater than that of Si_3N_4 containing Si-Y-Al-O-N glassy phase, the protective tribo-film of the former enhances the resistance to wear damage. The results of this work show that with appropriate control of the mixture of Si_3N_4, sintering additives and carbon nanopowders, monolithic Si_3N_4 with improved mechanical and wear performance at room temperature can be obtained.

10:20 AM

(ICACC-S1-073-2015) Hierarchial nanocomposite cermets: Next generation ceramic-metal composites

A. Sherman*[1]; M. grogan[1]; 1. Powdermet Inc, USA

The ability to combine the hardness, strength, friction and wear properties of ceramics with the toughness and ease of production of metals has long been the goal of composite science. By combining deformable, high strength and hardness nanocomposites with ductile phase toughening in a hierarchically controlled structure, novel composites have been produced with high hardness and with fracture toughness equal to steels. The structure, processing, properties, and performance including rolling contact fatigue, friction, and wear properties of hierarchically structured nanocomposites will be presented and discussed.

10:40 AM

(ICACC-S1-074-2015) Sliding wear behavior of TiC-stainless steel cermets

K. P. Plucknett*[1]; C. Onuoha[1]; Z. N. Farhat[1]; G. Kipouros[1]; 1. Dalhousie University, Canada

A range of titanium carbide-based cermets have been developed, using the steel grades 304L, 316L and 410L. The materials were fabricated using a simple melt infiltration processing route, with infiltration performed between 1475 and 1550°C, for up to 4 hours. The sliding wear response of these materials has been evaluated against a tungsten carbide-cobalt counter-face, to simulate an aggressive wear scenario, for loads up to 80 N. The wear track volume was then assessed using an optical profilometer, and then converted to a specific wear rate. It is shown that the materials show a complex transitional wear response. Initially, and at low loads abrasive wear arises (two-body transitioning to three-body). Ultimately, adhesive wear occurs, with the formation of homogeneous tribolayers that contain high oxygen contents. The overall wear response of these cermets will be reviewed in the context of other wear resistant cermet systems.

11:00 AM

(ICACC-S1-075-2015) Nanomechanical testing of Al/Al-Cu-Fe composites: correlation between chemical heterogeneities and mechanical properties

A. Joseph[1]; C. Tromas[1]; V. Gauthier-Brunet[1]; J. Monchoux[2]; A. Joulain*[1]; S. Dubois[1]; J. Bonneville[1]; 1. Pprime Institute - Poitiers, France; 2. CNRS, France

Metal Matrix Composites combine a light and ductile matrix with hard reinforcement particles. Reinforcement of the matrix results from load transfer between the matrix and the reinforcement particles and by modification of its microstructure (dislocation density, grain size, diffusion,…). Thanks to their mechanical (high hardness, high elastic modulus and yield stress) and tribological properties, Al-Cu-Fe particles appear as good candidates for reinforcement particles in Al matrix composites. Optimizing the mechanical properties of composites implies a deep understanding of the correlation between microstructure and deformation mechanisms. In this work, Al/Al-Cu-Fe composites have been produced by spark plasma sintering of Al-Cu-Fe and Al particles mixture. Large and regular nanoindentation arrays have been performed in order to build hardness maps across the different phases of the composite. The detailed analysis of the individual deformation curves show serrated behavior characteristic of dislocation pinning by solute atoms in Al matrix. These results are correlated with the SEM observations coupled with EDXS analysis. The comparison between chemical and hardness maps as well as the quantitative analysis of the deformation curves give evidence of a strong correlation between the chemical heterogeneities and mechanical properties in the Al matrix. .

11:20 AM

(ICACC-S1-076-2015) Hardmetals based on niobium carbide (NbC) versus casted MMCs based on NbC

M. Woydt*[1]; H. Mohrbacher[2]; 1. BAM Federal Institute for Materials Research and Testing, Germany; 2. Niobelcon bv/ba, Belgium

Hardmetals based on NbC showed recently pronounced wear resistances. As the solubility of NbC in alloys is much lower than for WC, liquid phase sintering is not consequently necessary. This paper presents a comparison under dry sliding (0,1-10 m/s at 22°C or 400°C) and dry oscillating (2/50/98% rel. humidity) of metal bonded and SPS sintered, binderless NbCs versus metallurgically synthesized MMCs with a very high content of NbC. The metallurgical route is not possible for tungsten carbide due to its high solubility in alloys.

11:40 AM

(ICACC-S1-077-2015) Indentation damage in TiC-316L stainless steel cermets: The effects of sharp versus blunt indentors

C. Jin*[1]; K. Plucknett[1]; 1. Dalhousie University, Canada

Cermets combine hard but brittle ceramics with a ductile metallic phase. Compared with conventional ‘hardmetals’, such as tungsten carbide-cobalt, cermets have lower mass while maintaining good mechanical and thermal properties, including high strength and toughness, good wear and corrosion resistance, together with high thermal conductivity. With a high melting point and low density, titanium carbide (TiC) is used in a wide variety of cermet applications, such as bearings, cutting tools, drawing dies, etc. In the present work, stainless steel binders (grade 316L) 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 1475°C and 1550°C, held for up to 240 minutes. Two basic types of indentation response were examined in this study; Hertzian (or “blunt”) and Vickers (or “sharp”) indenters. Two primary indentation-cracking patterns arose for Vickers indentation, namely median cracks or Palmqvist cracks, which relates to the volume fraction of ductile metal binder present, which was confirmed using sequential polishing and focused ion beam microscopy. Preliminary use of Herztian indentation, with various applied loads and contact sphere diameters, will also be reported.

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

Advanced Multifunctional Coatings

Room: Coquina Salon G

Session Chairs: Dongming Zhu, NASA Glenn Research Center; Gustavo Costa, NASA Glenn Research Center

9:00 AM

(ICACC-S2-041-2015) CSD and ALD combined opportunities for complex functional oxide bilayers growth and interface engineering

X. Obradors*[1]; T. Puig[1]; M. Coll[1]; J. Gázquez[1]; J. González[1]; R. Ortega[1]; J. Suñé[2]; 1. ICMAB - CSIC, Spain; 2. Univ. Autònoma de Barcelona, Spain

Epitaxial growth of complex functional oxides has generated a lot of interest for their outstanding physical properties (superconductivity, colossal magnetoresistance, ferroelectricity, resistive switching). In recent years, these materials have reached even more attraction since novel or improved functionalities are reached by artificially engineering the interfaces. Chemical Solution Deposition (CSD) and Atomic Layer Deposition (ALD) are foreseen as powerful chemical methods for growth of complex functional oxides, however their combined potentiality in interface engineering and nanoscale control has yet not been exploited. In this contribution we study the mutual benefit of combining both methodologies to reach bilayers with special interest in oxide electronics for superconductivity and resistive switching phenomena. Whereas CSD appears as a very competitive method for the epitaxial growth of YBa2Cu3O7-x and La0.7Sr0.3MnO3 oxide films with fine control of stoichiometry and homogeneity, ALD, as a unique chemical gas-phase thin-film deposition method, arises as a unique method to grow epitaxial CeO2 ultrathin films at the very low temperatures on top of the mentioned CSD layers. The functional properties of CeO2/YBCO and CeO2/LSMO have been evaluated in view of their potentiality as resistive switching elements and reconfigurable superconducting devices.

9:20 AM

(ICACC-S2-042-2015) Iron Nitride Thin Films Fabricated by RF Sputtering

X. Wang*[1]; H. Zeng[2]; J. Parry[2]; H. Kamat[1]; 1. Alfred University, USA; 2. University of Buffalo, USA

Iron nitride materials have unique magnetic properties, and may replace some of the rare earth magnetic materials. In a collaborative research between Alfred University and University of Buffalo (SUNY RF 4E), iron nitride thin films were fabricated by RF sputtering techniques. The film thickness varies from 50 nm to 300 nm, depending on the deposition parameters. Some of the materials properties will be reported, along with the magnetic and optical properties. Applications will be described, as well as prototype devices.

9:40 AM

(ICACC-S2-043-2015) Effect of the Processing Variables on TiO2 Film Formation during Room Temperature Granule Spray in Vacuum

D. Park*[1]; H. Kim[2]; B. Hahn[1]; J. Ryu[1]; J. Choi[1]; W. Yoon[1]; J. Kim[1]; C. Ahn[1]; C. Park[2]; 1. Korea Institute of Materials Science, Korea (the Republic of); 2. Pukyong National University, Korea (the Republic of)

Room temperature granule spray in vacuum (RTGSV) is a novel coating method by which highly dense ceramic films can be deposited at room temperature. Ceramic granules are carried by gas like compressed air and sprayed directly onto the substrates through a nozzle in vacuum. Since the granule feeding rate and the carrier gas flow rate are independently controlled, their effect on the microstructure and the deposition rate of the film can be systematically investigated. In this presentation, we report the experimental results of TiO2 film formation and discuss effects of the granule feeding rate, the compressed air (carrier gas) flow rate and the granule size on the deposition of TiO2 film.

10:20 AM

(ICACC-S2-044-2015) Plasma Electrolytic Oxidation of aluminium to produce hard and thick α-alumina ceramic coatings

J. A. Martin*[2]; A. Nominé[1]; G. Henrion[1]; T. Belmonte[1]; 1. Université de Lorraine, France; 2. Université de Lorraiine, France

Plasma Electrolytic Oxidation (PEO) is an electrochemical process to produce protective oxide coatings on light-weight metals. Growth of the oxide layer takes place at potentials above the dielectric breakdown voltage of the insulating oxide layer leading to the development of short-lived micro-plasma over the processed surface. The resulting coating exhibits improved surface performances in terms of wear protection and corrosion resistance promoted by high-temperature crystalline phases (α-alumina). PEO process gains a growing interest in various domains to replace conventional acid anodizing. The present communication gives new insight into the influence of some electrical parameters on the efficiency of the PEO of aluminum (current waveform, density and frequency). Correlations are established between the micro-plasma characteristics (density, lifetime, size) determined by fast video imaging (>125kfr/s) and the elaborated coatings (thickness, roughness, hardness, α-alumina content). It will be shown that the best layers in terms of hardness (> 1400Hv), growth kinetic (> 100μm/h) have been achieved using an asymmetric pulsed current combined with an high anodic current density (80A.dm-2) and an high pulsed frequency (900Hz). Within these specific electrical conditions, detrimental effects of numerous, big-size and long-live micro-plasma on the oxide layer are minimized.

10:40 AM

(ICACC-S2-045-2015) Magnetic properties of BiFeO3/LaFeO3 heterostructures

A. Z. Simoes*[1]; 1. UNESP, Brazil

BiFeO3 (BFO) and LaFeO3 (LFO) heterostructures were observed at room temperature on Pt/TiO2/SiO2/Si (100) substrates by the chemical solution deposition. The films were coherently grown at a temperature of 500°C for 2 hours. Bottom BFO layer in the heterostructure was able to promote the grain growth of LFO during the annealing process with huge crystallite size. Room temperature magnetic coercive field indicates that the BFO/LFO and LFO/BFO present different magnetic behavior. Dielectric permittivity and dielectric loss demonstrated only slight dispersion with frequency due the less two-dimensional stress in the plane of the film. Poor P–E hysteresis loop was observed for heterostructure due the large leakage current caused by the BFO sublayer subjected to a longer period of annealing time.

11:00 AM

(ICACC-S2-046-2015) The Effect of Nano-Cobalt Particles on Enamel Metal Interface by Electroplating Method

M. Jafari*[1]; 1. Najafabad Branch, Islamic Azad University, Iran (the Islamic Republic of)

In this research in order to increase the adhesion of enamel to metal substrate nano particles of cobalt was implemented by electroplating method. By changing time and current of electroplating different thickness of the intermediate layer of cobalt nanoparticles were obtained. The microstructure of metallic cobalt nano particles layer before and after sintering was investigated in order to find which phases have been formed. Then acid resistant enamel was applied on cobalt nano particles and the samples were fired at 850 C. Physical parameters such as impact testing was performed to evaluate the adhesion to metal substrate. The morphology of cobalt nanoparticles and intermediate layer after firing was investigated by SEM, XRD and EDS. The SEM microscopic was shown the saturated zone of dendrite cobalt components which grown at the interface to the enamel were identified. This dendrite structure causes to increase adhesion of enamel to metal substrate. The adhesion strength of cobalt metal has significantly increased with increasing cobalt coating time or thickness, also by increasing coating time superficial imperfections in the enamel surface has been significantly reduced.

S5: Next Generation Bioceramics and Biocomposites

Bioceramics IV

Room: Coquina Salon F

Session Chairs: Thierry Azaies, Universite Paris 6; Leena Hupa, Åbo Akademi University

8:30 AM

(ICACC-S5-030-2015) Submicron Spheres of Amorphous Calcium Phosphate forming in a Stirred SBF Solution at 55°C (Invited)

C. Tas*[1]; 1. University of Illinois, USA

X-ray-amorphous calcium phosphate (ACP) spheres were synthesized in a synthetic body fluid (SBF) solution heated to 55 to 70°C under constant stirring at 850 rpm. The specific SBF solution (Lac-SBF) was buffered by using Na-L-lactate and lactic acid, and did not contain any Tris or Hepes. The Lac-SBF solution of this study matched all concentrations of the inorganic electrolyte ions of the human blood plasma. The monodisperse ACP spheres synthesized at 55°C were 245 nm in diameter when the Lac-SBF solution contained 67 mg/L gelatin. Samples were characterized by powder X-ray diffraction, Fourier-transform infrared spectroscopy, scanning electron microscopy and inductively-coupled atomic emission spectroscopy.

8:50 AM

(ICACC-S5-031-2015) Finding Optimized Compositions for Bioactive Glasses in Novel Applications (Invited)

L. Hupa*[1]; 1. Åbo Akademi University, Finland

Most bioactive glass products used in clinical applications are based on just a few compositions manufactured in rather simple product forms such, e.g. monoliths or granules. However, new products which use glass fibers or thin walled porous structures are of increasing interest. Simultaneously, the clinical applications of bioactive glasses are emerging from bone grafting into tissue healing and tissue engineering. These types of new applications require glass compositions that allow the manufacture into desired shapes but, more importantly, provide optimized biochemical effects in the target use. The presentation reviews the most important requirements to be taken into account when tailoring bioactive glasses to bone graft materials, tissue engineering scaffolds, or continuous fibers to be used in polymer composites. Optimized glass compositions can be found based on various models describing the physical and chemical properties as functions of the oxide composition. Further, models describing the hydroxyapatite formation and bone tissue bonding can be used for additional information for such optimization. In novel clinical applications, the ability of the glasses to guide and stimulate new tissue growth, to give bacteriostatic properties or to provide mechanical support for the growing tissue are of primary interest.

9:20 AM

(ICACC-S5-032-2015) In vitro bioactivity study of Cobalt-Chromium(Co-Cr) alloys via chemical surface modification

L. Chao*[1]; M. Toshiki[1]; S. Yuki[2]; 1. Kyushu Institute of Technology, Japan; 2. Kyushu Institute of Technology, Japan

Although Co-Cr alloys are clinically utilized for hard tissue reconstruction, they are poor in bone-bonding ability, i.e. bioactivity. In this study, the bioactivity behavior of Co-Cr alloys was investigated via chemical surface modification which is the preparation of 11-Aminoundecylphosphonic acid (11-AUPA: [$C_{11}H_{27}BrNO_3P$]) self-assembled monolayers (SAMs) on alloys' surface for inducing apatite precipitation when soaking in simulated body fluid (SBF). After chemical treatment, the specimens were soaked in $CaCl_2$ solution, followed by soaking in SBF. After soaking in 11-AUPA solution, the contact angle values decreased obviously and the new presence of P 2p peak around 133.2 eV were observed in X-ray Photoelectron Spectroscopy (XPS) measurement results. These changes all demonstrated the immobilization of SAMs on the alloys' surface. After soaking in SBF, all samples were then examined by thin-film X-ray diffraction (TF-XRD) and scanning electron microscopy (SEM). With the pre-treatment of 11-AUPA solution, new broad peaks were detected at 26 and 32° in 2θ by TF-XRD and spherical particles about 2-3 μm in diameter were observed, which indicates the precipitation of apatite on the alloys' surface. This study shows the apatite formation on Co-Cr alloys in SBF could be successfully induced by chemical surface modification, which would lead to the improvement of bioactivity behavior.

9:40 AM

(ICACC-S5-033-2015) Constructing Cell-laden Nanofibrous Scaffolds through Concurrent Electrospinning and Cell Electrospraying

Q. Zhao*[1]; M. Wang[1]; 1. The University of Hong Kong, Hong Kong

Using conventional technology, it is difficult to obtain 3D cell-laden electrospun tissue engineering scaffolds. Normal cell seeding only puts cells on scaffold surfaces. We therefore investigated the fabrication of 3D cell-laden scaffolds using concurrent electrospinning and cell electrospraying. For cell electrospraying, coaxial electrospray was employed. The coaxial device had an inner tube, which was supplied with a cell suspension of human umbilical vein endothelial cells, and a coaxial outer tube, which was fed with a polymer blend solution (gelatin and sodium alginate; at different ratios). Electrospraying formed hollow microspheres (5~15 μm), encapsulating cells. Effects of electrospraying parameters were studied for the structure of microspheres. HUVEC cell viability was investigated after dissolving the water-soluble polymer shell and culturing the cells, and processing parameters were optimized for cell electrospraying. 3D cell-laden scaffolds consisting of PLGA nanofibers were constructed via concurrent electrospinning and cell electrospraying. Cells were released from electrosprayed particles by immersing in cell culture medium. Subsequently, in vitro biological studies were conducted to assess cell viability, cell location in scaffolds and cell proliferation. HUVEC cells exhibited good cell viability and cells proliferated with increasing culture time.

10:20 AM

(ICACC-S5-034-2015) Structural, phase stability and magnetic field assisted osteoinductive behavior of magnetoactive hydroxyapatite-iron oxide composites

S. K. Boda*[1]; B. Sahoo[1]; B. Basu[1]; 1. Indian Institute of Science, India

The application of magnetic fields for accelerated bone repair is clinically established. Herein, the efficacy of magnetoactive composites in modulating osteogenesis and matrix mineralization in the presence of static magnetic field (SMF) is investigated. Magnetic composites of HA-xFe3O4 (x = 5, 10, 20 and 40 wt%) were hot-pressed and characterized for the phase assemablage. Rietveld analysis of XRD data revealed an increase in the lattice parameters of hydroxyapatite (HA) while Mössbauer spectroscopy affirmed the formation of wustite (FeO) and Fe3+ doped HA along with the retention of the parent phases. The hysteresis loops observed in vibrating sample magnetometry (VSM) measurements divulged the ferromagnetic behavior of the composites. XPS analysis indicated significant reduction of Fe3+ to Fe2+ for x ≤ 10 wt%. A plethora of biological analysis expounded the potency of magnetic stimulation in inducing osteogenesis of human mesenchymal stem cells (hMSCs). The application of 100 mT (SMF) upregulated the expression of osteogenic markers (Runx2, ALP, Collagen, Osteocalcin and Osteopontin) as well as improved mineralization depicting the lineage switching of hMSCs to osteoblasts. In summary, the potential of SMF and magnetic biocomposites with tailored Fe3O4 content in driving the osteogenesis of stem cells is demonstrated in the current study.

10:40 AM

(ICACC-S5-035-2015) Synthesis and Characterization of CoCu Ferrite and Bioglass Composites for Hyperthermia Treatment of Cancer

V. Chalisgaonkar*[1]; K. Pandey[1]; A. K. Sampath[1]; H. Tripathi[1]; S. P. Singh[1]; R. Pyare[1]; 1. Indian Institute of Technology (BHU), India

Novel copper-cobalt ferrite/bioglass composites were prepared through sol-gel route and the effect of copper concentration on the magnetic properties was investigated and the particle size was measured by TEM. The composites were sintered at optimize temperature to get maximum densification and the constituent phases were analyzed by XRD and the major phases were identified as CoFe2O4 and Na2Ca2Si3O9. In vitro bioactivity of the composite was investigated in simulated body fluid (SBF) in physiological conditions. The HCA phase was identified by FTIR, SEM and XRD. The in vitro biocompatibility of the composite was assessed by human osteoblast cell attachment, viability and proliferation and the surface morphology was examined by SEM. The compressive strength and Young's modulus of the composites was measured. Thus the CoCu ferrite/ bioglass composite have higher potential for hyperthermia treatment of cancer.

11:00 AM

(ICACC-S5-036-2015) Structure–Bioactivity Relationship of Two Polymorphs of CaSiO3 Ceramics

B. Beyoglu*[1]; R. E. Riman[1]; B. Jadidian[1]; 1. Rutgers, State University of New Jersey, USA

CaSiO3 bioactive ceramics, because of their superior bioactivity and mechanical strength properties, are a promising biomaterial for bone replacement implant applications.Our goal in this study is to distinguish bioactivity differences for two polymorphs of CaSiO3 in order to select the most efficient CaSiO3 phase for bioactive implant production. The effect of crystal structure on its in vitro bioactivity behavior, the release rates of calcium and silicate ions and subsequent apatite phase precipitation, and mechanical strength is investigated experimentally. Pseudowollastonite (high temperature phase) has developed by applying heat treatment to wollastonite (low temperature phase).In vitro bioactivity test is applied to samples using Kokubo's conventional Simulated Body Fluid. Immediately after, Ca, S, P ion concentrations in SBF are determined by inductively couple plasma atomic emission spectroscopy (ICP). X-ray diffraction analysis, scanning electron microscopy (SEM), coupled with X-ray energy dispersive spectroscopy (EDS), compressive strength testing, pycnometry and mercury porosimetry are used to characterize samples before and after bioactivity tests. Cytotoxicity on osteoblast cells has evaluated. Results indicate that pseudowollastonite is a better biomedical implant material candidate by having superior bioactivity properties compared to wollastonite and increase in the strength of the implant.

S10: Virtual Materials (Computational) Design and Ceramic Genome

Modeling Defects and Related Properties

Room: Coquina Salon C

Session Chairs: Paul Rulis, University of Missouri - Kansas City; Xing-Qiu Chen, Institue of Metal Research

8:30 AM

(ICACC-S10-025-2015) Effects of irradiation and dopants on grain growth in nanocrystalline oxides (Invited)

Y. Zhang*[1]; D. Aidhy[1]; T. Varga[3]; F. Namavar[4]; W. J. Weber[2]; 1. Oak Ridge National Laboratory, USA; 2. University of Tennessee, USA; 3. Pacific Northwest National Laboratory, USA; 4. University of Nebraska Medical Center, USA

Nanocrystalline oxides are of high interests for a wide range of applications due to their exceptional size-dependent materials properties. Ceramic oxides are key materials for chemical, electronic, optical, space and nuclear industries, and nanostructured oxides are considered as potential candidates in advanced environmental and energy related applications. Cubic ceria (CeO2) and zirconia (ZrO2) are important materials for catalysis, sensors, fuel cells and coatings. They are also isostructural with urania, plutonia, and thoria-based nuclear fuels, and understanding the irradiation response of these materials is important for advanced nuclear energy systems. Ion beam doping and processing are effective approaches to tailor size-dependent material properties and functionality of oxide-based nanomaterials. Grain growth of nanocrystalline materials is generally thermally activated at elevated temperatures, but can also be controllably driven by irradiation at much lower temperature. Experimental results have shown that irradiation-induced disorder can lead to growth of the nanograins. Atomistic simulations have successfully modeled both thermal and irradiation-induced grain growth in these nanocrystalline oxides. Additional simulations have revealed criteria for selective doping to prevent grain growth by dopant-pinning of the grain boundaries. This work was supported by the U.S. DOE, BES, MSED.

9:00 AM

(ICACC-S10-026-2015) Nonlocal Exchange-Interaction Effects in Accurately Determining Vacancy Formation Enthalpy of Solids (Invited)

X. Chen*[1]; 1. Institue of Metal Research, Chinese Academy of Sciences, China

First-principles determination of the defect formation enthalpies has been long-term thought to be more successful for metals than semiconductors and insulators. However, a widely known fact is that the various conventional density functional theory (DFT) calculations with the typical semilocal approximations show the apparent failures to yield accurately those enthalpies of some typical metals and their related ceramics. Recently, the previously commonly assumed linear Arrhenius extrapolation to determine the vacancy formation enthalpies from the high-temperature data of measured vacancies has been demonstrated to have to be replaced by the non-Arrheniums local Gr\"ueisen theory. The large discrepancies between the conventional DFT-PBE data and the unrevised experimental vacancy formation enthalpies disappear for some materials, also further uncovering the previously suggested surface-correction or AM05 exchange-correlation functional were not successful to rectify these shortcoming. Even following the same revisions for some typical metals and their related ceramics, the large discrepancies are still robust. Here, we show the modern extensions of DFT based on nonlocal exchange interactions can further correct these failures. Our results shed light on improving the theoretical power to predict accurately defect formation energies and related thermodynamical properties.

9:30 AM

(ICACC-S10-027-2015) Composition dependent hardness of covalent solid solutions and its electronic structure origin (Invited)

Q. Hu*[1]; L. Vitos[2]; R. Yang[1]; 1. Insitute of Metal Research, Chinese Academy of Sciences, China; 2. Royal Institute of Technology, Sweden

Materials with high hardness are technologically important for many types of wear resistant coatings. The search for harder materials has a long history and remains one of the most active areas in materials science. Several hardness models based on electronic structure theory for perfect elemental materials/binary covalent and ionic compounds have been put forward. However, most of the engineering materials are alloys (solid solutions) and inevitably contain some impurities or defects such as vacancies. Theoretical predictions of the hardness of this kind of materials have rarely been touched in the past. We presented a hardness formula for multicomponent covalent solid solutions. Here the composition dependence of the hardness of some covalent/ionic solid solutions, predicted with this formula, taking the parameters from our first-principles calculations, will be reported in comparison with experimental results. Furthermore, the electronic structure origin of the composition dependence of the hardness will be discussed. We will show that the band-filling effect proposed in literature to account for the composition dependence of the hardness of e.g. TiCxN1-x fails for some of the systems. Instead, we suggest that the composition dependence is controlled by the competition between the band-filling effect and the strength of electronic states hybridization.

10:20 AM

(ICACC-S10-028-2015) Molecular Dynamic Simulations of Synergistic Effects in Ion Track Formation (Invited)

E. Zarkadoula*[1]; O. Pakarinen[1]; W. J. Weber[2]; Y. Zhang[1]; 1. Oak Ridge National Laboratory, USA; 2. University of Tennessee, USA

Molecular Dynamic (MD) simulations is an important tool for gaining insights into processes that take place during ion-solid interactions and are often not measurable in experiments. The effects of the interactions are partially due to nuclear stopping and partially due to interactions with the electrons. In high energy processes such as swift heavy ion irradiation, the electronic effects are more

dominant, and they are described by the inelastic thermal spike model. Swift heavy ion irradiation can result in the formation of trails of atomic disorder in the target, known as ion tracks. We use MD simulations in combination with the inelastic thermal spike model to study the effects of electronic energy loss on track formation in ceramics resulting from ions with energies up to tens of MeV. Systems of interest include $SrTiO_3$, a material widely studied for microelectronics, optoelectronics, and nuclear applications, and $ZrSiO_4$, proposed for immobilization of nuclear waste and plutonium. We find synergistic effects for electronic energy loss in the presence of pre-existing defects. These findings are in agreement with experimental results and our results reveal the ion track formation mechanism in these materials. Our work draws attentions to the importance of the electronic effects in high-energy irradiation events. This work was supported by the U.S. DOE, BES, MSED.

10:50 AM

(ICACC-S10-029-2015) Ab initio molecular dynamics approach of early stage oxidation of Cr2AlC (001) surface

N. Li*[1]; R. Sakidja[2]; W. Ching[2]; 1. Wuhan University of Technology, China; 2. University of Missouri-Kansas City, USA

Initial stage of oxidation of Cr2AlC (001) surface by oxygen atoms was investigated in atomic scale by ab initio molecular dynamics (AIMD) simulation at wide temperature range from 300 K to 1673 K. The results of the present simulation point to the oxygen atoms spontaneously dissociated on the Cr2AlC (0001) surface, strongly bond to the surface Al atoms, and formed Al-O bond whose mechanisms appear to be quite similar to that observed at the initial stage of oxidation on the Al (111) surface of FCC Al. The simulation also exhibited that the reacted with oxygen preferentially located in the back bonds of the surface dimer. Consecutive oxidation simulation with monolayer O atoms showed that the diffusion of oxygen atom into the subsurface of clean Cr2AlC (0001) surface can occur during long time of the present oxidation simulation. The present AIMD simulation also revealed that the oxidation at 300 K results in more stoichiometric oxide layer than that at 1673 K.

11:10 AM

(ICACC-S10-030-2015) Segregation and trapping of oxygen vacancies near the $SrTiO_3$ Σ3 (112) [-110] tilt grain boundary (Invited)

B. Liu*[1]; V. R. Cooper[1]; Y. Zhang[1]; W. J. Weber[2]; 1. Oak Ridge National Laboratory, USA; 2. University of Tennessee, USA

In nanocrystalline materials, structural discontinuities at grain boundaries (GBs) and the segregation of point defects to these GBs play a key role in defining the structural stability and macroscopic electrical/mechanical properties. In this study, the segregation of oxygen vacancies near the Σ3 (112) [-110] tilt GB in $SrTiO_3$ is explored using density functional theory. We find that oxygen vacancies segregate towards the GB, preferring to reside within the next nearest neighbor layer. The migration barriers of oxygen vacancies diffusing to the first nearest-neighbor layer of the GB are low, while those away from this layer are very high. The segregation and trapping of the oxygen vacancies in the first nearest-neighbor layer of the GB are attributed to the large local distortions, which can now accommodate the preferred six-fold coordination of Ti. This oxygen vacancy segregation is found to be crucial for stabilizing this tilt GB. These results also suggest that the electronic, transport, and capacitive properties of $SrTiO_3$ can be engineered through the control of GB structure, as well as grain size or layer thickness. This work was supported by the U.S. DOE, BES, MSED.

11:40 AM

(ICACC-S10-031-2015) Evolution of low energy structures in ZrC_x

Y. Zhang*[1]; B. Liu[2]; J. Wang[1]; 1. Institute of Metal research, China; 2. Oak Ridge National Laboratory, USA

Zirconium carbide, along with other binary transition metal carbides and nitrides (MX, M=Ti, Zr, Nb etc; X=C, N) is attracting increasingly attentions because of their unique properties at high temperatures and promising applications under extreme environments. The intrinsic carbon deficiency in non-stoichiometric ZrC_x is known significantly affecting the mechanical and thermal properties. Evolution of the pattern of carbon vacancies with their concentration and its influence on the phase stabilities and performances of ZrC_x are the crucial important questions but remain unclear for many years. In this work, we combine cluster expansion technique and first-principles calculations to investigate energetics and possible structures of a series of ZrC_x (x=0.5~1.0). The results show negative mixing enthalpies and ordering enthalpies of ZrCx in the broad composition range. These indicate that abundant C vacancies intend to form ordered low energy structures in ZrC_x. The origins of this tendency are attributed to the short-range interactions among C vacancies and the formation of maximum preferred C vacancy clusters. The present results are useful to understand and optimize macroscopic properties of ZrC_x with considerable intrinsic carbon deficiency.

S11: Advanced Materials and Innovative Processing Ideas for the Production Root Technology

Innovative Process Technologies with Enhanced Performances of Products I

Room: Coquina Salon E

Session Chairs: Ramesh Peelamedu, BTU Internatinoal; Sangmok Lee, KAIST

8:30 AM

(ICACC-S11-017-2015) Fabrication of Barium-Ferrite and Polymer Hybrid System with Highly Regulated 3D micro Structures (Invited)

T. Nakayama*[1]; M. Kanno[1]; H. Cho[1]; T. Suzuki[1]; H. Suematsu[1]; K. Niihara[1]; 1. Nagaoka univ of Tech, Japan

The orientation of Barium-Ferrite particles was controlled in polymer-based nanocomposite film using microscopic molds while applying a DC electric field. The Barium-Ferrite particles were dispersed by sonication in a prepolymer mixture of polysiloxane followed by a high speed mixing. The homogeneous suspension was cast on a microscopic mold with different patterns, which is attached to negative electrode during application of electric field before it became cross-linked. Analysis revealed that filament-like linear assembles of Barium-Ferrite particle were fabricated in polysiloxane/Barium-Ferrite hybrid films, and Barium-Ferrite particles composing filament-like linear assembles were aligned perpendicular to the film plane with high anisotropy. The structure and dimensions of filament-like linear assembles showed with thermal property of the composite, and could be changed depending on the type of used microscopic molds. The filament-like linear assembles formation induced by the type of microscopic molds and intensity of applied electric fields are discussed.

9:00 AM

(ICACC-S11-018-2015) Hybrid microwave drying of battery electrode slurries (Invited)

R. Peelamedu*[1]; D. A. Seccombe[1]; 1. BTU International, USA

One of the cost barriers of high performance lithium ion battery electrodes is the high electrode processing costs in manufacturing. The use of convection flotation drying technology to dry lithium ion battery electrodes can be extremely expensive due to the energy intensity of the air flotation requirements and the operation of the solvent recovery system. Any processing step towards a higher performance with considerable cost benefit should not be ignored. The footprint of the hybrid microwave system is considerably smaller and operates with a much lower thermal budget. In this presentation, we propose the use of a controlled microwave dryer for removal of water and organic solvents in both anode and cathode materials. Two- sided patch coating using water and NMP based slurries could be applied to a metal foil that would be fed through a microwave chamber in a continuous process. The foil would be supported by a microwave transparent support structure. The ability of microwaves to penetrate through several layers deeper would result in a complete solvent removal by the microwave system. The hybrid microwave technology has a very uniform temperature and drying distribution throughout the system. The potential for immediate coating compaction and the elimination for electrode de-humidification is possible.

9:30 AM

(ICACC-S11-019-2015) Sintering Combined with Coating for Developing High Performance Ceramics (Invited)

T. Goto*[1]; 1. IMR Tohoku University, Japan

Although novel sintering processes, such as SPS (spark plasma sintering) and micro-wave sintering, have been developed to produce high performance ceramics, it is still difficult to densify highly covalent materials, typically diamond and cubic boron nitride (cBN), at moderate pressure. The surface modification of powder by coating combined with SPS enables one to densify diamond powders. We have demonstrated amorphous SiC coating on diamond powders by rotary CVD, and prepared diamond (core)/ SiC (shell) powder which can be well sintered by SPS. Amorphous SiO2 layer were also coated on cBN, and cBN (core)/ SiO2 (shell) was densified by SPS. In cutting tool industry, WC-Co is common material, whereas W is a rare element and its usage should be minimized. TiCN powder was coated by WC layer forming TiCN(core)/ WC(shell) powder, which was mixed with Co forming W-less TiCN/ WC/Co cermets. CVD can prepare various core/shell powders simply changing source materials. SiC (core)/ SiO2 (shell) powder was consolidated by SPS having a high toughness of 8 MPam1/2. CVD can be expandable to mass production, and the combination of coating by CVD and SPS could be a promising technique to obtain high performance ceramics.

Innovative Process Technologies with Enhanced Performances of Products II

Room: Coquina Salon E

Session Chairs: Masahiro Yoshimura, National Cheng Kung Univ.; Taejin Hwang

10:20 AM

(ICACC-S11-020-2015) Electrochemical Assisted Microstructure Control for Ceramic Coatings on Metallic Materials by Growing Integration Layer [GIL] Method (Invited)

M. Yoshimura*[1]; 1. Cheng Kung University, Taiwan

Electric force is powerful tool for the formation and control of microstructures of ceramic films and coatings particularly via electrochemical reactions. We have studied on electrochemical ceramics films/coatings since 1989 succeeded to make BaTiO3 on Ti, then proposed a novel concept and technology: "Growing Integration Layer" [GIL] method for nano-/micro-structure controlled ceramics coating on metallic materials. Those GIL(s) can be prepared from a component of the metallic materials by electrochemical reactions in a solution at low temperature of RT-200 degree. CaTiO3/Al2O3 anti-oxidation coating could be fabricated on TiAl. On a Ti-base Bulk Metallic Glass, we could succeed to prepare bioactive titanate nano-mesh layer by hydrothermal-electrochemical techniques for 1 h at 90-120 degree. Similar bioactive oxide layers could be prepared on other Bulk Metallic Glasses and alloys. The GIL strategy is effective for many metallic alloys and bulk metallic glasses because they generally contain active component(s). [GIL] have particular features:1)Widely diffused interface(s), 2)Continuously graded layers grown from the bulk(substrate),3)Low temperature process, etc.

10:50 AM

(ICACC-S11-021-2015) Preparation of thick absorbent layer on the aluminum and the cupper plate for high-performance heat exchanger

T. Hwang*[2]; S. Cho[1]; 1. KITECH, Korea (the Republic of); 2. Department of Electronic Packaging Engineering(UST), Korea (the Republic of)

Porous zeolite particles modified with foreign metal ion are frequently used as an absorbent, which are attached on the surface of high-performance heat exchanger fins chiefly made of aluminum or, in less popular cases, cupper. The adsorption and desorption of water into and out of the porous particles noticeably increases the heat flux due to the latent heat by the phase change of water. However, the cyclic adsorption and desorption of water inevitably requires certain extent of mechanical and chemical durability of the absorbent layer. In this study, we employed silica binder prepared via the sol-gel chemical process to enhance the physicochemical properties of the deposited zeolite-based absorbent layer on both aluminum and cupper plates. Absorbent layers with thickness of several tens of micrometers were successfully prepared by a simple dip-coating method, and they showed an excellent adhesion to the metal plates during over 100 hours of salt-spray test.

11:10 AM

(ICACC-S11-022-2015) Fabrication of High-Strength Si_3N_4 Ceramics by Post-reaction Sintering Technique Using Waste Si Sludge (Invited)

J. Tatami*[1]; H. Sasano[1]; M. Iijima[1]; T. Takahashi[2]; 1. Yokohama National University, Japan; 2. Kanagawa Academy of Science and Technology, Japan

A lot of waste Si sludge are discharged from Si industry. In this study, we successfully fabricated high-strength Si_3N_4 ceramics by post-reaction sintering technique using the waste Si sludge. For reference, a commercial Si powder was also used as a raw material. Powder mixtures of the Si and sintering aids were prepared by wet ball milling. Although Si remained in the powder compacts of the commercial Si powder after nitridation, those of the waste Si sludge were fully nitrided. Furthermore, highly dense Si_3N_4 ceramics without coarser pores were obtained after post-reaction sintering using the waste Si sludge due to more homogenous microstructure in the reaction sintered Si3N4 body. The bending strength of the waste Si sludge was higher than that of the commercial Si because of homogenous microstructure.

11:40 AM

(ICACC-S11-023-2015) Properties of the metallic glass thin films fabricated by multicomponent single alloying target and its applications in various industrial fields

J. Sun*[1]; S. Shin[1]; K. Moon[1]; 1. Korea Institute of Industrial Technology, Korea (the Republic of)

Metallic glass alloys having dense packing structure have short range ordered structure with long range homogeneity. Therefore, they can provide complete corrosion protection and unique electrical properties. Recently, metallic glass thin films have received much attention to extend its application fields combining with PVC coating technologies. The metallic glass thin films can change the surface properties of the conventional bulk materials which need anticorrosion properties. However, multi-component alloying targets are required to fabricate the metallic glass thin films because metallic glass alloys contain more than three elements. Recently, many researchers have been reported the properties of the metallic glass thin films synthesized with multi-cathode systems or amorphous target. But, it is difficult to fabricate the large sized sputtering targets for mass production equipment with high toughness and thermal stability. In this study, newly developed sputtering target with glass forming ability and the properties of the metallic glass thin films will be introduced with respect to the various application fields such as bipolar plate in PEM fuel cell and decorative coatings for electric device and construction fields.

FS2: Advanced Ceramic Materials and Processing for Photonics and Energy

Structure and Applications

Room: Coquina Salon H

Session Chairs: Fiorenzo Vetrone, Université du Québec, Institut National de la Recherche Scientifique; Daniel Chua, National University of Singapore

8:30 AM

(ICACC-FS2-024-2015) Comparison between c-axis-aligned crystalline (CAAC) and nanocrystalline In-Ga-Zn-O which have different crystal morphologies

M. Takahashi[1]; K. Dairiki*[1]; K. Akimoto[2]; R. Tokumaru[1]; Y. Yamane[1]; N. Ishihara[1]; M. Tsubuku[1]; M. Nakashima[1]; J. Koezuka[2]; K. Okazaki[2]; S. Yamazaki[1]; 1. Semiconductor Energy Laboratory Co. Ltd., Japan; 2. Advanced Film Device Inc., Japan

A ceramic material of In-Ga-Zn-O (IGZO) has been attracting attention as novel semiconductor. In IGZO thin films of mass-produced field effect transistors (FETs), we have found two kinds of crystal morphology: c-axis aligned crystal (CAAC) and nanocrystal (nc). We compare CAAC-IGZO and nc-IGZO in this study. CAAC and nc have a difference in morphology. C-axes of crystals in CAAC-IGZO are substantially aligned but a- and b-axes are not aligned, while nc is constituted by crystals oriented in various directions. We measured the photo absorption coefficient due to deep defect states probably related to oxygen vacancies by constant photocurrent method. As a result, the amount of defects was smaller in CAAC. Furthermore, When a metal was deposited on an IGZO film, conductive region was generated in IGZO near the interface to metal and expanded by heating. An extension of this conductive region in CAAC was less than that of in nc. In addition, as we evaluated the diffusion of impurities (e.g. Cu) from the IGZO film surface in the depth direction, diffusion in CAAC was slower than that in nc. These results show that CAAC films have better control over defects, impurities and carriers, which affect semiconductor characteristics. Thus, we conclude that CAAC is preferable to nc in the production of minute FETs on a commercial level.

8:50 AM

(ICACC-FS2-025-2015) Carbon-based materials by Pulsed Laser Deposition and some applications (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 dimensions, such as graphite to graphene. There are many potential applications ranging from electronics to conductive coatings to biomedical technology. In order to obtain high quality materials as a precursor, the key focus has been in optimizing and finding the correct growth techniques. Pulsed laser deposition (PLD) has been widely known for its ability to deposit high quality hydrogen free diamond-like carbon films. In this talk, I will focus on the lesser known fact that the PLD technique can be used to deposit high quality graphene films at relatively low temperatures of 700 oC. In addition, by modifying the growth process, one can obtain graphite nanodots and through the formation of nanocomposites, particles such as ZnO can be embedded into the carbon matrix. Some applications of the graphene, graphite nanodots and nanocomposites will also be shown. For example, with careful design, flat-film electron emitters can be engineered to be as effective as tube-like emitters.

9:20 AM

(ICACC-FS2-026-2015) Lanthanide-Doped Nanoparticles: Versatile Near-Infrared Excited Optical Bioprobes (Invited)

F. Vetrone*[1]; 1. Université du Québec, Canada

Lanthanide-doped nanoparticles are emerging as useful tools in diagnostic medicine and therapeutics since they can be excited with near-infrared (NIR) light. This type of excitation mitigates some of the drawbacks associated with the use of UV as the excitation source since NIR light is silent to tissues and possesses greater tissue penetration capabilities. Moreover following NIR excitation, these nanoparticles can undergo conventional luminescence where the emission wavelengths are at lower energy than the excitation source or can undergo upconversion where the NIR light is (up)converted to higher energies. There has been an increasing interest in lanthanide-doped upconverting nanoparticles since it is possible to obtain UV/visible/NIR emissions using a single NIR excitation source and as such have been proposed for a wide variety of biomedical applications. Here, we present various types of NIR-excited nanoparticles and show how they could be used as multi-modal bioprobes for sensing, imaging as well as the diagnostics and therapeutics of cells.

10:10 AM

(ICACC-FS2-027-2015) Two photon polymerization of inorganic-organic hybrid materials for medical implant applications (Invited)

R. Narayan*[1]; 1. UNC/NCSU Joint Dept of Biomedical Engineering, USA

Two photon polymerization is a 3D printing technique in which ultrashort laser pulses are used to selectively polymerize photosensitive resins and form structures with micrometer and/or sub-micrometer scale features. The two photon polymerization process involves nearly simultaneous absorption of two photons by a small volume of the photosensitive resin within a short time frame. The nonlinear character of two photon absorption allows for processing of structures containing features below the diffraction limit. A structure with an arbitrary geometry may be processed by polymerizing the photosensitive resin along the laser trace, which is translated in three dimensions with a micropositioning system. This talk will consider processing of microstructured medical devices out of organically-modified ceramic materials using two photon polymerization. Use of two photon polymerization to create medically-relevant structures such as tissue engineering scaffolds and transdermal devices will be described. Use of in vitro studies for assessing two photon polymerization-processed organically-modified ceramic medical devices will also be considered.

10:40 AM

(ICACC-FS2-028-2015) Roll-to-Roll (R2R) Ultrathin Flexible Ceramic for Cost Effective Coating Deposition

J. A. Olenick*[1]; 1. ENrG Incorporated, USA

This paper presents ENrG's 2015 goal to produce an in-line, coatable format of its Thin E-Strate product. The 20 microns thick product, targeted between 100-300 meters long, with initial widths up to 5 centimeters, is being developed for customers capable of coating in R2R form. Unlike plastic films in which temperature and humidity affect R2R handling and alignment, Thin E-Strate is stable, inert and is translucent for two-sided coating registration. This flexible ceramic can handle higher temperature processing, does not absorb moisture and is corrosion resistant. Thin E-Strate, a flexible zirconia based ceramic membrane, was originally introduced in 2010 at 40 microns thick. Even though so thin, the membrane is gas-tight, fully dense, strong, thermal shock tolerant and chemically inert. Inherent properties of the membrane are fully compatible with many applications including wearable electronics, mechanical sensors, medical electronics, microbatteries, solar photovoltaic, power electronics, solid-state lighting, transparent infrared windows, fuel cells, and superconductors. These applications tap into additional membrane properties via coatings. Many of these market applications require the thin ceramic to be supplied in a R2R form versus sheets, for more economical coating. Material and application performance data will be presented as available across multiple market applications.

11:00 AM

(ICACC-FS2-029-2015) in situ Studies of the Thermal Stability of Group IV Binary and Ternary Alloys (Invited)

J. Fournier-Lupien[1]; G. Mussler[2]; S. Wirths[2]; S. Mantl[2]; D. Buca[2]; O. Moutanabbir*[1]; 1. Ecole Polytechnque de Montreal, Canada; 2. Forschungszentrum Juelich, Germany

Group IV binary (GeSn) and ternary (SiGeSn) alloys provide a wealth of opportunities to enable CMOS-compatible optoelectronic and photonic devices for chemical and biological sensing, spectroscopy, and free-space communication. Additionally, the control of the composition and structure of these alloys is also crucial to implement carbon-free energy conversion devices such thermoelectrics and high-efficiency solar cells. A deep understanding of the structural and morphological stability of GeSn and GeSiSn metastable alloys is of utmost importance in order to achieve the aforementioned technologies. Here, we present in situ investigations of their structural and elemental properties as a function of annealing temperature using low energy electron microscopy (LEEM), photoelectron emission microscopy (PEEM), and nano-Auger spectroscopy. These investigations have unraveled unprecedented insights into the stability of these layers as well as into the dynamics of phase separation in Sn-rich alloys. In the latter, we have traced the formation, evolution, surface diffusion of Sn-rich droplets and clusters. We have also indentified the interplay between Sn concentration and the critical temperature that triggers the alloy instabilities in both binary and ternary layers. A theoretical treatment including both thermodynamic and kinetic considerations was developed to discuss the observed phenomena.

Author Index

*** Denotes Presenter**

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