The American Ceramic Society

37th International Conference & Exposition on Advanced Ceramics and Composites

ABSTRACT BOOK

January 27–February 1, 2013
Daytona Beach, Florida

The American Ceramic Society
www.ceramics.org

Introduction

This volume contains abstracts for more than 849 presentations during the 37th International Conference & Exposition on Advanced Ceramics and Composites in Daytona Beach, Florida. The abstracts are reproduced as submitted by authors, a format that provides for longer, more detailed descriptions of papers. The American Ceramic Society accepts no responsibility for the content or quality of the abstract content. Abstracts are arranged by day, then by symposium and session title. An Author Index appears at the back of this book. The Meeting Guide contains locations of sessions with times, titles and authors of papers, but not presentation abstracts.

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.

MEETING REGULATIONS

The American Ceramic Society is a nonprofit scientific organization that facilitates the exchange of knowledge meetings and publication of papers for future reference. The Society owns and retains full right to control its publications and its meetings. The Society has an obligation to protect its members and meetings from intrusion by others who may wish to use the meetings for their own private promotion purpose. Literature found not to be in agreement with the Society's goals, in competition with Society services or of an offensive nature will not be displayed anywhere in the vicinity of the meeting. Promotional literature of any kind may not be displayed without the Society's permission and unless the Society provides tables for this purpose. Literature not conforming to this policy or displayed in other than designated areas will be disposed. The Society will not permit unauthorized scheduling of activities during its meeting by any person or group when those activities are conducted at its meeting place in interference with its programs and scheduled activities. The Society does not object to appropriate activities by others during its meetings if it is consulted with regard to time, place, and suitability. Any person or group wishing to conduct any activity at the time and location of the Society meeting must obtain permission from the Executive Director or Director of Meetings, giving full details regarding desired time, place and nature of activity.

During oral sessions conducted during Society meetings, **unauthorized photography, videotaping and audio recording is prohibited.** Failure to comply may result in the removal of the offender from the session or from the remainder of the meeting.

The American Ceramic Society plans to take photographs and video at the conference and reproduce them in educational, news or promotional materials, whether in print, electronic or other media, including The American Ceramic Society's website. By participating in the conference, you grant The American Ceramic Society the right to use your name and photograph for such purposes. All postings become the property of The American Ceramic Society.
Registration Requirements: Attendance at any meeting of the Society shall be limited to duly registered persons.
Disclaimer: Statements of fact and opinion are the responsibility of the authors alone and do not imply an opinion on the part of the officers, staff or members of The American Ceramic Society. The American Ceramic Society assumes no responsibility for the statements and opinions advanced by the contributors to its publications or by the speakers at its programs; nor does The American Ceramic Society assume any liability for losses or injuries suffered by attendees at its meetings. Registered names and trademarks, etc. used in its publications, even without specific indications thereof, are not to be considered unprotected by the law. Mention of trade names of commercial products does not constitute endorsement or recommendations for use by the publishers, editors or authors.
Final determination of the suitability of any information, procedure or products for use contemplated by any user, and the manner of that use, is the sole responsibility of the user. Expert advice should be obtained at all times when implementation is being considered, particularly where hazardous materials or processes are encountered.

Table of Contents

FS3: Nanomaterials for Sensing Applications: Fundamental Material Designs to Device Integration

2nd Global Young Investigators Forum

S1: Mechanical Behavior and Performance of Ceramics & Composites

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

S3: 10th International Symposium on Solid Oxide Fuel Cells (SOFC): Materials, Science and Technology

S4: Armor Ceramics

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

S7: 7th International Symposium on Nanostructured Materials and Nanocomposites

S8: 7th International Symposium on Advanced Processing and Manufacturing Technologies for Structural and Multifunctional Materials and Systems (APMT)

S9: Porous Ceramics: Novel Developments and Applications

S10: Virtual Materials (Computational) Design and Ceramic Genome

2nd Global Young Investigators Forum

S1: Mechanical Behavior and Performance of Ceramics & Composites

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

S3: 10th International Symposium on Solid Oxide Fuel Cells (SOFC): Materials, Science and Technology

S4: Armor Ceramics

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

S7: 7th International Symposium on Nanostructured Materials and Nanocomposites

S8: 7th International Symposium on Advanced Processing and Manufacturing Technologies for Structural and Multifunctional Materials and Systems (APMT)

S9: Porous Ceramics: Novel Developments and Applications

S10: Virtual Materials (Computational) Design and Ceramic Genome

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

S1: Mechanical Behavior and Performance of Ceramics & Composites

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

S4: Armor Ceramics

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

S8: 7th International Symposium on Advanced Processing and Manufacturing Technologies for Structural and Multifunctional Materials and Systems (APMT)

S9: Porous Ceramics: Novel Developments and Applications

FS2: Thermal Management Materials and Technologies

FS3: Nanomaterials for Sensing Applications: Fundamental Material Designs to Device Integration

S1: Mechanical Behavior and Performance of Ceramics & Composites

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

S3: 10th International Symposium on Solid Oxide Fuel Cells (SOFC): Materials, Science and Technology

S4: Armor Ceramics

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

S7: 7th International Symposium on Nanostructured Materials and Nanocomposites

S8: 7th International Symposium on Advanced Processing and Manufacturing Technologies for Structural and Multifunctional Materials and Systems (APMT)

S9: Porous Ceramics: Novel Developments and Applications

S10: Virtual Materials (Computational) Design and Ceramic Genome

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

S1: Mechanical Behavior and Performance of Ceramics & Composites

S3: 10th International Symposium on Solid Oxide Fuel Cells (SOFC): Materials, Science and Technology

S4: Armor Ceramics

S5: Next Generation Bioceramics and Biocomposites

S7: 7th International Symposium on Nanostructured Materials and Nanocomposites

S8: 7th International Symposium on Advanced Processing and Manufacturing Technologies for Structural and Multifunctional Materials and Systems (APMT)

S10: Virtual Materials (Computational) Design and Ceramic Genome

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

S13: Advanced Ceramics and Composites for Sustainable Nuclear Energy and Fusion Energy

Engineering Ceramics Summit of the Americas

S3: 10th International Symposium on Solid Oxide Fuel Cells (SOFC): Materials, Science and Technology

S5: Next Generation Bioceramics and Biocomposites

S7: 7th International Symposium on Nanostructured Materials and Nanocomposites

S11: Next Generation Technologies for Innovative Surface Coatings

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

S13: Advanced Ceramics and Composites for Sustainable Nuclear Energy and Fusion Energy

FS4: Advanced Ceramic Materials and Processing for Photonics and Energy

Engineering Ceramics Summit of the Americas

S1: Mechanical Behavior and Performance of Ceramics & Composites

S3: 10th International Symposium on Solid Oxide Fuel Cells (SOFC): Materials, Science and Technology

S5: Next Generation Bioceramics and Biocomposites

S7: 7th International Symposium on Nanostructured Materials and Nanocomposites

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

S13: Advanced Ceramics and Composites for Sustainable Nuclear Energy and Fusion Energy

FS1: Geopolymers and Chemically Bonded Ceramics

FS4: Advanced Ceramic Materials and Processing for Photonics and Energy

Engineering Ceramics Summit of the Americas

S1: Mechanical Behavior and Performance of Ceramics & Composites

S3: 10th International Symposium on Solid Oxide Fuel Cells (SOFC): Materials, Science and Technology

S4: Armor Ceramics

S5: Next Generation Bioceramics and Biocomposites

S7: 7th International Symposium on Nanostructured Materials and Nanocomposites

S11: Next Generation Technologies for Innovative Surface Coatings

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

S13: Advanced Ceramics and Composites for Sustainable Nuclear Energy and Fusion Energy

FS1: Geopolymers and Chemically Bonded Ceramics

FS4: Advanced Ceramic Materials and Processing for Photonics and Energy

Engineering Ceramics Summit of the Americas

S3: 10th International Symposium on Solid Oxide Fuel Cells (SOFC): Materials, Science and Technology

S5: Next Generation Bioceramics and Biocomposites

S11: Next Generation Technologies for Innovative Surface Coatings

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

S13: Advanced Ceramics and Composites for Sustainable Nuclear Energy and Fusion Energy

FS1: Geopolymers and Chemically Bonded Ceramics

FS4: Advanced Ceramic Materials and Processing for Photonics and Energy

Engineering Ceramics Summit of the Americas

Monday, January 28, 2013

Plenary Session

Plenary Session

Room: Coquina Salon D

9:00 AM

(ICACC-PL-001-2013) Failure of Ceramics under Externally Applied Loads and Internally Generated Pressures: Zirconia, a Unique Material (Invited)

A. Virkar*, University of Utah, USA

Stabilized zirconia exists in two crystallographic forms, cubic and tetragonal. Zirconia has been extensively investigated for various applications which exploit its ionic transport properties, its refractory properties and its excellent mechanical properties. Solid oxide fuel cells, sensors, electrolyzers, thermal barrier coatings, heating elements, ball bearings, medical implants, etc. are some of the applications. Tetragonal zirconia is known for its excellent mechanical properties attributed to t → m martensitic transformation and ferroelasticity. Excellent oxygen ion conductivity of zirconia is the reason for its use in fuel cells, electrolyzers. In many mechanical and electrochemical applications, zirconia exhibits failure in service under some conditions. The commonly experienced failure is under externally applied loads. Increase in fracture toughness and strength achieved through processing, microstructure control, etc. lead to greater reliability. This has been extensively investigated. However, cracking of zirconia also occurs under electrochemical conditions. Such failures occur under internally generated pressures. While cracking occurs in both types of failures, the origin and mechanisms can be very different in the two cases. Conventional approaches of increasing strength and toughness have little role in mitigating failures that often occur in electrochemical systems. Rather, ion and electron transport properties determine whether failures can be mitigated. Additionally, even the mechanism of cracking is also different from failures observed under externally applied loads. The two different modes of fracture will be compared and contrasted. In external loading, one seeks solutions to fracture mechanical problems by solving elasticity equations. In electrochemical systems with internally generated pressures, a coupling exists between electrochemical transport (e.g. solution to transport equations) and mechanics. This leads to different cracking patterns. Under external loading, failure is almost always catastrophic (barring subcritical crack growth related issues). However, under internal loading, failure is stable and not abrupt. The two different modes of failure will be compared and contrasted.

9:40 AM

(ICACC-PL-002-2013) Microstructural Evolution and Mechanical Properties of Engineering Ceramics (Invited)

T. Ohji*, National Institute of Advanced Industrial Science and Technology (AIST), Japan

Ceramic materials are composed of a variety of structural elements, including, defects, grains, particles, pores, fibers, layers, and interfaces at different scale levels. In terms of size, the structural elements can be classified into four categories: (1) atomic and molecular scale, (2) nano-scale (order of 10^{-6} mm), (3) micro-scale (order of 10^{-3} mm), and (4) macro-scale. It is possible to realize new or unique performance or markedly improve properties in ceramics, by controlling systematically these structural elements. Taking, as an instance, silicon nitride which is one of the most widely used engineering ceramics, this paper intends to show that the mechanical properties including strength, toughness, and creep resistance can be tremendously improved when the sizes, morphologies, orientation, distribution, etc. of grains and pores as well as grain boundary structure are carefully controlled. Examples are: (1) super strong silicon nitride with >2 GPa strength via refinement and alignment control of grains, (2) porous silicon nitride with high strength (>1 GPa), and high toughness (300-500 J/m^2; far higher than that of the dense) via morphology and alignment control of grains and pores, and (3) super heat resistant silicon nitride with strength retention up to 1500°C and toughness of ~800 J/m^2 (double that of cast iron). The paper also focuses on improved mechanical properties via microstructure control for high thermal conductivity silicon nitride, which is expected to be applied as substrate materials in future power devices.

10:40 AM

(ICACC-PL-004-2013) Designing Ceramics for Electrochemical Energy Storage Devices (Invited)

B. Dunn*, University of California, USA

The ability to design the chemistry and nanostructure of ceramics is having a profound effect on the performance of electrode materials for electrochemical energy storage. Some of the key advances in this field will be discussed in this presentation. In the lithium-ion battery field, improvements in energy and power densities are attributed to the development of nanoscale materials which exhibit shorter ion and electron diffusion lengths. The development of carbon coatings and core-shell materials represents another significant advance in the design of electrode materials. This approach enables new families of poorly conducting oxides to be used as insertion electrodes. Mesoporous transition metal oxides are also emerging as an important direction in the energy storage field. The mesoporous architecture provides electrolyte access to redox-active walls and enables higher energy densities to be attained. The energy storage field faces a number of future challenges and these items will also be discussed.

S1: Mechanical Behavior and Performance of Ceramics & Composites

Mechanics and Characterizations

Room: Coquina Salon D

Session Chairs: Rajan Tandon, Sandia National Lab; Pankaj Sarin, University of Illinois

1:30 PM

(ICACC-S1-001-2013) Measuring and understanding the fracture toughness in ceramics at the microstructural scale using microcantilever beams

A. D. Norton*, R. I. Todd, University of Oxford, United Kingdom

The measurement of fracture toughness of individual grain boundaries is important for understanding the properties of various ceramics, such as the change in fracture mode in alumina with dopants, or to model the structure of silicon nitride. Microcantilever beams, produced using Focussed Ion Beam milling and typically 20 x 4 x 3μm in size, can be used for this purpose. The Young's modulus of the microcantilever beams corresponded well with theoretical values and other results, hence validating the technique. Diffusion bonded sapphire was produced as a model "grain boundary", so that each beam and notch type would fracture along the same boundary. A straight-across notch, controlled flaw, or chevron notch were produced near to the fixed end (with a notch radius of around 45nm, measured using TEM). Beams were tested to failure using a nanoindenter; the load-displacement curves, and notch depth, were used to determine the fracture toughness. The three beam types produced on the same model grain boundary gave consistent results. After the development stages, the technique was used on various other samples, including different planes and directions of sapphire, and polycrystalline samples with / without dopants. The validity of the fracture toughness values is discussed with respect to the notch sharpness, slow-crack growth, and gallium implantation.

1:50 PM

(ICACC-S1-002-2013) Mesoscale Brittle Mechanical Testing Using Theta Specimens

B. Babcox*, M. Frecker, G. A. Lesieutre, J. H. Adair, Pennsylvania State University, USA

Mesoscale ceramic materials require innovative mechanical property testing to establish strength. In the present context, mesoscale refers to components with millimeter scale dimensions and features on a micron and submicron scale. One such test method involves using theta specimen, originally developed by Durelli et al. and more recently NIST researchers to determine elastic modulus. The theta specimen design is similar to the configuration of the Greek letter theta 'Θ'. The tests are performed on an Instron mechanical test system putting the theta specimen in compression, causing the central bar to be in tension and eventually fail. The mechanical properties of brittle materials are commonly determined by bend tests because of issues involved with fabrication and fixtures for brittle tensile specimens. The bend test values are used as a relative comparison among other brittle materials, but are not comparable to more ductile materials, tested in tension, not allowing direct mechanical property comparisons. Polycrystalline, zirconia-alumina theta specimens were fabricated, using the lost mold-rapid infiltration process developed by Antolino et al. with varying compositions of alumina. Testing was done on a conventional Instron 5866, showing the accessibility of theta specimen testing. Strength and fracture toughness increased with increasing alumina content.

2:10 PM

(ICACC-S1-003-2013) Torsion tests on brittle and tough joining materials

M. Ferraris*, M. Salvo, A. Ventrella, Politecnico di Torino, Italy

Results of an experimental investigation on epoxy-joined and glass-ceramic joined SiC tested in torsion will be presented. Torsion tests are proposed in ASTM F734-95 (2006) and ASTM F1362-09, but none of them is directly applicable to joined ceramics; these two ASTM standards have been adapted to joined SiC, by preparing butt-joined cylinders, tubes, and hourglass-shaped samples with reduced joined area. Silicon carbide samples have been joined by a glass-ceramic, which is a model brittle joining material and by an epoxy adhesive (AV119), chosen to obtain several joined samples in a reasonable time. Advantages and disadvantages of each configuration are discussed and compared, in particular when the joining material has a tough behavior. Torsion test seems to be appropriate for the determination of the shear strength of joined ceramics when also the joining material has a brittle behaviour.

2:30 PM

(ICACC-S1-004-2013) Role of Circumferential Cracking in Fracture from Cylindrical Inclusions in: LTCC-Gold via System

R. Tandon*, Sandia National Lab, USA

The strength and fracture behavior of a low-temperature co-fired (LTCC)-gold via microelectronic packaging system is analyzed. The biaxial fracture strength of the LTCC-gold via combination was ~ 60% lower than the base LTCC material. Planar and fracture surface examination of the samples revealed that circumferential (arc) cracking at the gold-LTCC interface was a prelude to fracture. Final fracture occurs due to the kinking of the arc crack into the LTCC matrix. Two dimensional stress intensity factor solutions for interfacial arc cracks around circular inclusions are used to derive the driving force for the arc crack. Under the combination of the radial (residual) tensile stress and biaxial (applied) loading, the crack driving force exhibits a maximum at arc angle of ~50°. Crack kinking into the matrix was experimentally determined to occur for crack angles ranging from 58°-88°, i.e., on the decreasing part of the strain energy release rate curves. The crack extension behavior is described based on interfacial fracture mechanics, and used to explain the lowered strength of the LTCC-gold via system. 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.

2:50 PM

(ICACC-S1-006-2013) Edge Chip Fracture Resistance of Ceramic and Composite Materials

G. Quinn*, A. Giuseppetti, K. Hoffman, J. Quinn, American Dental Association Foundation, USA

The edge chipping test was used to measure the fracture resistance of a variety of dental restorative materials including ceramics, glass ceramics, filled resin composites, and new composite materials. Materials included a feldspathic porcelain, leucite and lithium disilicate glass ceramics, a 3Y-TZP zirconia, a filled resin-matrix composite, a resin denture material, a new nanoceramic filled composite and a new interconnected resin-ceramic composite. Sharp conical, Vickers, and Rockwell C indenters were used. Data trends were analyzed with linear and power law functions. Various indices of chip resistance such as "edge toughness Te," "edge strength, SE(0.5)," and "edge chip resistance, ReA," were compared. Edge chip resistance varied significantly with the type of indenter used. In some cases the data was well fit by a simple linear trend, but in other instances, a power law fit was superior. Chipping resistance correlated strongly with fracture toughness

3:30 PM

(ICACC-S1-007-2013) Heat diffusivity measurements on ceramic foams and fibers with a laser spot and an IR camera

G. L. Vignoles*, University Bordeaux, France; C. Lorrette, CEA, France; G. Bresson, R. Backov, University Bordeaux, France

The heat diffusivity is rather easy to measure on material samples as soon as a flat sample of constant thickness can be produced; however this is not always possible. We will present and discuss two cases, both solved by the use of a laser spot, an IR camera, some image processing and data analysis. First, SiC foams were produced as small bulk samples without any clearly defined shape, excluding the possibility of using a rear-face recording of temperature evolution for the identification of heat diffusivity: methods based on the processing of front-face responses to a step impulse of a laser spot allowed the extraction of diffusivity and conductivity. Second, a bundle of isolated SiO2 fibers has been examined with the same laser spot; a distinct data extraction technique has been set up and validated.

3:50 PM

(ICACC-S1-008-2013) Effect of Calcium-Magnesium-Alumina-Silicate on Strain within the TGO Layer of Thermal Barrier Coatings

S. Siddiqui*, S. Scott, M. Ewen, K. Knipe, A. Manero, University of Central Florida, USA; J. Okasinski, J. Almer, Argonne National Laboratory, USA; L. Li, A. Feuerstein, Praxair Surface Technologies, USA; S. Raghavan, University of Central Florida, USA

In this study, the effect of Calcium-Magnesium-Alumina-Silicate (CMAS) on the Thermally Grown Oxide (TGO) strain in plasma-sprayed Thermal Barrier Coatings (TBC) was analyzed. A comparison was conducted between two low-density deposition TBC samples, one of which contains CMAS. Synchrotron in-situ x-ray diffraction was performed on the samples subjected to a thermal cycle in order to obtain high-resolution quantitative strain measurements at high temperature. The results from this experiment were used to identify variations in the strain relaxation within the TGO layer due to CMAS and the effects of this on TBC durability.

4:10 PM

(ICACC-S1-009-2013) Phase Transformations in $YTaO_4$ and the Effect of Zr-ion Doping

P. Sarin*, Z. D. Apostolov, D. R. Lowry, W. M. Kriven, University of Illinois at Urbana-Champaign, USA; S. Shian, D. R. Clarke, Harvard University, USA

Recent studies in the Y_2O_3-ZrO_2-Ta_2O_5 ternary system, specifically those on doping of $YTaO_4$ into ZrO_2, have demonstrated increased stability of the tetragonal ZrO_2 phase, resulting in lower modulus and thermal conductivity. The incorporation of ZrO_2 into the $YTaO_4$ structure has not been explored. $YTaO_4$ is known to exist as two main polymorphs: tetragonal (t-$YTaO_4$) and monoclinic (m-$YTaO_4$ and m'-$YTaO_4$) forms. The m'-$YTaO_4$ is stable only at low temperatures, and when heated to 1450°C, it transforms irreversibly to t-$YTaO_4$. The tetragonal phase to m-$YTaO_4$ phase upon cooling. In this study the phase transformations in $YTaO_4$ were studied in-situ, at high temperatures using synchrotron X-ray diffraction. In addition, the effect of addition of ZrO_2 (up to 20 mol%) on phase stability and transformation properties of $YTaO_4$ was evaluated. The phase transformation in m-$YTaO_4$ is ferroelastic ($I2/a \rightarrow I41/a$), reversible, and second-order in nature. Addition of ZrO_2 to $YTaO_4$ resulted in lowering of the $m \rightarrow t$ transformation temperature, from ~1450°C in pure $YTaO_4$ to ~900°C in 20 mol% ZrO_2 doped $YTaO_4$ system. Thermal expansions as functions of temperature and dopant concentration are presented. Atomic rearrangements associated with the incorporation of Zr ion in the structure, and its transformation, will be interpreted to elucidate the role of Zr-ion on stabilization of the t-$YTaO_4$ phase.

4:30 PM

(ICACC-S1-010-2013) Neutron Scattering of Ferroelastic Mixed Ionic Electronic Conducting LaCoO3 based Perovskite Under In-Situ Uniaxial Compression

N. Orlovskaya*, Y. Chen, University of Central Florida, USA; D. Ma, A. Stoica, K. An, Oak Ridge National Laboratory, USA

The crystal structure and texture development of ferroelastic LaCoO3 and La0.8Ca0.2CoO3 based perovskites have been investigated under uniaxial compression using VULCAN beam line at the Spallation Neutron Source, Oak Ridge National Laboratory. Texture development was directly observed during cyclic compression experiments. Both microscopic strain by extensometer and lattice strain in cobaltites were measured and compared during cyclic loading/unloading in-situ compression experiments. Both radial and lateral strains were measured during sample's compression thus allowing calculation of Poisson's ratio of the cobaltites. It was found that calculated Poisson's ration is not a constant for a given material under investigation but it exhibited strong stress dependence. In addition to the cyclic loading the room temperature creep of pure LaCoO3 was studied at the constant 70 MPa stress, which corresponds to the coercive stress of this ferroelastic material. The crystal structure development of LaCoO3 was studied during four hours of creep experiments.

4:50 PM

(ICACC-S1-011-2013) Characterization of structural behavior under re-entry type transformations in Ln_6WO_{12} (Ln= Y, Ho, Er, Yb)

Z. Apostolov*, P. Sarin, W. M. Kriven, University of Illinois at Urbana-Champaign, USA

The focus of this study was the low-fcc to rhombohedral (III→II, 1200- 1300°C) phase transformation in Ln_6WO_{12} (Ln= Y, Ho, Er, Yb), investigated by in-situ high-temperature synchrotron X-ray diffraction. The transformation was determined to be an irreversible, first order, diffusional ordering process, which occurred over a heating rate-dependent temperature range starting at 1270°C. The shape change of the rhombohedral unit cell consists of elongation along the [111] axis and contraction in the (111)plane, resulting in an overall volume decrease on heating. An abrupt discontinuity in both volume and rhombohedral angle (α) evolution was observed across the transformation region for all four compositions. Trends in lattice parameters, ΔV and $\Delta\alpha$ at room temperature and transformation were established according to Ln cation type. Additionally, results on preliminary investigations of the rhombohedral to high-fcc (II→I, 1600-1700°C) transformation will be presented and transformation characteristics compatible with both the III→II and II→I processes will be compared. While the two transitions seem to share similar order, thermal dependence and nature of evolution, the lattice parameters behavior, as well as the volume and shape changes at temperature are different in each.

5:10 PM

(ICACC-S1-012-2013) Acquisition Techniques for Synchrotron X-Ray Strain Measurements in Tubular TBC Specimens for Thermal Gradient Mechanical Testing

K. Knipe*, A. Manero, S. Das, S. Siddiqui, S. Scott, M. Ewen, University of Central Florida, USA; C. Meid, J. Schneider, DLR Aerospace, Germany; J. Okasinski, J. Almer, Argonne National Laboratory, USA; M. Bartsch, DLR Aerospace, Germany; S. Raghavan, University of Central Florida, USA

This research aims to develop techniques to accurately obtain in-situ strain measurements of thermal barrier coating systems (TBCs) applied to tubular specimens. EB-PVD coated tubular samples with internal cooling were designed to achieve a realistic temperature gradient over the coatings. Effects of the circular cross-section on the x-ray diffraction (XRD) strain measurements in the various layers, including the thermally grown oxide (TGO), are investigated using a high energy synchrotron. Multiple approaches for beam penetration, including both tangential and normal to the layers, along with variations in collection parameters are compared for their ability to attain high-resolution XRD rings of the internal layers. To account for the measurement through the layers, results from the acquisition techniques are analyzed to isolate the diffraction rings of the various materials. The techniques are compared to experiments aligning the x-ray beam parallel to the in-plane direction of flat specimens, providing insight for the compensation of the non-symmetrical material composition in the diffraction volume. Results are used to summarize the various techniques for obtaining depth-resolved strains through multi-layered coating systems and their outcomes will pave the way towards goals in achieving realistic in-situ testing of these coatings.

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

Environmental Barrier Coatings

Room: Ponce DeLeon
Session Chairs: Kang Lee, Rolls-Royce Corporation; Yiguang Wang, Northwestern Polytechnical University

1:30 PM

(ICACC-S2-001-2013) Environmental Barrier coatings for Ceramic Matrix Composites (Invited)

K. N. Lee*, Rolls-Royce Corporation, USA

SiC/SiC ceramic matrix composites (CMCs) are the most promising material system that has the temperature and structural capability to meet the needs of next generation gas turbine engines. One major barrier to the implementation of CMC hot section components is the lack of environmental durability in combustion environments. Water vapor in combustion environments causes rapid recession of CMCs. CMCs also suffer from severe hot corrosion in molten salts. Currently the most promising solution to preventing environmental attack is an external environmental barrier coating (EBC). EBC is a prime reliant coating and therefore a reliable EBC lifing method is needed for successful implementation of CMC components. Multiple sources responsible for EBC degradation, such as water vapor, CMAS, stresses, foreign objects, etc., are present in gas turbines and therefore strong interactions between various degradation modes are expected. EBC lifing will require thorough understanding of individual degradation mode as well as interactions among them. Generation of life validation data in relevant environments is also very important. This paper will discuss the evolution of EBCs and the current understanding on key issues for EBC durability and lifing.

2:00 PM

(ICACC-S2-002-2013) Progress in EBC Development for Silicon-based, Non-oxide Ceramics

C. Lewinsohn*, H. Anderson, J. Johnston, Ceramatec, Inc., USA; D. Zhu, NASA Glenn Research Center, USA

Hydrothermal corrosion is a lifetime-limiting mechanism for silicon-based, non-oxide ceramics in combustion environments. Many desirable coating materials are physically or chemically incompatible with the non-oxide substrate materials. A unique method of engineering bond-coats and coating systems for non-oxide systems has been developed and shown to improve the hydrothermal corrosion resistance of silicon nitride ad silicon carbide-based materials. Progress in work to investigate the effect of additions of oxidation resistant filler materials to polymer-derived bond coats for EBCs will be discussed. In the current work, additional data will be provided showing that the bond coat system can be adapted to composite silicon carbide. Initial results on the high-temperature durability of these coatings will be presented.

2:20 PM

(ICACC-S2-004-2013) The Influence of Ca-Mg-Al Silicates on Stresses and Phase Transformations in Yb-Silicate Environmental Barrier Coatings

F. Stolzenburg*, Northwestern University, USA; J. Almer, Argonne National Lab, USA; K. N. Lee, Rolls Royce Corporation, USA; B. J. Harder, NASA Glenn Research Center, USA; K. T. Faber, Northwestern University, USA

With the increasing importance of SiC/SiC composites for high-temperature structural applications and their known vulnerability to attack by water vapor at elevated temperatures, identifying environmental barrier coatings (EBCs) for these materials is paramount. Rare-earth silicates have been recognized as promising candidates for EBCs due to their excellent high temperature stability and well-suited thermal expansion coefficient. However, it is known that calcium magnesium aluminosilicates (CMAS), ubiquitous glassy engine deposits, react with EBCs, leading to changes in stress states, the formation of unwanted phases, and ultimately, premature failure. High-intensity X-rays in a transmission geometry at beamline 1-ID of the Advanced Photon Source were used to determine stresses and phase transformations in the coatings. In-situ heating and cooling experiments were performed to quantify the changes in stresses in these coatings as a function of temperature. The stress measurements were complemented by a more detailed analysis of the progression of the CMAS/Yb2Si2O7 interface and the formation of new phases using a combination of electron diffraction and X-ray diffraction techniques.

2:40 PM

(ICACC-S2-005-2013) The stability of rare-earth silicates in water-vapor environments (Invited)

Y. Wang*, Northwestern Polytechnical University, China

Rare-earth disilicates are very promising materials for environmental barrier coatings (EBCs). They exhibit excellent water-vapor corrosion resistance at high temperatures. However, which one has the best resistance in water-vapor environments, the mono-silicate or the disilicate, is still arguable. In this presentation, we studied the water-vapor corrosion behavior of seven kinds of rare-earth disilicates in water-vapor. The results indicated that the disilicates showed a better water-vapor resistance than that of mono-silicates. The structures of mono-silicates and disilicates were compared to verify our experiments. A corrosion mechanism based on these results was proposed.

3:30 PM

(ICACC-S2-006-2013) Single Crystal TiO_2 recession in high temperature water vapor

R. A. Golden*, University of Virginia, USA; X. Liu, University of Virginia, USA; J. Valentine, University of Virginia, USA; E. J. Opila, University of Virginia, USA

Stability of single crystal TiO_2 in high temperature water vapor was investigated. Liquid water was pumped at a controlled rate into a fused quartz capillary inside a high temperature tube furnace, where the large expansion of vaporization within the capillary accelerated the jet. The high velocity steam jet impinged on the sample under study. The capability of the system was first demonstrated for a fused quartz coupon where Si-O-H(g) formation is well known. The tests on TiO_2 single crystals were performed at 1290°C, a total pressure of 1 atm, a steam jet velocity on the order of 250 m/s and exposure times at or greater than 100 hours. Surface recession of the TiO_2 singles crystals was observed after exposure in the steam jet furnace presumably due to the formation of volatile Ti-O-H (g) species. The TiO_2 samples were characterized by Optical Microscopy, Optical Profilometry, X-ray Diffraction, Scanning Electron Microscopy, and Energy Dispersive Spectroscopy. Calculations of the Ti-O-H (g) partial pressure from recession were compared to several values in the literature. Results indicate that TiO_2 is not sufficiently stable in high temperature water vapor for applications in combustion environments.

3:50 PM

(ICACC-S2-007-2013) Plasma Spray – Physical Vapor Deposition of High Temperature Environmental Barrier Coatings for Turbine Blades

B. J. Harder*, D. Zhu, NASA Glenn Research Center, USA

Fuel efficiencies of gas turbine engines could be significantly improved with the incorporation of Si-based ceramic matrix composites (CMCs) as hot section components. These materials have lower densities and improved thermomechanical stability over superalloy-based systems. However, Si-based ceramics react with water vapor present in combustion conditions and therefore require environmental barrier coatings (EBCs) to prevent recession. To further improve the thermal capability and erosion resistance, a columnar topcoat can be added. Plasma Spray- Physical Vapor Deposition (PS-PVD) is a unique technique that fills the gap between conventional thermal spray and vapor phase methods, allowing tailoring of thin, dense layers or columnar microstructures necessary for these advanced coatings. In this work, multilayer coatings were applied to SiC/SiC CMC substrates via PS-PVD. The base EBC layer was dense rare-earth silicate, followed by a mixture layer to improve bonding. Multiple oxide materials were explored for the topcoat in order to maximize the thermal and erosion performance of the system. Coatings were characterized in the as-sprayed condition and after laser thermal conductivity and cyclic testing in dry and water-containing environments. Microscopy was used to investigate changes in morphology and X-ray diffraction was used to track phase structure and stability.

4:10 PM

(ICACC-S2-008-2013) Thermal Expansion and Phase Transitions of Rare Earth Disilicates and Monosilicates

T. S. Key*, E. E. Boakye, K. F. Presley, R. S. Hay, UES & AFRL/RXCC, USA

Rare earth disilicates and monosilicates are of interest as environmental barrier coatings for SiC-based composites. Stability of phases and minimization of thermal expansion mismatch are crucial. In this research, the thermal expansion and phase stability of Re2Si2O7 powders in the α, β and γ phases and Re2SiO5 powders in the X2 phase were examined by XRD between 20 and 1200°C (Re=Y, Ho, Er). Neutron diffraction was used to determine the bulk thermal expansion coefficients. This technique was applied to the γ phase, the X2 phase and a mixture of the two to assess the relative contributions of each phase. Because neutron diffraction allows transmission measurements through large, densely sintered samples, bulk thermal expansion coefficients can be calculated from the $\alpha 11$, $\alpha 22$ and $\alpha 33$ of each phase. These results will be compared to dilatometry and x ray powder diffraction measurements to determine how well the powder diffraction results agree with the bulk thermal expansion coefficients and to confirm whether a simple rule of mixtures is applicable when calculating the bulk thermal expansion coefficient of a mixture of the γ and X2 phases.

4:30 PM

(ICACC-S2-009-2013) Electrochemical Synthesis of Carbide Derived Carbon – A Novel Air Filter for Volatile Organic Compounds (VOCs)

S. Jaganathan*, W. Chih-Chiang, T. Wen-Ta, National Cheng Kung University, Taiwan; G. Yuri, A. J. Drexel Nanotechnology Institute, Drexel University, USA; Y. Masahiro, National Cheng Kung University, Taiwan

Glutaraldehyde is a cold sterilant specifically used for heat-sensitive instruments, such as endoscopes, bronchoscopes and dialysis equipment. In this study, we have used glutaraldehyde as the target pollutant which causes serious of health effect including asthma, breathing difficulties, respiratory irritation and skin rashes to those who are handling it in hospitals and laboratories. Carbide derived carbon (CDCs) can be used for a range of applications including purification of gases, water, biological fluids, organic and inorganic chemicals. CDCs shows pore-size dependent sorption and this property can be used for the purification of volatile organic compounds (VOCs), bacteria and virus. In this study, micro/nano structured carbon layer has been formed by selective electrochemical etching of SiC with HF in non-aqueous condition. The surface morphology and carbon enhancement on the etched SiC surface was confirmed with SEM, EDX, Raman and AFM analysis.The carbon enriched micro-mesoporous layer acts as a potential sorbent for the removal of glutaraldehyde specifically in gasious form. The GC analysis shows that glutaraldehyde is effectively sorbed on the surface of the etched SiC compared to nonetched SiC surface. The major advantages are, CDCs can reused several times after incinerating under vacuum or nitrogen atmosphere.

4:50 PM

(ICACC-S2-010-2013) Fabrication of slurry based Y-Si-Al-O environmental barrier coating on the porous Si_3 N_4

Y. Liu, C. Wang, H. Wang*, State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, China

An environmental barrier coating (EBC) was in urgent need for the porous Si_3 N_4 ceramic, which was treated as promising broadband wave-transparent material. Because the water collected from the moisture working condition by the pores would degenerate the dielectric properties sharply, and the porous structure also make the component vulnerable for the erosion and corrosion. In this paper, a dense Y-Si-Al-O ceramic coating with an $Y_2Si_2O_7$ transition layer was fabricated on porous Si_3 N_4 substrate by slurry spray method. The mixture of Y_2O_3, SiO_2, Al_2O_3 were precalcined at 1300°C in air, and ball-milled in ethanol to form slurry. The slurry was sprayed on the substrate and then sintered between 1350~1500°C under N_2 atmosphere after dry. A uniform deep grey sealing coating was formed. The $Y_2Si_2O_7$ layer prevented the melt of top layer from infiltrating into the porous substrate massively, so that a clear interface formed between the coating and substrate. The water-absorption of substrate dropped significantly after the coating was introduced. Furthermore, the mechanical properties, like strength and hardness, were improved, especially for the Vickers Hardness of the surface. The erosion resistance of the coating was far better than the porous Si_3N_4, while the dielectric properties were only slightly impacted by the coating.

5:10 PM

(ICACC-S2-011-2013) Effect of Cobalt Oxide on Willemite Crystalline Glazes at Moderate Temperature

N. Sharma*, N.A.S. (P.G.)College, India; L. K. Sharma, Central Glass and Ceramic Research Institute, India; H. Kaur, N.A.S. (P.G.)College, India

Crystalline glazes are one of the types of glazes which have high percentage of zinc oxide (more than 10%). The ZnO combines with free silica to form willemite (Zn2SiO4 or 2ZnO.SiO2) crystals. The size of the crystals is directly proportional to the soaking time at crystallization temperature. The attractiveness of these large crystals is increased by the addition of various transition metal oxides in different percentage (by weight-wt%) which give colour to them. The crystals get colour when the metal oxides fit into the lattice structure. In this research work, studies were carried out on cobalt (II) oxide in the range of 1-5wt % to stain the crystals blue. Cobalt oxide has the +2 valency which is common with zinc and therefore it competes for the same sites in lattice and new combinations are being formed. Samples were sintered at 1250oC for 10-40 minutes of soaking period to study the crystals morphology. XRD, SEM and EDAX techniques were used to study the lattice structure, morphology and combination of the crystals. It was found that cobalt moves into the lattice of the willemite by replacing Zn in the structure and forms CoxZn2-xSiO4 type of cobalt doped willemite crystals. The glaze with 3% Cobalt oxide was found to be best giving better crystallisation, formation and acceleration of Gahnite crystals. This behaviour was not visible in any of the other samples.

S4: Armor Ceramics

Transparent Ceramics & Glasses

Room: Coquina Salon E

Session Chairs: Parimal Patel, U.S. Army Research Laboratory; Jane Adams, U.S. Army Research Laboratory

1:30 PM

(ICACC-S4-001-2013) Mechanical Behaviors and Structure of Glass (Invited)

S. Ito*, Tokyo Institute of Technology, Japan

Glass is a transparent material with excellent characteristics and has been used in numerous fields. However, due to its brittle nature, its application field is restricted. Therefore, a strong demand for less brittle glass is rising. Although glass has very high intrinsic strength compared to practical materials, micro-cracks are easily formed by surface contact with hard materials and trigger the catastrophic fracture of glass. At the contact point, glass is subjected to large stress and shows first deformation due to densification and flow before cracking. Such deformation plays an important role for easier stress relaxation and hence lower brittleness, i.e., higher crack-resistance. However, when the contact stress exceeds a critical value, micro-cracks form around the contact point. These phenomena strongly depend on glass structure and composition. To reduce the probability of crack formation and subsequent crack propagation, physical and chemical tempering methods are currently used. By using such methods, crack formation resistance of glass can be enhanced higher than that of Al2O3 ceramic. To clarify the mechanism of deformation and fracture, we investigated network and void structures in glass by using molecular dynamics simulation and volume rendering methods. The mechanical behaviors of glass will be discussed in terms of nanostructure and composition of glass.

2:00 PM

(ICACC-S4-002-2013) Structure and Properties of Densified Glasses (Invited)

L. Huang*, Rensselaer Polytechnic Institute, USA

Experimental and computational techniques were combined to study the structure and properties of densified glasses. In experiments, silica and

silica-rich glasses were quenched from temperatures near the glass transition under pressures up to 4 GPa using a piston-cylinder apparatus. In molecular dynamics (MD) simulations, densified glasses were prepared by pressure-quenching or potential tuning. With the increase of the quenching pressure, density, hardness and elastic moduli of as-quenched glass increase substantially, and the anomalous behaviors (positive temperature derivative and negative pressure derivative of elastic moduli) in silica-rich glasses gradually diminish. Uniaxial tension, nano-indentation and fracture tests all show a brittle-to-ductile transition with increasing density and Poisson's ratio of densified glass. In densified glass, more and more silicon atoms become five coordinated with oxygen atoms with the increase of density. These five-coordinated silicon atoms create additional energy dissipation pathway and facilitate shear flow during mechanical tests and play a critical role in the mechanical behaviors of densified glass.

2:30 PM

(ICACC-S4-003-2013) MD Simulations of Structure and Mechanical Properties of Silica Glasses (Invited)

A. Cormack*, L. Adkins, Alfred University, USA

Molecular dynamics simulations of silica glasses have proved to be very useful for elucidating not just the structure of silica based glasses, but also their properties. In this talk, recent work on modeling the mechanical properties of silica, including its behavior under a tensile load, will be described. Initially, a bulk glass structure was modelled, but the work has been extended to include silica glass fibers, in which the key factor is the surface structure. Surface structural units, which may be characterized as defects, will be shown to be associated with the generation of flaws which then propagate as cracks through the fiber. The reactivity of the surface defect structures will also be discussed.

3:20 PM

(ICACC-S4-004-2013) Glass: A Highly Tunable and Versatile Material for Armor Applications

M. J. Davis*, SCHOTT North America, Inc., USA

Although glass of one type or another has been widely fielded now for decades for various protection applications, the breadth of glass compositions and associated properties has remained largely untapped. Historically, soda-lime (float) glass has been the mainstay of glass used in military armor systems, while borosilicate glasses have seen more recent attention. This review will present the rich diversity of glass types and associated properties to give the armor community a taste of the large property space attainable by this unique class of materials. Ranges of elastic, thermal, and optical properties will be reviewed, along with some open-literature reports that document the dependence of protection efficiency on glass type, even for the restricted range of compositions tested to date.

3:40 PM

(ICACC-S4-006-2013) Responses of Siliceous Materials to High Pressures

A. Wereszczak*, T. Morrissey, M. Ferber, Oak Ridge National Laboratory, USA; K. Bortle, E. Rodgers, ORISE, USA; Y. Vohra, University of Alabama - Birmingham, USA

Several silicate glasses, glass ceramics, and crystalline quartz were subjected to high pressure loading using spherical indentation, diamond anvil cell (DAC) testing, and laser shock impact. The chosen materials are all silica-based and are either presently used in armor applications, are candidates for such, or served as a relevant reference in this study. The three employed test methods were chosen because they can apply many GPa of pressure, are relatively quick and inexpensive to experimentally conduct, produce repeatable results, and induce a bulk material response. Small diameter diamond indenters were used to apply many GPa of Hertzian contact stress, and resulting indenter depth-of-penetration provided insights into apparent stress-strain response. A DAC was used to apply a hydrostatic pressure and each material's Raman spectra were interpreted as a function of pressure up to ~ 20 GPa. Laser shock impact testing applied many GPa in a couple tens of nanoseconds so this dynamic test method enabled a cursory examination of any rate effect at high pressures. The test methods and their produced stress states are described, and the mechanical and morphological responses of the materials caused by them are contrasted. Research sponsored by WFO sponsor US Army Tank-Automotive Research, Development and Engineering Center under contract DE-AC05-00OR22725 with UT-Battelle, LLC.

4:00 PM

(ICACC-S4-007-2013) Damage Mechanisms of Chemically Strengthened Glass Bars Due to High-Velocity Ball Impact

P. A. Jannotti*, G. Subhash, University of Florida, USA

Ball impact experiments were conducted at a range of velocities (52 – 345 m/s) on as-received and strengthened glass bars in order to assess the damage propagation characteristics and energy dissipation mechanisms. The damage morphology was captured by high-speed imaging using white light, photoelasticity and shadowgraph techniques. For the as-received glass, the damage front reached a velocity of 1617 – 2134 m/s (depending on impact velocity), and rapidly fell to zero within a short distance from the impact site. The damage front in the strengthened glass reached an initial velocity of 1593 –2617 m/s, but then remained at a constant velocity of ~1900 m/s until the glass bar was fully consumed. It is reasoned that the high level of stored energy due to chemical strengthening led to self-sustained damage front propagation independent of the energy imparted by the impacting ball. Also, the damage front velocity in the outer compressive region of the glass was higher than in the central tensile region of the glass with periodic bridging cracks developing between the two zones to form damage-free islands of material in the central regions. The contribution of major damage mechanisms (e.g., elastic wave propagation, bar dilation, particle ejection and friction) to the overall energy dissipated was quantified in a comprehensive energy balance using analytical equations available in literature.

4:20 PM

(ICACC-S4-008-2013) Modeling Multiple Impacts onto Glass Targets

T. Holmquist*, Southwest Research Institute, USA

Windshields (transparent armor) on armored vehicles are required to stop multiple impacts, and it is this requirement that typically drives the design. Transparent armor is complex, composed of multiple layers of glass and polymers. It would be helpful in the design process to have the ability to model the response of transparent armor when subjected to more than one impact. Holmquist and Johnson recently developed a constitutive model for glass. It has been demonstrated that the glass model produces computed results that are in good agreement with a number of experiments including single impacts onto thin glass-polycarbonate laminates, but nothing has been done to investigate the ability to model multiple impacts. This work assesses the ability to model multiple impacts onto relatively thin glass and glass-Lexan targets. Experimental data provided by Anderson et al. are used in this assessment. Computed results are presented that investigate the effects of mesh resolution, target lateral dimensions and model parameters on the evolution and extent of damage, and ultimately on the ability to accurately model multiple impacts.

4:40 PM

(ICACC-S4-009-2013) Brittle fracture evolution in projectile impact on a glass laminate: comparison between experiments and peridynamics results

F. Bobaru*, W. Hu, University of Nebraska-Lincoln, USA; J. Yu, C. Yen, ARL, USA

We present experimental and computational results for the impact of a small spherical projectile on a thin glass plate (with dimensions of

10.16 cm × 10.16 cm × 0.3 cm) backed by a similarly thin polycarbonate plate. The plates are restrained in a metal frame with a 5 cm by 5 cm central opening. We analyze the dependence of the damage patterns forming in the glass plate on increasing impact velocity. Three tests are conducted with projectile velocities of 61m/s, 100m/s and 200m/s. The experimental results are compared with those from peridynamic simulations of a model that uses some simplified boundary conditions. The main fracture patterns observed experimentally are well captured by the peridynamic model for each of the three projectile velocities tested. The trends observed experimentally for the rebound projectile velocity are also seen in the peridynamic results. We identify the boundary conditions as the cause for some differences between the computational results and the experiments. The peridynamic computational model allows us to understand the early stages of the complex damage evolution in the brittle glass layer of the multi-layered system. This research is a first step in the process of validating computational models capable of predicting dynamic brittle fracture and damage in multi-layered targets.

5:00 PM

(ICACC-S4-010-2013) Multiscale Modeling of Non-crystalline Ceramics (Glass)

G. A. Gazonas*, J. W. McCauley, P. Patel, U.S. Army Research Laboratory, USA

Under the auspices of the ARL Strategic Research Initiative for Materials in Extreme Environments, an interdisciplinary Director's Strategic Initiative research team (I. Batyrev, R. Becker, S. Izvekov, T. Jenkins, B. Rice, B. Schuster, N. Weingarten, and R. Wildman) was formed to develop a multiscale computational model for non-crystalline ceramics or glass ceramics that are used in a variety of transparent armor applications. For many years it has been known that the properties of glass can be modified and enhanced through compositional and processing modifications. Some glass formulations have been shown to exhibit enhanced performance against shaped-charge jets and kinetic energy projectiles but the fundamental reasons remain obscure. This is in part due to their various nanoscale short and long range atomic structural characteristics that are difficult to quantify experimentally. Multiscale computational methods are used which include quantum mechanical, molecular dynamics, peridynamic and continuum models to determine the fundamental physical deformation and failure mechanisms responsible for the performance of these materials. Intermediate range structure changes in glass are investigated by studying how density varies with pressure using the diamond anvil cell. Also discussed are edge-on-impact and fragmentation experiments conducted at the Ernst-Mach-Institute to validate our multiscale computational models.

5:20 PM

(ICACC-S4-011-2013) Quantum mechanical modeling of structure and elastic properties of AlON

I. G. Batyrev*, D. E. Taylor, J. W. McCauley, G. A. Gazonas, N. S. Weingarten, B. M. Rice, US Army Research Laboratory, USA

Quantum mechanical (QM) simulations of cubic aluminum oxinitride (AlON) spinel were performed using various methods for the initial structure generation and two density functional theory (DFT) methods based on plane waves and Gaussian basis functions. Special quasirandom structures (SQS) were generated by finding unit cells whose correlation functions most closely matched those of the infinitely random system. Another method of generating AlON structures was carried out using an evolutionary algorithm. Genetic operators of permutation, mutation, and heredity were coded in a shell script convenient for the queuing system of massively parallel computers. The results show that the constant anion model (McCauley, 1978) with random distribution of N atoms is the lowest energy configuration. The optimized structure of a 55 atom unit cell from the evolutionary algorithm was used to construct 220 and 440 atom simulation cells, which were re-optimized using DFT with a Gaussian basis set. The calculations resulted in a cubic spinel unit cell which was used for complete analytical evaluation of the second order elastic constants. The elastic constants were also evaluated numerically from energy-strain and stress-strain relations for the 55 atom unit cell. The calculated elastic constants are in overall agreement with experimental measurements of polycrystalline and single crystal AlON.

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

Li-ion Battery Technology - Advanced Electrodes

Room: Coquina Salon G

Session Chairs: Michelle Johannes, Naval Research Laboratory; Kiyoshi Kanamura, Tokyo Metropolitan University; Ilias Belharouak, Argonne National Laboratory

1:30 PM

(ICACC-S6-001-2013) All Solid State Batteries for High Energy Applications (Invited)

S. Lee*, T. Yersak, A. MacPherson, University of Colorado, USA; S. Kim, K. Oh, Seoul National University, Republic of Korea; C. Stoldt, University of Colorado, USA

Conversion battery materials are a promising alternative to oxide based intercalation materials for high energy density batteries. While conversion chemistries offer high capacities, they often suffer from a variety of capacity fade mechanisms. In the case of FeS2, the agglomeration of elemental iron (Fe0) nano-particles and the dissolution of polysulfides (Sn2-) results in rapid capacity fade. We demonstrate that a solid-state battery architecture enables the reversible, four electron storage of fully utilized synthetic cubic-FeS2 (pyrite). With a sulfide based glass electrolyte we successfully confine electro-active species and permit the safe use of a lithium metal anode. We also conclude that nano-particles of orthorhombic-FeS2 (marcasite) are regenerated upon recharge at 30-60°C. Our FeS2/Li solid-state cells deliver a specific energy density that is a nearly threefold improvement over the specific energy density of the state of the art LiNi1/3Mn1/3Co1/3O2/graphite cells (1340 Wh kg-1 versus 500 Wh kg-1 based on cathode and anode materials). Our demonstration of reversible four electron storage using a solid-state battery architecture provides important mechanistic insight for the design of advanced battery materials.

2:00 PM

(ICACC-S6-002-2013) Two Dimensional Transition Metal Carbides and Carbonitrides (MXenes) Anodes for Lithium Ion Batteries and Lithium Ion Capacitors

M. Naguib*, Drexel University, USA; J. Come, Université Paul Sabatier, France; Y. Dallagnese, O. Mashtalir, Drexel University, USA; P. Taberna, P. Simon, Université Paul Sabatier, France; M. W. Barsoum, Y. Gogotsi, Drexel University, USA

Recently, we reported on the fabrication of a new family of two-dimensional (2-D) sheets of early transition metal carbides and carbonitrides produced by the exfoliation of the MAX phases. MAX phases are a large family of layered ternary carbides and nitrides, where "M" is an early transition metal, "A" is A-groups 13-16 element and "X" is C and/or N. We labeled this new family "MXene" to indicate the selective etching of the A layers from the MAX phases and highlight their similarity to graphene. Cold pressed discs of MXenes showed hydrophilic behavior and electrical conductivity compared to multilayer graphene. The good conductivity and their morphology make them attractive for electrochemical energy storage applications. More recently, we reported on the use of Ti_2C as an anode material in lithium-ion batteries that can be cycled at high rates. Herein, we report on the synthesis and performance of other MXene members, viz. Nb_2C, $(Ti_{0.5}N_{b0.5})_2C$, Ti_3C_2, $Ti_3(C_{0.5}N_{0.5})_2$ and Ta_4C_3, as anodes in

LIBs. The effect of different forms carbon additives to this new anodes system is presented. Also, we report on the performance of MXene/activated carbon asymmetric cell.

2:20 PM

(ICACC-S6-003-2013) Preparation and Property of Li2MSiO4/Graphene Cathode Materials

Y. Cen, Y. Yao, Worcester Polytechnic Institute, USA; C. Wang, Qingdao University of Science and Technology, China; R. D. Sisson*, J. Liang, Worcester Polytechnic Institute, USA

One challenge of modern power sources today is to meet the energy demand of advanced applications including electric vehicles (EVs). Recently, silicates with the general formula of Li2MSiO4 (M = Mn, Fe) have attracted attention of many researchers, as they can accommodate insertion/extraction of two lithium ions per formula unit and provide a theoretical capacity of ~330 mAh/g. Furthermore, it would be interesting to find out if Li2MSiO4 with mixed M of Fe, Mn and Co will provide superior performance to the pure phases as observed in the case of the layered cathodes (e.g. Li(Co1/3Mn1/3Ni1/3)O2). However, one of the major drawbacks of the silicate materials is their low electric conductivities. On the other hand, graphene, as a novel allotrope in nano carbon family and a mono layer of carbon with sp2 carbon lattice, has 0 eV of bandgap between the graphene layers and a high conductivity. Thus, we examined the use of graphene to prepare graphene/silicate nano composites to enhance the conductivity and reversibility of the silicate cathode material. In our work, Li2MSiO4 with mixed Fe and Mn was prepared by sol-gel synthesis method to obtain nano-scale structures. The precursor was coated with graphene and calcinated for complete crystallization. The improved electrochemical performance of grapheme/silicate composites indicates that it is a viable approach to advance the use of lithium silicates in Li-ion batteries.

2:40 PM

(ICACC-S6-005-2013) Ion Beam Mixing to Improve Ge Thin Film Li Ion Battery Anodes (Invited)

K. S. Jones*, N. Rudawski, R. G. Elliman, University of Florida, USA

Conversion electrode materials such as Ge experience large volumetric changes of ~400 % during cycling. In nonporous film electrodes, this ultimately leads to loss of electrical contact due delamination at the electrode/current collector interface. This talk will review recent work done using ion implantation to improve the cycling performance of these materials. Via a phenomenon known as ion beam mixing, it is possible to improve the adhesion strength of the electrode (film) to the current collector (substrate) resulting in a dramatic improvement in electrochemical performance of a conversion electrode. This talk will discuss the role of doses on cycling behavior. Cells for electrochemical testing were prepared in sealed pouches in a half-cell configuration. The morphological and structural evolution of the electrodes was evaluated with high-resolution cross-sectional transmission electron microscopy and scanning electron microscopy. Nanoindentation was performed on virgin electrodes to evaluate the role of implant dose on the strength of adhesion of the film to the substrate. Dramatic improvements in the electrochemical performance of the electrodes were observed at certain doses and the minimum dose necessary to effect improvements in the cycling performance was determined.

3:30 PM

(ICACC-S6-006-2013) Lithium-ion storage- Advanced High Rate and Energy anode materials (Invited)

S. Mitra*, U. Sen, A. Tripathi, P. Veluri, Indian Institute of Technology Bombay, India

If, both high power and energy requirements are accomplished by Lithium-ion battery, it would be useful for power quality applications like electric vehicles, renewable storage etc. Even though inexpensive high power cathode (lithium-iron phosphate) has been realized for high power applications but development of high rate and energy density anode materials are scarcely reported or used in practical Lithium-ion battery. Present Lithium-ion battery uses carbon or graphite –based anode in most of the cases and lacks inherent safety issues due to two main reasons: 1) carbon/graphite intercalates lithium at near lithium potential, and 2) there is no significant indication of oxygen removal in the voltage profile while we use Lithium cobalt oxide (LiCoO2) as cathode. In our group, we use conversion and alloy-dealloying type high energy density anode materials to avoid such issues. Herein we report, anode materials like molybdenum-sulphide, tin-oxide, iron-oxide –based anode materials for high rate and capacity energy storage, power capability and their cycle-life against Lithium for a new generation lithium-ion battery applications.

4:00 PM

(ICACC-S6-008-2013) Synthesis and characterization of olivine-type $LiFePO_4$ cathode material prepared by a polymeric steric entrapment precursor route

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

A fine and pure olivine structure $LiFePO_4$ (triphylite) was synthesized using an organic–inorganic steric entrapment solution, from precursor chemicals of $LiNO_3$, $Fe(NO_3)_3•9H_2O$ and $(NH_4)_2HPO_4$ stoichiometrically dissolved in distilled water. A long-chain polymer such as polyvinyl alcohol ($–[CH_2–CHOH]_{-n}$ or PVA) having a degree of polymerization corresponding to a molecular weight of 9,000 to 10,000 was used as the organic carrier for the precursors, which served for the physical entrapment of the metal ions in the dried network. Normally, when calcined and crystallized in air, this method leads to the synthesis of compounds where the cations in their highest oxidation state. However, in this study we found a way to make compounds having lower oxidation states (e.g. Fe^{+2} versus Fe^{+3}) which may have wider applications in the synthesis of other compounds having variable oxidation states, with potential applications in electronic ceramics of complex chemistry. The resulting $LiFePO_4$ or ($Li_2O•2FeO•P_2O_5$) powders were characterized by TG/DTA thermal analysis, X-ray diffractometry (XRD), scanning electron microscopy (SEM), Brunauer-Emmett-Teller (BET) nitrogen absorption and particle size analysis. Finally, the effect of carbon content from the organic carrier and the resulting electrochemical properties are discussed.

4:20 PM

(ICACC-S6-007-2013) Potential meso-structured Li (Mn0.9Fe0.05Mg0.05)PO4/C cathode material for high rate energy storage application

V. Ramar*, P. Balaya, NUS, Singapore

LiMnPO4 (LMP) offers high specific energy 701 Whkg-1 vs. Li/Li+ owing to its Mn2+/ Mn3+ redox couple which is compatible with the existing electrolytes. However, LMP suffers from sluggish Li+ ions diffusion and poor electronic conductivity. It has been reported that manganese is more electro-chemically active in Mn-Fe solid solution than in LMP. However, the specific energy of those solid solutions is limited by the Fe/Mn proportion. On other hand, inactive cationic doping seems to be interesting than the solid solution due to improved electrochemical performance at higher potential with a flat single redox profiles and hence higher specific energy. In this regard, the meso-structured LiMn0.9Fe0.1-xMgxPO4/C (where x = 0.0, 0.03 and 0.05) and LiMn0.95Mg0.05PO4/C were successfully prepared by a simple scalable soft template approach assisted high energy ball milling to overcome the above cited limitations. The optimized composition LiMn0.9Fe0.05Mg0.05PO4/C exhibits excellent storage performance of 162, 156, 143, 120, 106 and 81 mAhg-1 at 0.1, 0.2, 0.5, 1, 2 and 5C respectively. This composition also exhibits superior capacity retention (97%) at 1C over 200 cycles. It appears that this synthetic approach offers well connected meso-structured grains with high surface area which possibly favour improved storage performance.

4:40 PM

(ICACC-S6-004-2013) Decoration of Graphene with Sn Nanoparticles through Surface Functionalization using Diazonium Chemistry for Lithium-ion Battery Application

G. Zeb*, P. Gaskell, McGill University, Canada; X. Xiao, General Motors, USA; T. Szkopek, M. Cerruti, McGill University, Canada

The composite of graphene/Sn nanoparticles (NP) is a promising anode material for high energy density Li ion batteries. A uniform dispersion of Sn NP with controlled size is necessary to obtain high electrochemical performance. Previous studies showed that oxygenated groups remaining on reduced graphene oxide act as nucleation sites for NP formation. The efficiency of these methods is limited by poor functionalization. In this study, we have investigated functionalization of graphene nano-platelets (GNP) with aminophenyl functionalization for obtaining Sn NP with controlled size. We grafted aminophenyl groups on GNP using diazonium chemistry. The grafting was verified by X-ray photoelectron spectroscopy and Raman spectroscopy. Next, we immersed the aminophenyl functionalized GNP (A-GNP) in an aqueous solution of SnCl2, citric acid and ascorbic acid and subsequently reduced by NaBH4 to obtained Sn NP on A-GNP. We observed very high density and homogeneous dispersion of Sn NP of average size 30 nm on A-GNP. In contrast, we observed significantly lower density of Sn NP on unfunctionalized GNP with inhomogeneous dispersion. We attribute the higher density of Sn NP on A-GNP to higher density of defects on GNP produced by aminophenyl functionalization. Our Li ion coin-cell tests demonstrated high and stable discharge capacity for Sn NP/A-GNP.

S7: 7th International Symposium on Nanostructured Materials and Nanocomposites

Synthesis and Applications of Functional Nanostructures I

Room: Coquina Salon B
Session Chair: Sanjay Mathur, University of Cologne

1:30 PM

(ICACC-S7-001-2013) Nanostructured ceramics: Processing, characterisation and commercialisation (Invited)

J. Binner*, B. Vaidhyanathan, C. Reilly, S. Saremi, M. Tong, Y. Zhang, S. Ghanizadeh, S. Huang, P. Ramanujam, S. Venugopal, P. Zhang, Loughborough University, United Kingdom

The ability to produce genuinely nanostructured ceramics with mean grain sizes <100 nm has been achieved for yttria partially stabilised zirconia (YSZ) and is being developed for alumina, barium titanate (BT), zirconia toughened alumina (ZTA) and yttrium aluminium garnet (YAG) under a range of different Government and industrially-funded projects. Prototype components have already been produced and characterised for the YSZ, BT and ZTA and the work on YSZ was licensed to an industrial company in early 2012 for subsequent commercialisation. This presentation will highlight the key steps, indicate the challenges that have been overcome and those that still remain and demonstrate the achievements and applications.

2:00 PM

(ICACC-S7-002-2013) Phase-selective synthesis of rare earth phosphors at the nanoscale from ionic liquids (Invited)

A. Mudring*, Ruhr-Universitaet Bochum, Germany

A significant amount of electricity could be saved if more energy-efficient light sources were used. Various countries have already banned or are currently planning to ban conventional incandescent lamps which suffer from poor luminous efficiency since most of the energy is converted to heat. Light sources with higher energy efficiency are compact fluorescent lamps (CFLs) used for instance in home illumination or light emitting diodes (LEDs) found in traffic lights. However, their current manufacturing process employs hazardous and rare materials, which should be replaced by environmentally safer ones, and therefore diminishing their impact on health and environment during production and end-of-life processes. In order to make such a light bulb competitive, novel smart materials - nano energy-conversion phosphors - will be coated on the respective device by a new technique relying on ionic liquids. Ionic liquids can be made in such as way that they are safer to use than conventional organic solvents; they help to eliminate toxic and difficult synthesis steps, reaction times and temperatures can be reduced, less chemicals are needed, smaller particles are obtained and, most importantly, it is possible to obtain high-quality phosphors from them.

2:30 PM

(ICACC-S7-003-2013) Zinc oxide particles: The growth and characterization (Invited)

Z. Crnjak Orel*, National Institute of Chemistry, Slovenia

In this contribution, the preparation (batch reactors and or continuous segmented flow tubular reactor –SFTR) of stable and non-agglomerated ZnO nano-to-submicrometer sized particles of different shapes (spherical, wires, needles, rods, etc.) and sizes with narrow particle size distribution is presented. We will show the assumed growth mechanism of ZnO particles. It follows the "non-classical crystallization" concept as it was observed by the combining of the advanced in-situ SAXS method and the ex-situ electron microscopy (FE-SEM and TEM). The mechanism predicts the self-assembling of nanobuilding units (5-10 nm) into larger microstructures with prompt crystallization. At the same time, the growth based on the direct attachment of ions from the solution also occurs in minor extension. Particle growth was also monitored indirectly via in-situ pH measurements. The synthesized ZnO nanoparticles were further used for the preparation of polymer/inorganic-material-based nanocomposites. We found that the presence of a very small quantity of ZnO based nanomaterial in the PMMA showed sufficient UV shielding (efficiently absorb UV light up to 370 nm) and at the same time good transparency in the visible-light region. According to TEM, homogeneous dispersion of ZnO particles in the amorphous PMMA matrix was achieved. Thermal stability of the ZnO/PMMA nanocomposites is considerably improved.

Synthesis and Applications of Functional Nanostructures II

Room: Coquina Salon B
Session Chairs: Anja-Verena Mudring, Ruhr-Universitaet Bochum; K. Byrappa, University of Mysore

3:20 PM

(ICACC-S7-004-2013) Tuning of Bandgap and Nanoporosity in Hydrothermally Prepared Metal Oxide Semiconductors using Positron Annihilation Lifetime Spectroscopy (Invited)

K. Byrappa*, University of Mysore, India; K. Namratha, C. Ranganathaiah, University with Potential for Excellence Building, India

Metal oxides exhibit excellent multi-functional characteristics with a broad range of applications as semiconductors, in optical devices, piezoelectric devices, surface acoustic wave devices, sensors, transparent electrodes, solar cells, antibacterial, antioxidant, drug delivery, hypothermia, etc. TiO2 has several other specific applications and the common ones are as photocatalyst, dye sensitized solar cells, white pigment, ceramic glazes, sun screen and UV absorbers, also as electronic data storage, and so on. Similarly, zinc oxide is well-known as n-type wide band gap semiconductor ($\Delta E = 3.37$ eV at 300 K) with a large exciton energy of 60 meV and thermal energy of 27 meV. Due to bright UV-luminescence, ZnO is a perspective material for the manufacture of UV-light emitting diodes, UV lasers operating at room temperature and display devices. Moreover, ZnO quantum dots with very low toxicity, high photostability, biofriendly and biodegradable have been demonstrated. However, it is interesting to note that these physico-chemical characteristics depend mainly upon the band gap and the tuning of band gap and its significance to photocatalytic properties has not been understood in the literature.

3:50 PM

(ICACC-S7-005-2013) Effect of grain size on the thermal conductivity of La-doped SrTiO3 nanoceramics

V. Buscaglia*, M. Buscaglia, National Research Council, Italy; F. Maglia, U. Anselmi Tamburini, University of Pavia, Italy; D. Marrè, University of Genoa, Italy; I. Pallecchi, National Research Council, Italy; A. Ianculescu, Polytechnics University of Bucharest, Romania; M. Fabrizio, National Research Council, Italy

Donor-doped SrTiO3 shows a high electrical conductivity and a large Seebeck coefficient and, consequently, has attracted attention as a potential thermoelectric material. However its figure of merit is limited by the high (10 W m-1 K-1 at RT) thermal conductivity. A major reduction of thermal conductivity of bulk materials can be attained by decreasing the phonon mean-free path through nanostructuring. In this contribution the influence of grain size on the thermal conductivity of La-doped (10 at.%) SrTiO3 ceramics will be illustrated. Dense ceramics with grain size between 24 and 82 nm were fabricated by spark plasma sintering (SPS) at 800-1100°C from two different types of nanopowders. Coarse grained ceramics were prepared by annealing some SPSed samples at higher temperature. Thermal conductivity measurements were performed in the temperature range 10–300 K. The data show a progressive reduction of the thermal conductivity with decreasing grain size. One order of magnitude reduction (from 10 to 1 W m-1 K-1) has been observed at room temperature for the ceramics with a grain size of 24 nm in comparison to the reference data for single crystals. The decrease is even larger at low temperature. Three factors contribute to this reduction: scattering of phonons by La ions and other lattice point defects, scattering by grain boundaries and a dilution effect caused by the residual porosity.

4:10 PM

(ICACC-S7-006-2013) Polymer-Derived Ceramics - Nanodomain Structure and Energetics

G. Mera*, Technische Universität Darmstadt, Germany; A. Navrotsky, University of California at Davis, USA; H. Kleebe, Technische Universität Darmstadt, Germany; S. Sen, University of California at Davis, USA; R. Riedel, Technische Universität Darmstadt, Germany

Controlled pyrolysis and processing of suitable “homemade” silicon-based polymers enables to control and to tune the final structure of amorphous polymer derived ceramics (PDCs). A particular feature of PDCs is the nanodomains presence. The nanodomains of 1-3 nm in size are found to influence the properties and thermal stability of these materials. As recently observed, the chemical bonding at the interface between nanodomains has a strong influence on the stability of these ceramics and is expected to introduce new properties in the materials. The emphasis of this work is on the intimate relationship between the precursors (molecular structure/architecture) and the resulting PDCs (phase composition, nano/microstructure and energetics) in the ternary systems SiCN and SiOC. Particularly, carbon-rich SiCN PDCs, due to the graphene phase formation already at very low temperatures, were reported as multifunctional materials finding application as micro- and meso-porous nanostructured ceramics or as anode materials in Li-ion batteries. The energetics of SiCN and SiOC PDCs were studied by oxidative solution calorimetry in molten oxide solvents at 700-800 °C. Spectroscopic methods such as solid-state NMR, SAXS and Raman spectroscopy, together with TEM and STEM were applied as powerful methods for the characterization of nanodomains in PDCs.

4:30 PM

(ICACC-S7-010-2013) Water Vapor Facilitated Synthesis of Single-Crystal Platinum Nanoparticles

T. Cheng*, K. L. More, Oak Ridge National Lab, USA

Single crystal (SC) Pt nano-particles exhibited broad application in automobile pollution control, sensors and fuel cells. The single crystal platinum particles in a range of nano to micron were synthesized at the Pt/SiC interface in water vapor at 800-1200 °C. Formation of the Pt particles is possibly due to water vapor-facilitated oxidation of the platinum silicide resulted from interaction between SiC/Pt. The single crystal Pt formed in water vapor exhibits an octahedral shape, growing along (111) direction as increasing exposure time. Spherical Pt nanoparticels were formed in the presence of Y and Al elements serving as the sintering aids for SiC. Size and shape of platinium SC nano particles largely depend on water vapor temperature, reaction time and metal impurites.

4:50 PM

(ICACC-S7-007-2013) Novel Synthesis and Analysis of Ce-doped TiO2 Nanotubes

P. N. Lisboa-Filho*, UNESP-São Paulo State University, Brazil; L. B. Arruda, UNESP -São Paulo State University, Brazil

Nanoscale tubular structures have been intensively studied due to their unique physical properties. In this context, nanosized materials derived from titanium dioxide (TiO2) have been investigated for a number of applications, especially those for solar energy conversion, photocatalysis and gas sensor devices. One of the distinctive characteristic of this material is that TiO2 has a wide band gap, however it does not absorb in the visible light region. 1-D Ce-doped TiO2 exhibit large increase on the absorption capacity in the visible region if compared to samples without doping, caused by a charge transfer between the electron of f-layer of ions Ce and the valence band of TiO2. Moreover, valence fluctuations in cerium states may occur under oxidation and reduction resulting different microstructural and optical properties . Nanotubes of TiO2/Ti1-xCexO2 were synthesized by an alternative chemical route, directly in alkali-medium treatment with subsequent washing in water and HCl aqueous solution to obtaining 1D-nanostructures. X-ray diffraction (XRD) and transmission electron microscopy (TEM) measurements show that the synthesized samples preserve the anatase phase and that the nanotubes are formed of multiple walls, with homogeneous size distribution. The formation process of TiO2 nanotubes under alkaline conditions was determined by infrared spectroscopy (FTIR) measures in combination with the TEM analyses.

S8: 7th International Symposium on Advanced Processing and Manufacturing Technologies for Structural and Multifunctional Materials and Systems (APMT)

Novel Processing for Functional Materials

Room: Coquina Salon A
Session Chairs: Ian Nettleship, University of Pittsburgh; Paul Bowen, EPFL

1:30 PM

(ICACC-S8-001-2013) Fundamental Issues in the Processing of Transparent Aluminas : From Interparticle Forces to Porous Ceramic Coatings and Dense Transparent Ceramics (Invited)

P. Bowen*, EPFL, Switzerland

Two aspects of alumina processing will be presented i): dispersion of nanosized transition aluminas for porous coatings for ink-jet paper and ii) the use of sub-micron aluminas for transparent polycrystalline alumina (PCA). First we illustrate the importance of small steric barriers that are sufficient to disperse 20-40 nm particles and describe their application for industrial transparent coatings. Secondly we investigate the effects of Mg, La and Y dopants (nitrates) on alumina powder suspensions which cause a yield stress to appear. This change in rheological properties rendered granulation of the powders for dry-pressing impossible. Inter-particle force calculations were used to determine the minimum particle separation which was then used to calculate a predicted yield stress from a yield stress model for suspensions (YODEL). The model predictions compare very well with the measured yield stresses. The choice of key parameters for the model that are difficult to measure explicitly will be discussed. From these predictions the use of polyacrylic acid (PAA) allowed us to reduce the yield stress and produce transparent PCA from freeze granulated powders. The mechanism of dispersion was more subtle than simple electrosteric repulsion with in fact the complexation of the PAA with the Mg, La and Y ions playing a significant role.

2:00 PM

(ICACC-S8-002-2013) UBE's Functional Ceramics Synthesized from Bountiful Resources (Invited)

T. Ishikawa*, Ube Industries, Ltd., Japan

Ube Industries have produced many types of functional ceramics. These ceramics are classified into three groups which are "Fine ceramic powders with very high purity", "Thermo-structural ceramics", and "Precursor ceramics". All of them are synthesized from bountiful resources of the earth. Main resources of UBE's functional ceramics are Mg, Ca, and Si. As you may know, the surface region of the earth is composed of MgSiO3 with a perovskite crystalline structure. And, Ca is brought from the shelf of coral. So, Ca is a great blessing from the sea. Using these bountiful resources, UBE developed "silicon nitride powder", "Mg-based ceramic powders", and "Ca-based ceramic powders". These ceramic powders show the highest purity compared with comparative powders. And also, UBE developed several types of precursor ceramics, that is to say, SiC-based fibers (Tyranno) with high heat-resistance and excellent mechanical properties, photocatalytic fiber with very high quantum efficiency, and so on. Today, I would like to talk about the fundamental information of these functional ceramics along with some applications.

2:30 PM

(ICACC-S8-003-2013) What the difference between Aerosol Deposition and Cold Spray techniques as the kinetic spray coating? (Invited)

J. Akedo*, National Institute of Advanced Industrial Science and Technology (AIST), Japan

Recently, Aerosol Deposition (AD) method has been made attention as room temperature ceramic coating technique. AD method is a unique approach for depositing ceramic films, where solid state submicron metal and ceramics particles (both oxide and non-oxide) are accelerated by gas flow up to 100 - 500 m/s and then impacted onto a substrate. It can form rapidly a thick dense, uniform and hard ceramic layer at room temperature without additional heating for solidifying starting powders, even in low vacuums, using relatively cheap and simple production facilities. It is expected to reduce energy, cost, difficulty to fabricate the thin or thick film with complicate material compositions and the number of processes during fabricating electronic devices and others, as well as to improve their performances substantially. Cold Spray (CS) method is well known in the field of thermal spray coating technology as similar technique of AD method. CS method is spraying of solid state metal particles onto the substrate in atmospheric pressure. AD method allows making both metal and ceramic dense layers. On the other hand, CS method only allows making metal layer. In this report, the deference of the principle between AD method and CS method as the kinetic spray coating will be presented.

3:20 PM

(ICACC-S8-004-2013) High Efficiency Low Temperature Recycling Technology for Lithium Ion Batteries (Invited)

Y. Wang*, H. Zou, D. Apelian, Worcester Polytechnic Institute, USA

The rechargeable secondary Lithium ion (Li-ion) battery is expected to grow to more than $6.3 billion by 2012 from ~$4.6 billion in 2006. With the development of personnel electronics, hybrid and electric vehicles, Li-ion batteries will be more in demand. However, Li-ion batteries are not widely recycled because it is not economically justifiable (in contrast, at present more than 97% Lead-acid batteries are recycled). So far, no commercial methods are available to recycle Li-ion batteries economically and efficiently because of the complex chemistry of Li-ion batteries. Considering our limited resources, environmental impact, and national security, Li-ion batteries must be recycled. A new methodology with low temperature and high efficiency is developed in order to recycle Li-ion batteries economically and with industrial viability. The separation and synthesis of cathode materials (most valuable in Li-ion batteries) from recycled components are the main focus of the research.

3:50 PM

(ICACC-S8-005-2013) Processing and Characterization of Multiferroic Composite Films Using Metal-Organic Precursor Solutions (Invited)

W. Sakamoto*, Y. Kawabata, D. Maeda, M. Moriya, T. Yogo, Nagoya University, Japan

Multiferroic materials, which simultaneously exhibit ferroelectricity and ferromagnetism, have recently been receiving much attention because of their scientific interest. The composite thin films combining ferroelectric and ferromagnetic phases have higher feasibilities for practical applications due to their larger magnetoelectric coupling at room temperature than the single-phase multiferroic materials. In this study, we selected Pb(Zr,Ti)O3 (PZT) or BiFeO3-PbTiO3 (BF-PT) as a ferroelectric and CoFe2O4 (CFO) as a ferromagnetic for the fabrication of nano-composite films. Tailored metal-organic precursor solutions for preparing PZT, BF-PT and CFO were alternately spin-coated on Si-based substrates to fabricate layered PZT/CFO and BF-PT/CFO films. On the other hand, CFO nano-fibers were prepared from a CFO precursor solution by the electro-spinning. The CFO fibers were placed on a substrate, and then the PZT or BF-PT precursor film was deposited to form a spinel CFO nano-fibers embedded perovskite PZT or BF-PT film. The PZT/CFO and BF-PT/CFO composite films exhibited typical ferroelectric P-E and ferromagnetic M-H hysteresis loops simultaneously at room temperature. The detailed properties and the effect of processing conditions on microstructure and properties of the nano-composite films are also discussed.

4:20 PM

(ICACC-S8-006-2013) The Design and Processing of Bioreactor Ceramics for In-Vitro Culturing of Human Cells

I. Nettleship*, A. Finoli, E. Schmelzer, J. Gerlach, University of Pittsburgh, USA

In-vitro expansion and maintenance of large volumes of human cells will be a key prerequisite for the widespread implementation of regenerative medicine therapies and in-vitro drug testing. Bioreactor systems will be well suited to this application. The basic design requirements of composite materials used for 3D culturing of cells in perfusion bioreactor cores will be considered. The presentation will focus on the design of a porous calcium phosphate-hydrogel composite bioreactor core in which the levels of structure are informed by key features of the natural microenvironment or "niche" inside the human body. In this case the reactor core is being designed for culturing of liver cells and tissue. Specific topics to be discussed include: (i) the effect of the calcium phosphate ceramic and the hydrogel on the culturing of human cells and (ii) processing of the multiscale, macropore structure required for perfusion of the cells by media.

4:40 PM

(ICACC-S8-007-2013) Novel approach to produce spherical, porous, multilayer and hollow ceramic beads

C. J. Espinoza Santos*, B. Walusiak, S. Hayes, E. K. Mendoza, W. M. Kriven, University of Illinois at Urbana-Champaign, USA

The purpose of this of study was to investigate a novel forming method to produce spherical ceramic beads for the study of stress wave propagation of granular media. The process involves preparing a slurry with a small amount of PVA binder and dispersant. The moisture content of the slurry is adjusted until 20% moisture is retained. After drying, the mixture is fairly solid when left at rest, but will begin to flow when vibrated (shear thinning). With correct moisture content under an applied vibration, the material can then be vibrated within square enclosures to form spheres. First, the vibration lowers the viscosity of the slurry enough for it to be shaped easily. Second, the vibration keeps the slurry from sticking to the vibrating table during the forming process. Lastly, the vibration causes the spheres to agitate in a random manner, which constantly rounds them out. Together with the appropriate containment and a slight circular motion, very round spheres are formed as the slurry vibrates and slowly dries out, resulting in hard, dense green bodies. This process has the potential of producing beads for many other applications such as ceramic beads for milling, catalyst supports, encapsulation of drugs, and water filtration.

5:00 PM

(ICACC-S8-008-2013) Effect of Additives on Electrical Resistivity of Liquid-Phase Sintered Silicon Carbide Ceramics

Y. Kim*, K. Lim, The UNiversity of Seoul, Republic of Korea; K. Kim, Konkuk University, Republic of Korea

The influence of additive composition on the electrical resistivity of hot-pressed liquid-phase sintered (LPS)-SiC was investigated using various additives containing Y_2O_3, yttrium nitrate, and AlN-RE_2O_3 (RE=Nd, Eu, Gd, Ho, Er, Lu) mixtures. It was found that all specimens could be sintered to densities >95% of the theoretical density by adding 5 wt% in situ-synthesized nano-sized SiC and a small amount of additives. Six out of seven SiC ceramics showed very low electrical resistivity on the order of 10^{-4} Ωm. This low electrical resistivity was attributed to the growth of nitrogen-doped SiC grains and the confinement of non-conducting RE-containing phases in the junction areas. The SiC ceramics sintered with AlN-Lu_2O_3 showed a relatively high electrical resistivity (~10^{-2} Ωm) due to its lower carrier density (~10^{17} cm-3), which was caused by the appreciable $\beta \rightarrow \alpha$ phase transformation of SiC. The occurrence of this phase transformation led to the growth of faceted grains, resulting in a weak interface between SiC grains.

S9: Porous Ceramics: Novel Developments and Applications

Processing Methods for Porous Ceramics I

Room: Coquina Salon C
Session Chair: Paolo Colombo, University of Padova

1:30 PM

(ICACC-S9-001-2013) Particle-stabilized ceramic foams: from discovery to invention to innovation (Invited)

U. T. Gonzenbach*, de Cavis Ltd., Switzerland; P. N. Sturzenegger, B. S. Seeber, ETH Zürich, Switzerland; U. Ebneter, de Cavis Ltd., Switzerland; P. Elser, M. Heer, L. J. Gauckler, ETH Zürich, Switzerland

More than a hundred years ago, Ramsden and Pickering discovered the ability of fine particles to stabilize oil-water interfaces. Interestingly, little work appeared afterwards and it was only recently that the principles of particle stabilization were applied to the formation of liquid ceramic foams. Such foams are technically important soft matter and crucial as intermediates for the production of porous ceramics. However, their thermodynamically unstable nature is a critical issue that can be drastically improved using particles as foam stabilizers. For efficient stabilization, particle wettability needs to be tailored to promote particle attachment to the liquid-gas interface. Our invention of in-situ particle hydrophobization is a powerful method to tailor wettability of colloidal particles via adsorption of short-chain amphiphilic molecules in order to enable the formation of stable wet foams. This presentation takes you on a journey from the early discovery of emulsion stabilization with fine particles to the long road from invention to innovation in the area of particle-stabilized ceramic foams. It gives an overview over our activities in this field and describes our method in detail, focusing on the parameters controlling foam formation as well as the processing of wet foams into porous ceramics and their outstanding mechanical, thermal, electrical and microstructural properties.

2:00 PM

(ICACC-S9-002-2013) Development of highly closed porous ceramics for thermal insulator

M. Fukushima*, Y. Yoshizawa, National Institute of AIST, Japan

Efficient use of heat energy and its energy-saving concerns over glass, ceramic and iron-steel industries require high temperature operations are prompting researchers to investigate more effective and affordable thermal insulators and refractory to be used, for example, for the improvement of porosity, stationary closed porosities, inhibition of radiation and convection flow, and improved strength. We will propose gelation freezing route as a cost-effective and versatile method for the drastic improvement of thermal conductivity and compressive strength. This novel route can make it a possible to prepare macroporous ceramics with tailored higher closed porosity with controlled pore size and improved strength as well. The freezing conditions (temperature and direction) and compositions led to a decrease of thermal conductivity and an increase of compressive strength of obtained materials. In addition, permeation behaviour was studied. Results presented were compared to commercial various thermal insulators.

2:20 PM

(ICACC-S9-003-2013) High Performance Porous Si3N4 Ceramics with Microstructural Design (Invited)

J. Yang*, Xi'an Jiaotong University, China

Silicon-based porous structural ceramics: Si3N4, SiAlON, Si3N4/SiC nanocomposites, are fabricated by pressureless sintering, partial hot-pressing (PHP), restrained sintering by reaction bonding (RSRB), by tailoring the composition, microstructure and sintering condition. The porous Si3N4 ceramics with fine elongated fibrous β-Si3N4 grains have a high strength, toughness and strain tolerance, and the porous SiAlON ceramics has a good corrosion resistance. Porous Si3N4 ceramics with rod-like pores were synthesized by pressureless sintering of green compacts prepared using slip casting of slurries containing Si3N4, sintering additives and organic whiskers. Porosities ranging from 0% to 45% were obtained by the whisker contents (corresponding to 0–60 vol% whisker). Carbothermal nitridation (CT/N) of SiO2 was proposed. Fine elongated fibrous β-Si3N4 grains were developed in the seeded samples with stoichiometric C-SiO2 ratio and Y2O3 as the sintering additive, when sintered at 1,700-1,750 °C in nitrogen atmosphere. Outstanding strength of 5 times of that for the seed-free samples had been resulted. Recently we proposed a new concept of the high purity porous Si3N4 ceramics, fabricated by the following process: pressureless sintering of the porous Si3N4, removing of the oxide grain boundary, silicon infiltration, nitridation. The samples occupy the fibrous β-Si3N4 grains, and good thermal and corrosion resistance.

Processing Methods for Porous Ceramics II

Room: Coquina Salon C
Session Chair: Alberto Ortona, SUPSI

3:20 PM

(ICACC-S9-004-2013) Foaming methods for the production of porous ceramics based on ZrB2 and SiC (Invited)

V. Medri*, M. Mazzocchi, A. Ruffini, D. Sciti, E. Landi, CNR-ISTEC, Italy

Different methods of direct and indirect foaming were applied to produce porous ceramics based on ZrB2 and/or SiC. Clot forming was used to produce highly porous ZrB2 ceramics by exploiting the foaming property of ovalbumin and its ability to thicken after heating around 80°C. SiC foams were developed by in situ foam formation in alkaline environment using a low temperature process such as a chemical consolidation. An alkali aluminosilicates binder was used. The foaming agent was metallic silicon iimpurity in SiC powder. Replica method was used to produce ZrB2-SiC porous composite. Polyurethane templates generated empty ceramic struts that decrease mechanical performances. Foams from PU showed very low compressive strength: 0.7 MPa with porosity ≥85 vol% and 0.3 MPa with porosity ≥88 vol%. Thank to hydrophilic surfaces, cellulose or natural sea sponges were permeated by the suspension, yielding open cells with dense wall structure after sintering, thus increasing mechanical strength up to 4.8 MPa. Finally, the possibility to shape into graded porous structures by freeze casting was investigated on ZrB2 and ZrB2-SiC composites. The total porosity was about 63-64 vol % and hierarchical architectures with anisotropic porosity were realized, which showed porosity formed by mainly unidirectional channels separated by ceramic plates. The compressive strength was improved compared to sponge-templated foams.

3:50 PM

(ICACC-S9-005-2013) Formation mechanism of porous zirconia with a high volume fraction of fine closed pores

S. Hashimoto*, T. Umeda, Nagoya Institute of Technology, Japan; K. Hirao, N. Kondo, Y. Zhou, H. Hyuga, National Institute of Advanced Industrial Science and Technology (AIST), Japan; S. Honda, Y. Iwamoto, Nagoya Institute of Technology, Japan

A novel technique to make a porous ZrO2 with a high volume fraction of fine closed pores has been developed. It was found that ZrO2 sintered bodies containing small amount of impurities exhibited larger volume expansion related to the formation of closed pore as heated at 1700 degree C. These closed pores are considered to be formed due to vaporization of impurities. Particularly, Si, Ti, P and Ca are the possible impurities to form the pores during heating, because the elements were mainly detected by Glow Discharge (GD) mass analysis in the ZrO2 body having such unusual characteristics. Therefore, in this study, several impurities such as SiO2, TiO2 and/or hydroxyl apatite were added to 3 mol% Y2O3 partially stabilized ZrO2 (3Y-PSZ) and formation of closed pores was investigated. A porous ZrO2 with fine closed pores ~ 30% in volume fraction was successfully fabricated by adding 1 mass % of SiO2, 1 mass % of TiO2 and 1 mass % of hydroxyl apatite as impurities at the same time and by two step heating technique. Closed pore size and morphology of the porous ZrO2 bodies were investigated and formation mechanism of the closed pores was discussed in chemical thermodynamics.

4:10 PM

(ICACC-S9-006-2013) Fabrication and filtration behavior of ceramic foams decorated with ceramic nanowires

M. Fukushima*, National Institute of AIST, Japan; M. Innocentini, Universidade de Ribeirão Preto, Brazil; J. Coury, Universidade Federal de São Carlos, Brazil; Y. Yoshizawa, National Institute of AIST, Japan; P. Colombo, Università di Padova, Italy

Silicon oxynitride (Si2N2O) nanowires (NWs) were grown in situ on the cell walls of silicon carbide and alumina foams by coating preceramic polymers containing a Co-based catalyst, followed by pyrolysis in nitrogen at temperatures ranging from 1250°C to 1450°C. The relationship between different processing factors (type of substrate and preceramic polymer, pyrolysis temperature) and the growth of NWs was examined. Varying processing factors were found to be effective for controlling the growth of NWs. The use of a preceramic polymer containing a high amount of carbon as well as silica impurities present in the SiC foams led to a larger amount of longer NWs, homogeneously covering the ceramic struts of the porous substrates. Ceramic foams with and without NWs were then tested for air permeability and aerosol filtration at room temperature. The results showed that the ceramic foam decorated with NWs is a very promising alternative as an aerosol filter, since the permeability and efficiency curves are similar to those of commercial HEPA filter. The overall morphology, growing mechanism, filtration efficiency and permeability of the ceramic foam decorated with various amounts and length of NWs on ceramic foams were investigated.

4:30 PM

(ICACC-S9-007-2013) Possible Mechanisms to Wet Foam Stabilization Forming Porous Ceramics

A. Pokhrel*, S. Nam, I. Kim, Hanseo University, Republic of Korea

Experimental data's are presented to show the influence of colloidal particles on the stability of the colloidal suspension, later resulting in the stabilization of air-water emulsions. This gave rise to the stability of the wet foam which leads to the well-structured porous ceramics on sintering. Colloidal particles that are partially wetted by both the aqueous and hydrophobized phases are capable of effectively stabilizing foams. The effectiveness of these particles and resultant effects of these solids in stabilizing foams depends on the factors such as particle size, inter-particle interactions, and the wettability of the particles. Here we describe the fundamental understanding of the mechanisms which is essential in governing the stability of these foams to produce porous ceramics. Colloidal particles stabilized foams, by providing steric hindrance to the coalescence of bubbles and modifying the rheological properties of the interface.

4:50 PM

(ICACC-S9-008-2013) Silicon Oxycarbide Foams from Silicone Precursors

H. Chen*, T. Parthasarathy, M. Cinibulk, M. Chen, AFRL, USA

Silicon oxycarbide foams were synthesized by pyrolysis of self-rising silicone foams. Silicone foams were first prepared by either physical blowing or chemical blowing. In the physical blowing method, dichloromethane was used as the blowing agent. In the chemical blowing method, hydrogen was produced in-situ at room temperature as a chemical blowing agent. Silicone foams were converted to silicone oxycarbide foams after being pyrolyzed in an inter atmosphere. The structural features of the ceramic foams were characterized using SEM and X-Ray CT scan. The bulk density, pore size, and pore openness were correlated to processing conditions including foam formulation, rising temperature, and filler contents. The mechanical and thermal properties of the ceramic foams were evaluated and correlated to the structural features. The silicone derived ceramic foam is a promising candidate for structural thermal insulation material in high temperature applications. This work was partially supported through the U.S. Air Force Contract FA8650-10-D-5226.

5:10 PM

(ICACC-S9-009-2013) The Synthesis of Mesoporous SiC Ceramics from Block Copolymer Precursors

X. Yang*, L. An, University of Central Florida, USA

Mesoporous non-oxide ceramics are promising for many applications due to their high thermal stability, excellent corrosive resistance, chemical inertness, and bio compatibility. In this paper, we report the direct synthesis of mesoporous SiC ceramics from the self-assembled micelles of polyvinylsilazane-block-polystyrene copolymer without templates. In this process, PVSZ-b-PS di-block copolymer was first synthesized from VSZ and styrene monomers. By using the selected solvent, the copolymer was self-assembled into micelle structure with PS as the core and PVSZ as the shell. Such micelles were then used as starting block to synthesized porous ceramics by pyrolysis at elevated temperatures. By this process, both bulk and thin film porous SiC were synthesized. The synthesis and conversion of the copolymer were characterized by TEM, SEM and BET to understand the processing and resultant porous materials.

5:30 PM

(ICACC-S9-010-2013) Superparamagnetic single phase cubic mesoporous CuFe2O4 synthesized by nanocasting from vinyl-functionalized Cubic mesoporous silica

N. Najmoddin, M. S. Toprak*, KTH - Royal Institute of Technology, Sweden; A. Beitollahi, H. Rezaie, IUST - Iran University of Science and Technology, Islamic Republic of Iran; M. Muhammed, KTH - Royal Institute of Technology, Sweden

Spinel ferrites with the formula of MFe2O4, where M represents a divalent metal ion, have shown great potential for applications due to their unique optical, electrical and magnetic properties. These materials are technologically important and have been used in many applications including magnetic recording media and magnetic fluids for the storage and/or retrieval of information, magnetic resonance imaging (MRI) enhancement, catalysis, magnetically guided drug delivery, sensors, and pigments. Copper ferrite has two crystallographic spinel structures: the high-temperature cubic phase (c-CuFe2O4), and the low-temperature tetragonal phase (t CuFe2O4). The high temperature single phase cubic structure (with a higher magnetization) was only obtained as a metastable phase at room temperature by rapid quenching. The method we propose is hard templating approach that is capable of forming the high temperature cubic phase at relatively low temperature, with a high phase purity, and without the need of quenching. In this method, Cu(NO3)2.3H2O and Fe(NO3)3.9H2O were used as precursors, and vinyl- functionalized mesoporous silica was utilized as hard template. We will present the details of the developed route along with the thorough characterization results of the fabricated mesoporous CuFe2O4.

FS2: Thermal Management Materials and Technologies

Thermal Management Materials and Technologies

Room: Coquina Salon H
Session Chair: Andrew Gyekenyesi, OAI/NASA GRC

1:30 PM

(ICACC-FS2-001-2013) Evaluation of Graphite Foam in Thermal Energy Storage Applications

P. G. Stansberry*, E. Pancost, GrafTech International Holdings, USA

Enhanced performance in electronics, aerospace, and military systems require improved solutions in thermal management. Some of the solutions include developing new and novel materials that exhibit high thermal conductivity, dimensional stability at high temperature, high surface area, and low density. Graphite foam is an attractive candidate in thermal management systems because it can be manufactured with ligament thermal conductivities in excess of 1,500 W/m-K and bulk thermal conductivities greater than 150 W/m-K. These qualities, in combination with an open-pore structure and low density, offer distinct advantages over other types of materials. In order to understand the performance of graphite foam for thermal management a thermal energy storage device (TESD) was constructed using graphite foam cores and paraffinic phase change material (PCM). Heat transfer fluid at controlled temperature and flow rate was conveyed through a graphite foam core on the acquisition/rejection side of the TESD, which was interfaced with a graphite foam core saturated with PCM. The heating and cooling responses of the graphite foam infiltrated with PCM are reported and modeled.

1:50 PM

(ICACC-FS2-002-2013) Joining and Characterization of Graphite Foam-to-Metal Joints

M. Singh, R. Asthana*, C. E. Smith, A. L. Gyekenyesi, University of Wisconsin-Stout, USA

Variable-density, high-conductivity graphite foams were joined to titanium, 430 stainless steel, Cu-clad-Mo and Inconel 625 using two silver-based braze alloys, Cusil-ABA and Palcusil-5 with similar liquidus temperatures (TL~815°C). Well-bonded joints with partially infiltrated foam with interfaces enriched in Ti formed in Cusil-ABA joints with all metallic substrates. Low-density foams showed greatest braze penetration and penetration distance decreased with increasing foam density. Initial tension test results on foam/Ti joints made using Cusil-ABA revealed that joints were stronger than foams. Palcusil-5 formed sound foam/metal joints but showed reduced braze penetration and no interfacial segregation of Pd except in foam/Palcusil-5/steel joints which exhibited near-zero infiltration and a discontinuously bonded interface. To obtain high conductivity joints for higher operating temperatures than Cusil-ABA, foam/steel joints were fabricated using Ticusil braze (TL: 900°C, kTicusil: 219 W.m-1-K-1) with different percentages (5, 10 and 15 wt%) of AlN powders. The powders were used to preserve the conductivity while controlling the interlayer thermal expansion and enhancing the joint strength. Microstructural observations are presented together with the projections of thermal conductivity, thermal expansion, and braze strength with the Ticusil-AlN braze treated as a two-phase metal-matrix composite.

2:10 PM

(ICACC-FS2-003-2013) High-Temperature Foam-Reinforced Thermal Insulation

J. J. Stiglich*, B. Williams, Ultramet, USA

Ultramet has developed a highly insulating and lightweight thermal protection material by combining an open-cell carbon or ceramic foam skeleton with an ultralow-density aerogel filler material. The foam serves as an easily machinable structural reinforcement for the very low-strength aerogel insulator and defines the shape of the component. In the foam-aerogel composite structure, the aerogel exists in small discrete cells and is supported by the foam skeleton. The combined density of the composite insulator is as low as 0.1 g/cm3, and the thermal conductivity is <1 W/mK at 2000°C. Single-piece panels up to 30” square are feasible. The benefits of structural foam as a reinforcement for chopped fiber phenolic ablators has also been demonstrated in arcjet testing to heat flux levels of >1000 W/cm2 in which low erosion rates and heat transfer were indicated. The foam helps retain the char layer by physical reinforcement, and the network of interconnected passages allows pyrolysis gases to escape with less disruption of the char layer. The benefits of foam reinforcement of both nonablating and ablating insulators will be discussed.

FS3: Nanomaterials for Sensing Applications: Fundamental Material Designs to Device Integration

Nanomaterials for Sensing Applications

Room: Coquina Salon H
Session Chair: Francisco Hernandez-Ramirez, Catalonia Institute for Energy Research and University of Barcelona

3:20 PM

(ICACC-FS3-001-2013) The surface chemistry effects on the gas response of metal oxide nanocrystals. A combined experimental and theoretical investigation (Invited)

M. Epifani*, CNR-IMM, Italy

The importance of metal oxides (MOXs) nanocrystals for improving the performances of chemoresistive gas-sensors is well established. On the other hand, when comparing the literature results, the sensing properties span a very broad range, depending on the processing route, the material morphology and so on. This spread of the results can not be fully explained by the dependence of the gas response on the particle size. The details of the surface chemistry of the active oxide must also be taken into account. This task was undertaken by coupling DFT modeling of the gaseous analyte – MOX interaction with experimental study of the material surface chemistry and structure. Three examples will be presented of our investigations in this field: i) the NO2 sensing properties of SnO2 nanocrystals; ii) the alkane sensing properties of SnO2 nanocrystals; iii) the ammonia sensing properties of Cr-doped WO3 nanocrystals. In the first two studies, the reduced surface of the SnO2 nanocrystasl was investigated by XPS, electrical measurements and cathodoluminescence spectroscopy.

3:50 PM

(ICACC-FS3-002-2013) New nanostructured SiOC aerogels for gas sensing applications

G. Soraru*, University of Trento, Italy; A. Parakkulam Ramaswamy, German Aerospace Research Centre [DLR], Germany; A. Karakuscu, A. Ponzoni, E. Comini, G. Faglia, G. Sberveglieri, University of Brescia, Italy

Due to their unique nanostructure in which silica nanosized clusters are encased into a graphene network, polymer-derived SiCO ceramics combine very high temperature stability with un-usual functional properties such as semiconductivity, piezoresistivity and luminescence. Accordingly, SiCO ceramics have been proposed as anode for Li-ion batteries, as white light LEDs and high temperature pressure sensors for operation in harsh environments. Here we show, for the first time, that that highly porous SiCO aerogels obtained through a pyrolysis process from ambient-dried hybrid silica aerogels, can be used as gas sensors for H2 and NO2. Our results show that sensors responded to H2 with highest magnitude at temperatures above 500°C. On the other hand, the fastest response and recovery times occurred at lower temperatures (≤300°C) for NO2.

4:10 PM

(ICACC-FS3-003-2013) Synthesis, Dispersion and Functionalization of SiO2 Nanowires for Biosensing Applications

P. Sekhar*, H. Sarraf, H. Mekonen, Washington State University Vancouver, USA

As one-dimensional nanostructures, silica (SiO2) nanowires have received increasing attention as potential building blocks for nanoscale electronic, optical and biosensor devices. The mechanism of SiO2 nanowire growth follows a combination of vapor-liquid-solid and oxide assisted growth lending to their inexpensive synthesis. Selective growth of amorphous silica nanowires by evaporation of silicon monoxide in an inert gas atmosphere using a Pd-coated silicon wafer as a substrate was achieved. Nanowires grow with diameters ranging from 50 to 200 nm. It is a disadvantage of nanowires having an insufficiently uniform length. For example, the current entangled nanowire architecture inhibits their biosensing applications. In particular, sensitivity and selectivity can be significantly improved upon uniform placement of nanowires. For biosensing applications, nanowires require surface functionalization. In order to have uniform length and functionalize the complete surface of each individual nanowire, a good dispersion method is required. In this investigation, various advanced dispersion methodologies such as ultrasonics will be explored. Ultrasonication leads to smaller nanowires and increased uniformity.

4:30 PM

(ICACC-FS3-005-2013) A Novel Platform of Solar-Driven Self-Powered Gas Sensors

A. A. Gad*, M. Hoffmann, Chair of Inorganic Chemistry, Germany; J. Prades, University of Barcelona, Spain; F. Hernandez-Ramirez, Catalonia Institute for Energy Research (IREC), Spain; H. Shen, S. Mathur, Chair of Inorganic Chemistry, Germany

A novel sensing concept was developed; namely solar diode sensor (SDS), based on the integration and correlation of different complementary functionalities originated from a singular nanomaterial. In this regard the gas sensing and the solar energy harvesting abilities of metal oxide semiconductors were utilized to deliver a self-sustained gas sensing signal without any external power sources. The proof of concept was demonstrated in our previous work. Herein we proof the generality of the SDS concept to other nanomaterials such as planar metal oxide based systems and radial p-n heterojunctions. The electrical properties of the obtained systems were evaluated by measuring current-voltage (I–V) and capacitance-voltage (C–V) characteristics. The fabricated sensors were capable of detecting oxidising and reducing gases with reproducible response at room temperature by solely using solar illumination. The radial heterojunction based SDS devices showed better sensitivities toward oxidizing gases as compared to their planar counterparts. These results showed the impact of the material design on the sensor performance as well as the generality of the SDS concept as a new sensing approach paving the way to commercially appealing and easy to use self-powered nanodevices with smart functionalities that go beyond the ones available in macro-scale devices.

4:50 PM

(ICACC-FS3-006-2013) Development of single-, few- and multiple-nanowire gas-FET devices on ceramic substrates

B. W. Mwakikunga*, Council for Scientific and Industrial Research, South Africa; T. Singh, I. Giebelhaus, T. Fischer, A. Lepcha, A. E. Gad, S. Mathur, University of Cologne, Germany

This presentation will introduce our efforts on the development of field effect transistors (FETs) for resistive-type gas sensors and discuss the role of the gate voltage in selecting the type of analyte gas. We have examined a quick and cost-effective method for fabricating single, and multiple nanowire FETs on insulating alumina ceramic substrates, which entails patterning the drain, source and gate on the surface of ceramic alumina substrates without the need of a clean room, electron beam and focussed ion beam facilities. Transfer of nanowires to the contacts is accomplished by the in situ on-chip growth techniques viz. electro-spinning, hydrothermal synthesis and CVD techniques made possible due to the high-temperature stability of the ceramic substrate. Some preliminary gas-FET devices of TiO2 nano-structured micro-fibres, ZnO nanorods and SnO2 nanowires from this fabrication method will be presented.

5:10 PM

(ICACC-FS3-007-2013) Synthesis and Structural Studies of Some Lanthanide Complexes of Mesogenic Schiff-base, N,N'-di-(4'-octadecyloxybenzoate)salicylidene-l",3"-diamino-2"-propanol

S. Singh*, Banaras Hindu University, India

A mesogenic Schiff-base, N,N'-di-(4'-octadecyloxybenzoate)salicylidene-l",3"-diamino-2"-propanol (H2L5) was synthesized and its structure studied by elemental analyses and FAB mass, NMR & IR spectra. The Schiff-base, H2L5, upon condensation with hydrated lanthanide(III) nitrates, yields LnIII complexes of the general composition [Ln(L5H2)3(NO3)](NO3)2, where Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy and Ho. The bidentate bonding of the Schiff-base in the nematogenic LaIII complex, as implied on the basis of IR & NMR spectral data. As per spectral studies of LnIII complexes, the Zwiterionic-species of the ligand coordinates (as L5H2) to the LnIII ions through only two phenolate oxygens, rendering the overall geometry around LnIII to eight-coordinated polyhedron, possibly distorted Square Antiprism.

5:30 PM

(ICACC-FS3-004-2013) Polymer derived ceramic sensors for ultra-high temperature application

G. Shao*, University of Central Florida, USA; D. Freese, R. Gongora, C. Xu, University of central florida, USA; L. An, University of Central Florida, USA

Polymer derived ceramics are a new classic of high-temperature materials which are thermally decomposed from polymeric precursors. The materials are promising for ultra-high temperature applications because of their excellent high temperature stability, high oxidation and corrosion resistance, and tunable electronic properties. In this paper, we fabricate a set of high temperature sensors fabricated by using polymer-derived SiAlCNs. The performance of these sensors are characterized and discussed.

2nd Global Young Investigators Forum

Applications: Ceramic Sensors and Actuators, Energy Generation and Storage, Photo-catalysis I

Room: Coquina Salon F
Session Chairs: Thomas Fischer, University of Cologne; Fernando Torres Andon, Karolinska Institutet

1:30 PM

(ICACC-GYIF-001-2013) Energetics of $La_{9.33+x}(SiO_4)_6O_{2+3x/2}$: Solid Oxide Fuel Cell Electrolyte Materials

S. Hosseini*, A. Navrotsky, UC Davis, USA

Lanthanum silicate oxyapatite materials, $La_{9.33+x}(SiO_4)_6O_{2+3x/2}$, are attracting interest as a new family of fast oxide-ion conductors with potential use in solid oxide fuel cells (SOFCs), oxygen sensors and ceramic membranes. Their complex structure brings a new conduction mechanism, interstitial oxide ion conduction, which makes them exciting candidates for solid electrolyte research. Recent studies have reported that the non-stoichiometric compositions with cation vacancies or oxygen excess show higher conductivity than the stoichiometric system. To study the thermodynamic stability of these materials, energetic studies have been done on two series: $La_{9.33+x}(SiO_4)_6O_{2+3x/2}$ (x = 0, 0.33 and 0.67) and $La_{10-x}Sr_x(SiO_4)_6O_{3-0.5x}$ (10 - x = 9.00 and 8.00) by high temperature oxide melt solution calorimetry using molten $2PbO\text{-}B_2O_3$ solvent at 1078 K. The enthalpies of formation from oxides are, ΔHof-oxides: $La_{9.33}Si_6O_{26} = -769.86 \pm 11.22$, $La_{9.73}Si_6O_{26.60} = -801.67 \pm 12.10$, $La_{10}Si_6O_{27} = -818.36 \pm 8.35$, $La_9Sr_1(SiO_4)_6O_{26.5} = -889.23 \pm 18.98$ and $La_8Sr_2(SiO_4)_6O_{26} = -925.26 \pm 18.97$ (kJ/mol). The endothermic enthalpy of defect formation is 133.8 ± 17.5 kJ/mole of interstitial oxide ions, and 272.2 ± 21.6 kJ/mol of oxygen vacancies. Cation vacancy content is the dominant factor in determining the energetics of lanthanum silicate apatite materials.

1:50 PM

(ICACC-GYIF-002-2013) Grain Boundary Electrical Properties of Ionic Conductors Based on Solid Solutions of Nd, Ga and Ge Oxides

H. J. Avila-Paredes*, H. Chávez-Cárdenas, A. Deolarte-Carreón, Universidad Autónoma Metropolitana Unidad Iztapalapa, Mexico

The aim of this work is to study the effects of synthesis method, grain size and dopant content on the total and specific grain boundary conductivities of oxy-cuspidine structured materials. This work is inscribed in the field of Solid Oxide Fuel Cells, as oxides with a cuspidine structure have recently been proposed as promising solid electrolyte candidates. However most of the studies on the electrical properties of these materials are based on DC measurements, so that the bulk and grain boundary contributions have not been determined. Samples of Ge-doped $Nd_4Ga_2O_9$ and $Nd_4Ga_{1.28}O_{7.92}$ were synthesized by a citrate and a conventional solid state reaction methods. Pellets were prepared by a Field Assisted Sintering Technique and characterized by SEM, XRD and Impedance Spectroscopy. The bulk conductivities were higher than the specific grain boundary conductivities, indicating a grain boundary blocking effect. Consistently, samples with a smaller average grain size presented the lower total conductivities. Those prepared by the citrate method showed a higher total ionic conductivity. Moreover, the total, bulk and grain boundary conductivities increase with dopant (Ge) content. The specific grain boundary conductivity and its activation energy values are consistent to the resistive nature of grain boundaries in these materials, which has to be considered for applications.

2:10 PM

(ICACC-GYIF-003-2013) Carbon/Metal Oxide Nanocomposites as Electrode Materials for Lithium-Ion Batteries

R. Mueller*, S. Mathur, M. Büyükyazi, A. Lepcha, University of Cologne, Germany

New approaches in low cost production, structuring and integration of nanostructured electrode materials into batteries are of great current interest. Especially, composite materials of metal oxides with carbon (e.g. graphite, graphene) were shown to significantly enhance the performance of lithium-ion battery electrodes. Here, we present the straightforward fabrication of C/MOx cathode and anode materials by electrospinning and microwave assisted synthesis, highlighting the great potential of such hybrid materials. The electrospinning method offers great potential in the 1-D nanofiber design and production of cathode materials with complex structure and composition. By judicious choice of precursor solutions in sol-gel type electrospinning and the calcination of fiber networks under inert atmosphere the successful production of self-supporting cathodes could be shown for C/LiFe1-yMnyPO4 and C/Li3V2(PO4)3 systems. Furthermore, based on a microwave assisted synthesis graphene/metal oxide anode materials could be obtained by reduction of graphene oxide with M2+ ions (M = Sn, Fe, Co). The direct conversion reaction offers the advantage of an effective separation of single and few layered graphene by in situ formed oxide nanoparticles, whereby the graphene sheets can further act as a buffer material compensating the tremendous structural changes of the oxide phase involved during battery cycling.

2:30 PM

(ICACC-GYIF-004-2013) Synthesis of 1D-Nanostructures $LiFeO_2/C$ and $Fe\text{-}Fe_3O_4/C$ as Anode Materials and their Electrochemical Measurements in Lithium-Ion Batteries

M. Büyükyazi*, R. von Hagen, S. Mathur, University of Cologne, Germany

Lithium-ion batteries have been a great success for portable electronic devices, because of their great cycle stability, the missing memory effect as well as the high energy density (120-170 Wh/kg). Among the materials applicable for lithium-ion battery anodes, transition metal oxides like Co_3O_4 or Fe_2O_3 have drawn attention due to their higher theoretical capacity compared to other materials. Transition metal oxides can in principle deliver a charge capacity, that is about 3 times larger than that of commercial graphite with a theoretical capacity of 377 mAh/g, which is the most commonly used anode material. Amongst all, iron oxide nanomaterials are the most promising candidates for anode materials and have received much attention as promising new electrode materials. In addition, carbonaceous materials have also attracted increasing attention because of the high electrical conductivity of carbon. Therefore, a combination of carbon with metal oxides promise improved anode materials which might exhibit better cycling performances in lithium-ion batteries due to the higher conductivity. Herein we report the fabrication and the electrochemical measurements of novel 1D-nanostructures $LiFeO_2$/C and Fe-Fe_3O_4/C, synthesized by electrospinning, which promise enhanced electrochemical performances as anode materials in lithium-ion batteries.

2:50 PM

(ICACC-GYIF-005-2013) Modification of the electric properties in carbonaceous materials by deposition of SnO2 nanowires via CVD

A. Gutierrez-Pardo, University of Seville, Spain, Spain; R. Fiz*, S. Mathur, University of Cologne, Germany; J. Ramirez-Rico, University of Seville, Spain, Spain

Properties in porous carbonaceous materials made from natural precursors can be modified by CVD, coating them with different materials, particularly metal oxides which show tunable properties due to their semiconducting nature. The control of the parameters in the process such as temperature and time, can control the morphology and properties of the nanostructures. In this work, samples of BioSiC and partially graphitized BioC are used as substrate, and Au is deposited by sputtering as catalyst for the growth of SnO2 nanowires using Sn(OtBu)4 as precursor which decomposes at elevated temperatures. Without additional catalyst, thin films of SnO2 cover the surface of the substrate are expected, but nanostructures are also obtained, maybe due to the residual metals that remains in the substrates, silicon in BioSiC and nickel for the graphitization process in BioC. The materials obtained are characterized by SEM, TEM, X-Ray diffraction, Raman and physisorption. The observed differences in samples made in different conditions are shown and discussed.

Applications: Ceramic Sensors and Actuators, Energy Generation and Storage, Photo-catalysis II

Room: Coquina Salon F
Session Chairs: Seyedeh Mahboobeh Hosseini, UC Davis; Ralf Mueller, University of Cologne

3:30 PM

(ICACC-GYIF-006-2013) Nanochemistry: The gigantic growth of a dwarf

T. Fischer*, S. Mathur, University of Cologne, Germany

Although "nano" had ever been there, the evolution of new analytical tools opened the broad field of research especially dedicated to the nanoscale after 1990. Starting in the field of renewable energy generation, distribution and storage, to medical applications and sensors, new nanostructured ceramic materials are essential to improve existing technology and open doors to completely new developments based on a material design based on the molecular level. From precursor development over material synthesis to surface functionalization of ceramics a profound level of understanding in the field of materials science, physics, chemistry and engineering is essential and demands a high level of interdisciplinary research. This talk will discuss the synthesis and application of nanostructured materials from the point of view of a molecular chemist and how chemistry can contribute to the ever growing field of ceramic technology and research.

3:50 PM

(ICACC-GYIF-007-2013) Metal oxide/semiconductor decorated multilayer Graphene oxide: photocatalysis and electrocatalysis

K. Ojha*, P. K. Chowdhury, A. K. Ganguli, Indian Institute of Technology, Delhi, India

Graphene based hybrid materials are important for their very high electronic mobility which can be utilized for photovoltaic properties and is significant for the future energy industry. In a hybrid graphene-semiconductor material the 2D planar π-conjugated graphene sheets inhibit the recombination of electron-hole pairs generated from the conjugated semiconductor. Synthesis of graphene based hybrid materials is still a matter of interest. Here we discuss our efforts to synthesize multilayer graphene-metal oxide hybrid materials where metal oxide particles are uniformly embedded in between the graphene layers. Photocatalytic efficiency of nanostructured metal oxides like TiO2, has been modified by graphene conjugation. We also discuss the synthesis of graphene-CdS/CdTe composite. We have investigated how the surface chemistry and distribution of the semiconductor material on graphene layers control their electronic and photophysical properties which have significance in photocatalysis and electrocatalysis.

4:10 PM

(ICACC-GYIF-008-2013) Production and characterization of nanocomposites consisting of electroless deposited Ag on semiconducting oxide nanostructures

F. L. Miguel*, F. Soldera, Saarland University, Germany; T. Fischer, R. Müller, S. Mathur, University of Cologne, Germany; F. Mücklich, Saarland University, Germany

Ag thin coatings were applied by means of the electroless deposition technique on semiconducting oxide nanostructures. These consisted on TiO2 nanorods and SnO2 nanowires obtained through chemical vapor deposition (CVD) and vapor-liquid-solid (VLS) growth, conforming oriented and disordered arrangements. Novel composites with both reinforced metal matrix and core-shell configurations were produced. The resulting materials were analyzed through SEM imaging of cross sections after focused ion beam (FIB) milling and partially through FIB-SEM tomography. This method allowed the qualitative and quantitative analysis of the microstructure. In the case of the composite comprising a Ag matrix reinforced with SnO2 nanowires, the porosity was measured at 0.1%. This new composite is intended to be applied as electrode material at electrical contacts, for which enhanced physical and mechanical properties are to be expected with respect to the current Ag-SnO2 material produced through powder metallurgy. Examples of the awaited improvements would be the reduction of oxide agglomeration because of the attachment of the nanowires to the substrate and their mutual entanglement, lower porosity contents and increased thermal and electrical conductivities, all these leading to longer service life of the devices.

4:30 PM

(ICACC-GYIF-009-2013) Nb2O5 Nanorods and SnO2/Nb2O5 Heterostructures as Humidity Sensors

R. Fiz*, Universität zu Köln, Germany; F. Hernandez-Ramirez, Catalonia Institute for Energy Research (IREC), Germany; T. Fischer, Universität zu Köln, Germany; L. Llopez-Conesa, S. Estrade, F. Peiro, University of Barcelona, Germany; S. Mathur, Universität zu Köln, Germany

Single crystalline niobium pentoxide (Nb2O5) nanorods synthesized by chemical vapor deposition (CVD) of niobium isopropoxide [Nb2(OiPr)10] and its donor-substituted alkenolate modification [Nb(OiPr)4(C8H5NOF3)] exhibited high sensitivity towards humidity at low temperature. HR-TEM and computing simulation studies showed the low density of defects in the pristine Nb2O5 nanostructures, which was supported by the observed high resistivity. However, poor electrical conductivity is not attractive for device applications. To modulate the properties of Nb2O5 structures, SnO2/Nb2O5 core-shell heterostructures were grown by a two-step CVD and used as humidity sensors. Thickness and morphology of the Nb2O5 shell could be controlled through the variation of the CVD parameters, which allows the tuning of the resistance in the heterostructure, directly related to the Nb2O5 content. This nano-architecture based on SnO2-Nb2O5 junctions integrates the high sensitivity of Nb2O5 shell towards moisture with the good electrical conductivity of SnO2, enabling the design of better humidity sensors than those fabricated with bare Nb2O5 nanorods alone.

4:50 PM

(ICACC-GYIF-010-2013) Dielectric and Piezoelectric Properties of Sr and La co-doped PZT Ceramics

V. Kalem*, Selcuk University, Turkey; M. Timuçin, Middle East Technical University, Turkey

PZT based piezoelectric ceramics doped with Sr^2+ and La^3+ in various levels, designated as PSLZT, were prepared by conventional processing techniques. The effect of the Zr/Ti ratio on the structural, dielectric and piezoelectric properties were investigated. XRD results showed that all PSLZT compositions had perovskite structure in which decreasing Zr/Ti ratio increased the tetragonality. The morphotropic phase boundary (MPB) appeared as a region extending from Zr/Ti ratio of 50/50 to 58/42. The PSLZT ceramic with a Zr/Ti ratio of 54/46 exhibited a remarkably high piezoelectric strain coefficient of 640 pC/N with attending parameters of dielectric constant (1800), electromechanical coupling coefficient (0.56), mechanical quality factor (70), and Curie temperature (272 C). This soft PSLZT ceramic composition is a good candidate for electromechanical applications where quick switching and high operation temperature are needed.

5:10 PM

(ICACC-GYIF-011-2013) ZnO-quantum dots-polymer as hybrid nanocomposite for photovoltaics

A. Sugunan*, Y. Zhao, X. Yang, M. Toprak, M. Muhammed, Royal Institute of Technology (KTH), Sweden

Oxide ceramics have been investigated as photo-anode for dye-sensitized solar cells. Recombination losses and the need for a fluid electrolyte is a challenge in this type of solar cell. Here we investigate an all solid-state hybrid nanocomposite consisting of aligned ZnO nanowires as photoanode, semiconductor quantum dots and poly-3-hexylthiophene as the optically active and hole conducting material. We have tailored the band-levels by varying the material choice and dimensions in order to minimize recombination losses. The ceramic oxide is employed as the electron conducting channel and the semiconducting polymer as the hole conducting channel. We have also performed preliminary I-V measurements to show the localization of the carriers within different layers.

Tuesday, January 29, 2013

S1: Mechanical Behavior and Performance of Ceramics & Composites

Processing, Microstructure and Mechanical Properties Correlation I

Room: Coquina Salon D
Session Chairs: Jon Salem, NASA Glenn Research Center; Yanchun Zhou, Aerospace Research Institute of Materials & Processing Technology

8:00 AM

(ICACC-S1-013-2013) The effect of the addition of ceria stabilised zirconia on the creep of mullite

D. Glymond*, F. Giuliani, Imperial College London, United Kingdom; M. Vick, M. Pan, Naval Research Laboratory, USA; L. J. Vandeperre, Imperial College London, United Kingdom

Mullite is considered a promising candidate for ceramic recuperators in turbo propelled engines, due to due to its low thermal conductivity, adequate thermal shock resistance, low cost, low density, thermodynamic stability, and reasonable strength at high temperatures. Unfortunately, the limited fracture toughness of mullite (~1.5-2 MPa m1/2) is considered too low. Improving the fracture toughness to about 5 MPa m1/2 is possible by the addition of ceria stabilised zirconia (CSZ). However, the addition of CSZ to mullite may also affect other properties. In this paper the effect of the addition of CSZ on the creep resistance is investigated by comparing mullite-zirconia composites made with two commercially available mullite powders against the creep behaviour baselines of pure mullite made from the same mullite powders.

8:20 AM

(ICACC-S1-014-2013) Characterizations of ZrO2-stabilized YTaO4: Thermal conductivity and in-situ Raman micro-analysis

S. Shian*, M. Gurak, Harvard University, USA; P. Sarin, W. M. Kriven, University of Illinois at Urbana-Champaign, USA; D. R. Clarke, Harvard University, USA

Because of its structural similarity to Yttria-stabilized zirconia ceramics, ZrO2-YTaO4 compositions have recently been studied and are reported to have promising characteristics, such as resistance to low-temperature degradation, low thermal conductivity, and efficient host for phosphors, to be potentially exploited in medical implants, high temperature thermal barrier coating (TBC), and x-ray detector applications. However, little is known with regard to the high temperature phase evolution and the effect of ZrO2 stabilization into YTaO4 structures. To address this, we prepared bulk YTaO4 from its metal salt precursors and characterize its microstructure, crystal structure, and thermal properties at a range of temperature, (from 25C to 1500C) and at various ZrO2 doping concentration (up to 20%). In-situ Raman spectroscopy revealed the presence of monoclinic and tetragonal phases at low and high temperature, respectively, where the transformation temperature is influenced by the concentration of ZrO2 doping. We will present analyses of the Raman spectra such as peak shifts, intensity, and width, to the structural changes, such as cation distribution, and lattice parameters or strain within the samples and their correlation to the measured thermal conductivity and observed microstructures.

8:40 AM

(ICACC-S1-015-2013) Doping as a way to control microstructure and mechanical properties of Al2O3-ZrO2 composites

L. Gremillard*, K. Biotteau-Deheuvels, J. Chevalier, INSA, France

Although current orthopedic ceramic biomaterials provide an effective immediate solution for many patients, concerns have arisen over their short- and long-term clinical success revealing the need for improved materials. Existing ceramics have already showed their own limits. For example, the brittleness of alumina increases the risk of acetabular cups fracture; Yttria Stabilized Zirconia is prone to hydrothermal degradation, decreasing lifetime of implants. Zirconia-toughened alumina (ZTA) composites provide both good stability and great mechanical properties, and a proven biocompatibility. Such composites are already commercialized all around the world and are commonly called “micro-composites”. The aim of our research is to show how doping ZTA with different dopant oxide can alter the microstructure and the reinforcement mechanisms of the composite. In controlling the microstructures, the pinning effect of zirconia was preponderant as compared to the dopant effect on grain boundaries mobility in most cases. Only high addition of both calcium and silica resulted in increased alumina grain boundaries mobility (thus intragranular composites), for high temperature and low amount of zirconia. Depending on the zirconia content, dopants and sintering temperature, different toughening mechanisms are observed: toughening by phase-transformation, microcracking or internal stresses.

9:00 AM

(ICACC-S1-016-2013) High-Temperature Creep Behavior of SiOC Polymer-Derived Ceramic Nanocomposites: Microstructural and Phase Composition Effects

E. Ionescu*, H. Kleebe, R. Riedel, Technische Universitaet Darmstadt, Germany

In the present work, dense monolithic polymer-derived ceramic nanocomposites (SiOC, SiZrOC and SiHfOC) were synthesized via hot pressing techniques and evaluated with respect to their compression creep behavior at temperatures beyond 1000 °C. The creep rates, stress exponents as well as activation energies were determined. The high temperature creep in all materials has been shown to rely on viscous flow, which occurs via diffusion processes. In the quaternary materials (i.e., SiZrOC and SiHfOC), higher creep rates and activation energies were determined as compared to those of monolithic SiOC. The increase of the creep rates upon modification of SiOC with Zr/Hf relies on the significant decrease of the volume fraction of segregated carbon; whereas the increase of the activation energies corresponds to an increase of the size of the silica nanodomains upon Zr/Hf modification. Within this context, a model is proposed, which correlates the phase composition as well as network architecture of the investigated samples with their creep behavior and agrees well with the experimentally determined data.

9:20 AM

(ICACC-S1-017-2013) Processing, microstructure and creep behaviour of alumina-SiC micro-nanocomposites

H. Reveron*, M. Jaafar, C. Esnouf, G. Fantozzi, MATEIS Laboratory - Insa de Lyon, France

The purpose of this study is to understand the processing-microstructure-creep properties relationships in order to develop highly creep resistant alumina-SiC nanocomposites. Nanocomposites can be divided into micro-nanocomposites (fine inclusions in a coarse matrix) and nano-nanocomposites (dispersion of two nanophases). Since in pure alumina creep resistance decreases with decreasing grain size, only the so-called micro-nanocomposites were here developed. Conventional sintering (CS), hot-pressing (HP) and Spark plasma Sintering (SPS) techniques were successfully applied to prepare dense alumina-5vol% SiC micro-nanocomposites with different microstructures (inter, inter-intra and intragranular types) and containing fine SiC particles of two different size. Bending tests at 1200°C under stresses from 90 to 140 MPa were used to characterize the creep behaviour. Microstructural features were examined by SEM and TEM. The results show that creep resistance depends on microstructural features obtained throughout processing. Particularly, in the case of almost intergranular materials sintered by SPS, creep deformation is mainly controlled through a lattice-dislocation mechanism (stress exponent >4) and an effective manner for further improvement of the creep resistance is to reduce the SiC particle size in order to increase the number of fine particles located at the grain boundaries.

10:00 AM

(ICACC-S1-018-2013) Pressure-Induced Transformation Toughening in 10 mol% Yttria Stabilized Zirconia–β-eucryptite Composites

S. Ramalingam*, I. E. Reimanis, Colorado School of Mines, USA

A novel mechanism for transformation toughening of ceramic composites using pressure-induced transformations is proposed. β-eucryptite ($LiAlSiO4$) transforms to ε-eucryptite at about 0.8 GPa hydrostatic pressure. A micromechanical model that captures toughening from the dilatation during transformation ($\varepsilon \rightarrow \beta$) and anti-toughening from tensile thermal residual stresses in the matrix predicts a net increase in toughness for 10 mol% yttria stabilized zirconia–β-eucryptite composites compared with zirconia. To validate these results, composites of zirconia with eucryptite of different volume fractions were made by hot pressing and fracture toughness of the different composites were measured through the modified indentation toughness technique. This research identifies the key parameters required for achieving transformation toughening using pressure-induced phase transformations.

10:20 AM

(ICACC-S1-019-2013) Investigation into the effect of common ceramic core additives on the crystallisation and sintering of amorphous silica

B. Taylor*, Birmingham University, United Kingdom; S. Welch, Rolls Royce PLC, United Kingdom; S. Blackburn, Birmingham University, United Kingdom

Aero engine turbine blades are commonly produced via investment casting methods and utilise sacrificial ceramic cores to provide internal features such as cooling channels. During the firing process the conversion of the main ingredient (amorphous silica) into β-cristobalite plays a significant role, as it directly affects the dimensional stability, shrinkage and leachability of the core. The formulation used to produce cores has evolved over the years in an iterative fashion, resulting in a deficit of understanding regarding the role of each component in the now complex formulation. Techniques such as dilatometry, DSC, XRD and SEM were utilised to evaluate common additives such as zirconium silicate, alumina, aluminosilicate, MgO and cristobalite seed. The degree of crystallisation and densification of the ceramic were studied, up to typical casting temperatures (circa 1530°C) and compared for an array of formulations. It was shown that aluminosilicate and zirconium silicate in particular make a considerable contribution to the rate of shrinkage and crystallisation. A mathematical model is proposed that allows empirical predictions of these key variables for all formulations.

10:40 AM

(ICACC-S1-020-2013) Crack Propagation in Tooth Enamel is Regulated by Enamel Apatite Crystallographic Dimensions

F. Tamimi*, E. Ghadimi, H. Eimar, B. Marelli, S. Nazhat, H. Vali, McGill University, Canada

Tooth enamel is a composite material made of an inorganic phase of apatite nanocrystals (96% w/w) and an organic phase (4% w/w). Surprisingly, the relative contribution of the constituents of enamel to its toughness is largely unknown. The aim of this study was to investigate how the crystallographic dimensions of enamel can regulate its crack propagation. A group of 26 extracted sound teeth were collected and prepared for mechanical and physical-chemical analysis. Average crack length was calculated by measuring the propagation of cracks created by Vicker's indentation fracture. The enamel cell lattice parameter and crystal dimensions were calculated from X-ray Diffraction and the chemical composition was analyzed with Fourier transform infrared spectroscopy. Crack propagation was correlated to the enamel crystallographic dimensions and chemical composition. The average length of cracks in enamel was positively correlated with its crystal dimensions along c-axis following the Hall-Petch model for polycrystalline materials. Also, it was found that the protein content of tooth enamel had no significant effect on crack propagation. Accordingly, it seems that the size of enamel apatite nanocrystals is the major factor that regulates crack formation in teeth.

11:00 AM

(ICACC-S1-021-2013) Processing and Mechanical Characterization of ZnO/Polyester Woven Carbon Fiber Composites

H. Park*, K. Kong, Ulsan National Institute of Science and Technology, Republic of Korea; H. Kim, LG Hausys R&D Center, Republic of Korea

The ZnO functional properties have interest on scientific and technical researches about development of polymer composites. Most researches on ZnO polymer composites are restrictedly studied for piezoelectric sensors. In this research we investigate the inherently mechanical properties by incident impact test for ZnO/polymer woven carbon fiber composites. One of the interesting our research is impact energy absorption on woven carbon fibers according to the various concentrations of ZnO growth, which were developed by hydrothermal process. The impact behavior of woven carbon fiber composites was shown differently with ZnO growth or not. The energy balance equation for addressing impact energy absorption was adopted by using image analysis of the deformed shape. Also, the tensile modulus in the VARTM-processed composites exhibited significantly enhanced fracture toughness at higher ZnO concentrations.

11:20 AM

(ICACC-S1-022-2013) Solid-solution of nitrogen-containing rare earth aluminates R2AlO3N

Y. Jiang*, L. Wu, Y. Chen, W. Sun, Z. Huang, Beifang University of Nationalities, China

AlN-rare earth oxide is often used as an efficient sintering aid in the manufacture of SiC ceramic. There is no any compound formed in the SiC-R2O3 system. However a compound R2AlO3N exists in AlN-R2O3 subsystems, which melts at about ~1700°C. It would be benefit to early-step densification of SiC sintering. Present work carried out the study on the reaction between SiC and R2AlO3N. It was found that Solid-solution of SiC substituted by AlN in R2AlO3N. The sintered samples were analysis by XRD and EPMA. The phase diagrams of SiC-AlN-R2O3 systems were present.

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

Thermal Barrier Coatings I

Room: Ponce DeLeon
Session Chairs: Ali Goodarzi, Amirkabir University; Seongwon Kim, Korea Institute of Ceramic Engineering and Technology

8:00 AM

(ICACC-S2-012-2013) Luminescence-Based Diagnostics of Thermal Barrier Coating Health and Performance (Invited)

J. I. Eldridge*, NASA Glenn Research Center, USA

For advanced turbine engines designed for higher temperature operation, a diagnostic capability for the health and performance of thermal barrier coatings (TBCs) will be essential to indicate when a mitigating action needs to be taken before premature TBC failure threatens engine performance or safety. In particular, it is shown that rare-earth-doped luminescent sublayers can be integrated into the TBC structure to produce luminescence emission that can be monitored to assess TBC erosion and delamination progression, and to map surface and subsurface temperatures as a measure of TBC performance. The design and implementation of these TBCs with integrated luminescent sublayers are presented. Results of monitoring debond progression are examined to evaluate the effects of furnace cycling, heat flux, and cooling holes on TBC life. It is demonstrated that integration of the rare-earth-doped sublayers by electron beam physical vapor deposition (EB-PVD) is achieved with no reduction in TBC life. Examples of subsurface temperature monitoring using Eu-doped YSZ sublayers will be shown. In addition, a new phosphor, Cr-doped $GdAlO_3$, is shown to retain ultra-bright luminescence at high temperature, and therefore is being developed for practical luminescence-based surface temperature mapping in the highly radiant turbine engine environment.

8:30 AM

(ICACC-S2-013-2013) TEM Characterization of Zirconate-based Oxides for Thermal Barrier Coatings (TBCs) (Invited)

S. Kim*, S. Lee, Y. Oh, H. Kim, Korea Institute of Ceramic Engineering and Technology, Republic of Korea; B. Jang, National Institute of Materials Science, Japan

Among candidate materials for future TBCs, zirconate-based oxides with fluorite and/or pyrochlore are prevailing ones. While the cubic fluorite phase of rare-earth oxide has the space group of Fm3(-)m, the cubic pyrochlore phase corresponds to the space group of Fd3(-)m. Furthermore, the pyrochlore structure is characterized by the cation occupancy of the special crystallographic sites and the oxygen vacancy at the 8a site. This ordering of cations in the pyrochlore structure results in additional peaks from superlattice in XRD compared with the fluorite structure. In this study, phase structures of zirconate-based oxide systems are characterized especially by transmission electron microscopy. Several compositions from La2(Zr1-xCex)2O7 or (La1-yGdy)2Zr2O7 are fabricated using solid-state reaction for this study. Each composition exhibits pyrochlore or fluorite or both phases after heat treatment. For the developed phases among these compositions, crystallographic structures and microstructures are characterized by transmission electron microscopy, especially with electron diffraction.

9:00 AM

(ICACC-S2-014-2013) Multilayer Thermal Barrier Coatings: Interplay among coating design, processing and properties

S. Sampath, G. Dwivedi, V. Viswanathan*, Y. Chen, Stony Brook University, USA

The continued need for increments in gas turbine operating temperatures has necessitated developments in new thermal barrier materials and their processing. Of particular interest in recent years is the potential for rare earth zirconates as candidate TBCs to replace yttria stabilized zirconia (YSZ). Gadolium zirconate (Gd_2ZrO_7) in particular is now being used in aero-engines as they not only provide lower conductivity but also resistant to environmental damage from ingested sand particles (categorized as CMAS for calcium magnesium alumino-silicate). Gd_2ZrO_7 however has several challenges including low fracture toughness, incompatibility with the thermally grown alumina and low erosion resistance. Multilayer concepts based on combinations of YSZ and Gd_2ZrO_7 have been developed to address the multifunctional requirements and have shown some promise in applications. This paper seeks successive approaches utilizing advances in processing science and control for layer by layer optimization of coating microstructure and properties so as to meet multifunctional obligations for instance compatibility with thermally grown oxide, porous low conductivity coating followed by erosion and CMAS resistant top coat. The paper will demonstrate the advantages of plasma spray for such layered coating system along with identification of critical challenges.

9:20 AM

(ICACC-S2-015-2013) Cycle Duration Effects on Thermal Barrier Coating Life- Experiments and Predictive Modeling

E. Jordan, S. Ahmadian*, C. Thistle, University of Connecticut, USA

Cyclic furnace tests were conducted on Air Plasma Sprayed (APS) Thermal Barrier Coating (TBC) samples which were coated with NiCoCrAlY on a single crystal nickel base superalloy at three temperatures and several cycling frequencies. All failures occurred in the top coat consistent with engine experience. From these tests the following were determined, cyclic life, oxidation kinetics with activation energy and bond coat rumpling rate the last two of which were used as input to subsequent modeling. The cyclic tests were modeled with the finite element method utilizing a realistic top coat constitutive model that included viscoplastic behavior and tensile compression behavior asymmetry consistent with available experimental data by allowing tensile stress no larger than 50 MPa which is consistent with recent Raman measurements. Rumpling produced by far the largest strains in the topcoat where failure occurred. Accumulated inelastic strain was used as a damage measure and qualitatively predicted not only temperature effects but the effects of cycling rate. An understanding of the relative importance of cycling rate and time at temperature is critical for mission analysis of aviation and peak power electrical generator gas turbines which see a variety of cycle durations.

10:00 AM

(ICACC-S2-017-2013) Thermodynamics of ZrHf-mixed silicates for environmental barrier coatings for Tyranno-hex materials (Invited)

A. Goodarzi*, H. Taylor, Harvard University, USA

The synthesis and characterization of Zr/Hf-mixed silicates, which are promising as an environmental barrier coating (EBC) on Tyranno-hex materials, have been carried out. The coefficient of thermal expansion (CTE), the corrosion resistance against high-temperature water vapor, and the drops of strength and elastic modulus after exposure for high-temperature water vapor were investigated. Furthermore, the chemical stability of the Zr/Hf-mixed silicates under high-temperature water vapor and oxygen gas was thermodynamically investigated. The CTE value can change to (3.6–5.1)×10−6 K−1 when the Zr/Hf ratio fluctuates. The weight losses of the mixed silicate samples after exposure for high-temperature water vapor were very small. The contents of the main component elements, such as Zr, Hf, and Si in the samples, were unchanged within the error limits by the exposure. The flexural strength and bending modulus of the samples decreased by 5–21 and 6–29% due to the exposure, respectively. The chemical stability of the Zr/Hf mixed silicates under the experimental conditions was discussed.

10:30 AM

(ICACC-S2-018-2013) Microstructural and Phase Evolution in Yttria-Stabilized Zirconia Thermal Barrier Coatings Deposited via Plasma Spray-Physical Vapor Deposition (PS-PVD)

M. P. Schmitt*, The Pennsylvania State University, USA; B. J. Harder, D. Zhu, NASA Glenn Research Center, USA; D. E. Wolfe, The Pennsylvania State University, USA

With gas turbine engine operating temperatures constantly rising to increase power and efficiency, current 7 wt% yttria stabilized zirconia (7YSZ) thermal barrier coating (TBC) materials are no longer sufficient due to phase instability. This instability has been studied for air plasma spray (APS) and electron beam-physical vapor deposition (EB-PVD) TBCs, but not for Plasma Spray-Physical Vapor Deposition (PS-PVD) coatings. Standard 7YSZ coatings were deposited using PS-PVD at NASA Glenn Research Center. PS-PVD processing uses high power plasma at pressures from 100-150 Pa to heat feedstock material and deposit microstructures via the vapor phase similar to traditional evaporation methods like EB-PVD. Coatings were processed with varying sample rotation, power and chamber pressure in order to optimize performance at elevated temperatures. Coating microstructures were characterized using electron microscopy before and after heat treatments up to 1300°C for 1000 hours. X-ray diffraction and Rietveld refinement was used to measure crystallite size, lattice parameter and phase fraction as a function of the heat treatments. The results were compared to data from a baseline 7YSZ EB-PVD coating to evaluate the differences in elevated temperature stability between the two deposition techniques.

10:50 AM

(ICACC-S2-019-2013) New Chemistries with the Potential to form Novel High Fracture Toughness Thermal Barrier Coating Materials

M. D. Hill*, Trans-Tech Inc., USA

Although second generations thermal barrier coating materials have a lower thermal conductivity than the industry standard yttria stabilized zirconia (YSZ), they suffer from the fact that the fracture toughness of the coatings is significantly less than YSZ. Novel chemistries will be presented which have the potential to show improved fracture toughness relative to current low thermal conductivity materials. The focus is on creating a dispersed second phase with a high aspect ratio to allow for crack bridging. In addition, potential chemistries showing multiple toughening mechanisms (ferroelastic toughening and crack bridging) will be presented as well.

11:10 AM

(ICACC-S2-020-2013) Mechanism of Mullite Formation By Aluminium Filler-Controlled Pyrolysis of Polymethylsiloxane

J. Anggono*, Petra Christian University, Indonesia; B. Derby, University of Manchester, United Kingdom

This research developed free-standing bodies of mullite formed via active filler controlled pyrolysis of polymethylsiloxane/aluminium powder (PMS/Al) precursor mixtures. This research was part of a programme with an objective of developing a mullite ceramic coating for SiC/SiC composites used in the combustion chamber of land-based gas turbine engines. The Al flakes powders of 73 μm was used in mixtures with PMS with a ratio of PMS/Al close to that required to form 3:2 mullite (81/19 vol.%). The green bodies were pyrolysed by heating in air at temperatures 400-1700oC. The reaction sequence has been characterised using simultaneous TGA/DSC, X-ray diffraction, and microstructural study using SEM and EPMA. Those results have been reported somewhere else. TEM study was also carried out and completed our previous work. It proposed three different mechanisms or steps of mullite formation via active-filler controlled pyrolysis of polymethylsiloxane (AFCOP). The first mechanism is a reaction between amorphous SiO2 and α-Al2O3 (corundum). The second mechanism is solid-state sintering between SiO2 (cristobalite) and α-Al2O3 (corundum) and the last mechanism is at higher temperature (>1650oC) through liquid-phase assisted sintering between SiO2 (liquid) and α-Al2O3.

11:30 AM

(ICACC-S2-016-2013) Comparison in Foreign Object Damage (FOD) between Air Plasma Sprayed and EB-PVD Thermal Barrier Coatings (TBCs) (Invited)

D. Faucett, S. Lei, S. R. Choi*, Naval Air Systems Command, USA

Thermal barrier coatings (TBCs), due to their brittle nature, are highly susceptible to damage by impacting foreign particles when the impacting kinetic energy exceeds certain limits. The damage, termed foreign object damage (FOD), results in various issues/problems to coatings as well as to substrates from delamination to cracking to catastrophic failure depending on the severity of impact. Comparison in FOD behavior between air plasma sprayed and EB-PVD thermal barrier coatings (TBCs) was made at ambient temperature using actual aeroengine components. FOD testing was conducted with a ballistic impact gun in a range of impact velocities from 50 to 340 m/s. Three different projectile materials of hardened steel, silicon nitride, and borosilicate glass spherical projectiles were employed for a given TBC system. The damage was characterized and assessed with respect to major variables such as impact velocity and projectile material. A phenomenological model to describe spallation and delamination of coatings will be presented. Preliminary high-temperature FOD data will also be compared with ambient-temperature counterparts.

S3: 10th International Symposium on Solid Oxide Fuel Cells (SOFC): Materials, Science and Technology

SOFC Applications

Room: Coquina Salon H
Session Chairs: Narottam Bansal, NASA Glenn Research Center; N.Q. Minh, University of California, San Diego

8:00 AM

(ICACC-S3-001-2013) Role of Solid Oxide Fuel Cells in a Balanced Energy Strategy (Invited)

E. D. Wachsman*, C. A. Marlowe, K. Lee, University of Maryland, USA

Fuel cells are the most efficient technology to convert chemical energy to electricity and thus could have a major impact on reducing fuel consumption and CO2 emissions. H2 is an energy carrier, not an energy resource. Unfortunately, fuel cells have been linked perceptually and programatically to an H2 economy. Moreover, the tremendous infrastructural cost of creating an H2 economy has relegated fuel cells to a "future technology". This perception has resulted in a drastic reduction in funding by the US DOE in favor of vehicle electrification. In fact, solid oxide fuel cells (SOFCs) are fuel flexible, capable of operating on both conventional fuels (natural gas and gasoline) and future alternative fuels (H2 and biofuels). The primary technical challenge for SOFCs has been high operating temperature and its impact on cost, reliability, and (for transportation applications) start-up time. Significant reductions in operating temperature have been achieved over the last decade without sacrificing power density, thus, reducing cost, improving reliability, and putting SOFCs on the path toward near term commercial viability in a number of stationary power applications. Moreover, recent increases in power density and further temperature reductions have made transportation applications feasible. Thus it seems clear that SOFCs are an important part of a balanced energy R&D portfolio, with or without an H2 infrastructure.

8:30 AM

(ICACC-S3-002-2013) SECA Program Status (Invited)

B. White, J. Stoffa*, Dept. of Energy, USA

Development of an electric power generation technology that efficiently and economically utilizes coal and natural gas while meeting current and projected environmental and water conservation requirements is of crucial importance to the United States. With that objective, 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 private industry, academia, and national laboratories. The FE Fuel Cell Program, embodied in the Solid State Energy Conversion Alliance (SECA), has three parts: Cost Reduction, Coal-Based Systems, and Core Technology. The Cost Reduction effort is aimed at reducing the manufactured cost of SOFC stacks and associated complete power blocks. Low-cost power blocks should enable initial market entry in distributed generation applications. The Coal-Based Systems goal is the development of large (>100 MW) integrated gasification fuel cell (IGFC) power systems for the production of near-zero-emission electric power from coal. Program efforts in the Core Technology area involve research and development on rigorously-prioritized technical hurdles, focusing on materials, processing and design optimization. Progress and recent developments in the SECA program will be presented.

9:00 AM

(ICACC-S3-003-2013) SOFC-system for high efficient power generation from biogas

A. Lindermeir*, R. Dietrich, J. Oelze, CUTEC Institut GmbH, Germany

Biogas is a renewable energy carrier with growing importance, but power generation using motor-driven CHP-units suffers from electrical efficiencies far below 50 %. Additionally, biogas might have fluctuating qualities and/or low methane contents that can cause sudden shutdowns of the CHP. In contrary, solid oxide fuel cell (SOFC) systems offer an overall efficiency of >50 % even for small-scale units and/or low-calorific biogas. Though SOFC-stack development is not available yet in the desired range, commercial stack modules are established for the evaluation of system concepts. A biogas-fed 1 kW SOFC-system based on a commercial SOFC stack module is presented. Methane is reformed by combined dry- and steam-reforming with carbon dioxide from biogas, water is added to compensate the fluctuations in the biogas for a soot-free operation. The system was characterized in the lab and subsequently operated on a biogas plant. Electrical power of 850 to 1,000 W and efficiencies between 39 and 52 % were received depending on the biogas methane content. These results were confirmed with synthetic biogas yielding an electric power output of 1,000 W and an efficiency of 53 % during a 500 h test period without any degradation. The presentation will discuss the features of the system concept, the results of the component development and -tests and experiences with the system operation on the biogas plant.

9:20 AM

(ICACC-S3-004-2013) Development of a portable propane driven 300 W SOFC-system

C. Szepanski, A. Lindermeir*, R. Dietrich, CUTEC Institut GmbH, Germany

The Lower Saxony SOFC Research Cluster was initiated to build a demonstrator for an SOFC based stand-alone power generator with a net system electrical power of 300 W, a high net efficiency of >35 %, compact mass and volume (less than 40 liters and 40 kg), time to full load in less than 4 hours and the ability for autarkic startup and operation. Innovations realized within this network project are a stacked, planar design of all main components to increase thermal integration and reduce system volumem, endothermic propane reforming with anode offgas to increase electrical efficiency without complex water treatment and an operation management with reduced sensor hardware to decrease internal energy consumption and overall costs. Anode offgas recycle in conjunction with a combined afterburner/reforming-unit in counter flow configuration is used for the generation of SOFC fuel gas. For the recirculation of the anode offgas a piston compressor was designed and evaluated. A heat exchanger tailored to the specific boundary conditions and an advanced compression system with active control of stack compression was developed. To minimize thermal losses the system casing is purged with the cathode air. Reformer and Afterburner operation has been evaluated as well as stack performance with Syngas. With the completed system assembly and ongoing operation and evaluation, we can report that the planar design approach is valid.

10:00 AM

(ICACC-S3-005-2013) Development and Application of SOFC-MEA Technology at INER (Invited)

M. Lee*, T. Lin, R. Lee, Institute of Nuclear Energy Research, Taiwan

The Institute of Nuclear Energy Research initiated the development of the SOFC technology in 2003. Now, substantial progresses have been achieved on the related techniques. Fabrication processes for planar anode/electrolyte-supported-cell (ASC/ESC) by conventional methods and metallic-supported-cell (MSC) by atmospheric plasma spraying are well established. At this stage, the maximum power densities of INER's ASCs are 652 mW/cm2 at 800 oC for IT-SOFC and 608 mW/cm2 at 650 oC for LT-SOFC. The power densities of INER's MSCs are 540 and 473 mW/cm2 at 0.7 V and 700 oC for a cell and a stack tests respectively. Durability tests for ASCs/MSCs at constant current densities of 300/400 mA/cm2 indicate that the degradation rates are less than 1% / 1,000 hr. Comparable or higher performance is now achieved with respect to the commercial cells. Innovative materials, structures, and the fabrication process for SOFC-MEA are improved to upgrade the MEA qualities and enhance the cost reduction. The diverse SOFC-MEAs are developed for specific issues to simultaneously solve the problems of energy and CO2 greenhouse effect. An 1-kW SOFC power system is designated and a pilot-scale production line of SOFC-MEA is constructed and operated at INER. Efforts are continuously input to solve the fatal problems, select the best type of SOFC-MEA, and assure the right choice for commercialization of the SOFC industry.

10:30 AM

(ICACC-S3-006-2013) Development of Solid Oxide Fuel Cell Stack Modules for High Efficiency Power Generation (Invited)

H. Ghezel-Ayagh*, FuelCell Energy, Inc., USA

FuelCell Energy (FCE) is developing SOFC systems and technology for very efficient, economically viable, coal-to-electricity power plants utilizing synthesis gas (syngas) from a coal gasifier through a cooperative agreement with the U.S. Department of Energy (DOE) Office of Fossil Energy's Solid State Energy Conversion Alliance (SECA) program. One of the key objectives of the multiphase project is implementation of an innovative system concept in design of a Baseline Power Plant (500 MW) to achieve an electrical efficiency of >55% based on higher heating value (HHV) of coal, exclusive of power requirements for CO2 compression. The Baseline system is designed to remove at least 90% of carbon in the syngas for sequestration as CO2. The coal-based power plant is targeted to have a cost of $700/kW (2007 US dollars) for the SOFC power block. In addition to the 500 MW Baseline Power Plant system, a small-scale (60 kW nominal) Proof-of-Concept Module (PCM) system is also being developed. The 60 kW natural gas fueled system is suitable for dispersed power generation applications. FCE efforts are focused on the stack tower and module development, and the development of the PCM system.

11:00 AM

(ICACC-S3-007-2013) Portable LPG-fueled microtubular SOFC (Invited)

S. Kuehn*, S. Kaeding, L. Winkler, eZelleron GmbH, Germany

The demand for mobile power increases steadily. Mobile devices always seem to be out of power exactly when you need them. Batteries can fulfill the users "thirst" for power only in a short term range. Batteries need a long-term non-mobile recharging time. Thus, for the long-term mobile power supply without recharging interruptions or for mobile recharging of devices gas batteries are the best choice. eZelleron's gas battery is a hybrid system of battery and fuel cell. For the user it feels like a standard battery with up to 30 times more energy per weight than a battery. The fuel cell can be easily fueled by everywhere available gases like propane, butane, camping gas or LPG. The fuel cell is a Solid Oxide Fuel Cell (SOFC), bringing the advantage of fuel flexibility and being free from noble metals. However, SOFCs have known issues, like slow start-up and bad cyclability. In this presentation it is shown, how to overcome these issues by engineering the microstructure an using ceramic manufacturing technologies like electrophoretic deposition for high quality thin films. The mass-manufactured eZelleron microtubular SOFC is operational within seconds. Hence this is a potential technology for mobile/portable power supply of devices.

11:30 AM

(ICACC-S3-008-2013) Demonstration of a Highly Efficient SOFC Power System Using Adiabatic Steam Reforming and Anode Gas Recirculation (Invited)

V. Sprenkle*, M. Powell, K. Meinhardt, L. Chick, Pacific Northwest National Laboratory, USA

Solid oxide fuel cells (SOFC) are currently being developed for a wide range of applications because of their high efficiency at multiple power levels. Applications range from 1-2 kW residential combined heat and power applications, 100-250kW sized systems for distributed generation and grid extension to MW scale power plants utilizing coal. This paper reports on the development of a highly efficient, small-scale SOFC power system operating on methane. The system uses adiabatic steam reforming of the methane and anode gas recirculation to achieve high net electrical efficiencies vs the lower heating value (LHV) of the fuel , The anode exit gas is recirculated and all of the heat and water required for the endothermic reforming reaction are provided by the anode gas as it emerges from the SOFC stack. Although the single-pass fuel utilization is only about 55%, because of the anode gas recirculation, the overall fuel utilization is up to 93%. The demonstrated system achieved gross power output of 1650 to 2150 watts with a maximum net LHV efficiency of 56.7% at 1720 watts. Overall system efficiency could be further improved to over 60% with use of properly sized blowers.

S4: Armor Ceramics

Brittle Materials Modeling

Room: Coquina Salon E
Session Chair: Brian Leavy, ARL

8:00 AM

(ICACC-S4-012-2013) Multiscale Modeling of Brittle Fracture with Peridynamics (Invited)

S. A. Silling*, Sandia National Laboratories, USA

The peridynamic theory is an extension of traditional solid mechanics that treats discontinuous media, including the evolution of discontinuities such as fracture, on the same mathematical basis as classically smooth media. The basic equations are integro-differential equations that, unlike the classical partial differential equations of solid mechanics, remain valid on singularities such as propagating cracks. Since peridynamics is a strongly nonlocal theory, peridynamic material models contain a length scale that characterizes the interaction distance between material points. By changing this length scale in a way that preserves the bulk elastic properties, greater spatial resolution in a simulation can be focused on a growing crack tip or other evolving singularity. This leads to a consistent way to treat fracture at the smallest physically relevant length scale within a larger model, without remeshing or coupling dissimilar methods. The peridynamic multiscale method appears to provide a promising new approach to understanding material failure. This talk will first review the basics of the peridynamic theory. The new multiscale method will then be discussed, with computational examples drawn from penetration mechanics, brittle fracture, and damage progression in heterogeneous media.

8:30 AM

(ICACC-S4-013-2013) Constitutive and Adaptive Kinematic Modelling of Dynamic Fracture in Ceramic Armour

N. Petrinic*, S. Falco, E. Barbieri, S. Knell, E. López-López, University of Oxford, United Kingdom; T. Rodriguez Suarez, Universidad de Oviedo, Spain; R. I. Todd, University of Oxford, United Kingdom

This paper focuses on dense ceramic materials with polycrystalline microstructure and a statistically representative distribution of flaws. A physically based constitutive model coupled with a non-local kinematic model has been developed to simulate the phenomena surrounding progressive dynamic cracking, fracture and fragmentation caused by ballistic impact at length scales an order of magnitude larger than the average size of the underlying structural units (grains). The model relies on decoupling the volumetric and deviatoric aspects of the deformation in order to simulate the pressure, temperature and strain rate dependent behaviour by using a thermodynamically consistent modelling approach and the principles of continuum damage mechanics. This approach allows for the simulation of strain localisation before engaging the non-local criteria for insertion and evolution of discontinuities as cohesive or contact interfaces. The results are compared against ballistic experiments involving ultra-high-speed photography and post-mortem material characterisation including microscopy and diffraction techniques to obtain high resolution tomographic and residual stress information.

8:50 AM

(ICACC-S4-014-2013) 3D Mechanism-Based Modeling of the Failure of Brittle Materials under Dynamic Multiaxial Loading

G. Hu*, K. Ramesh, Johns Hopkins University, USA

A 3D mechanism-based constitutive model is developed to capture the failure of brittle materials under dynamic multiaxial loading conditions. The micromechanics is that of a wing-crack mechanism, assuming a defect density and flaw distributions in both orientation and size. Interactions among cracks are modeled by means of a crack-matrix-effective-medium approach. A tensorial damage parameter, incorporating the anisotropic effects, is calculated based upon the crack length and orientation development under local stress fields. At low confining stresses, the wing-cracking mechanism dominates, leading to the degradation of the modulus and peak strength of the material, whereas at high enough confining stresses, the crack mechanism is completely shut-down and the dislocation mechanism is activated. The effects of loading rates, stress states and active mechanisms are explored through parametric studies.

9:10 AM

(ICACC-S4-015-2013) Simulations of Edge-on Impact (EOI) using a micromechanics damage model

A. L. Tonge*, K. T. Ramesh, The Johns Hopkins University, USA

Mechanism based constitutive models can link subscale physical processes, microstructural characteristics, and numerical discretization in a physically meaningful way, which is necessary for informative or predictive simulations of impact and penetration events in ceramic materials. In this work, we present a mechanism based brittle material model which accounts for thermodynamic effects through the use of an equation of state, the cooperative growth of microcracks through the use of micromechanics based damage, and the flow of comminuted material through a viscoplastic granular flow model. We relate the microstructure to the distribution of defects within the material and use this as input to the micromechanics model. After defining a parent distribution of defects, which is representative of the bulk material, we recognize that each material point represents a finite volume of material drawn from this parent distribution. This introduces macroscopic variability into the simulations. We simulate the edge on impact tests. For these simulations, we constrain many of the model parameters using available literature values and fit the remaining values based on quasi-static and dynamic test data. Simulation results are compared to high speed images taken during the experiments. Our objective is to assist in the development of predictive models for brittle materials subjected to impact loading.

9:30 AM

(ICACC-S4-016-2013) Current Numerical Efforts on Predicting the Ballistic Impact of W-Based Penetrators on Confined Hot-Pressed Boron Carbide Targets Behavior

C. G. Fountzoulas*, J. C. LaSalvia, WMRD, USA

LaSalvia et al. studied experimentally the interaction of confined hot-pressed boron carbide (B4C) targets impacted by laboratory-scale tungsten-based long-rod penetrators. Fountzoulas et al. studied by modeling and simulation the ballistic behavior of the above targets. To satisfactorily replicate the experimental damage of the targets and penetrator during impact, various parameters of the Johnson-Holmquist models, known as JH-1 and JH-2 respectively were iteratively modified. Despite numerous iterations, the damage replication of the target was only partially successful. The fracture of B4C was able to be replicated to some extent but without being able to stop its penetration by the projectile, a disagreement with the experimental observations. Recent microstructural characterization of the failed target has revealed the existence of localized amorphous B4C. However, the ability of a numerical model to realistically predict the response of ceramic armor to ballistic impact depends mainly on the selection of appropriate material models and availability of appropriate data. This effort will examine the simulating capability of the Johnson-Holmquist-Beissel strength and failure material models, which include phase presence, to accurately model tensile failure in order to accurately simulate the ballistic response of B4C.

Materials in Extreme Dynamic Environments (MEDE)

Room: Coquina Salon E
Session Chair: James McCauley, U.S. Army Research Laboratory

10:20 AM

(ICACC-S4-017-2013) Materials in Extreme Dynamic Environments - A Collaborative Research Alliance(CRA) (Invited)

J. H. Beatty*, US Army Research Laboratory, USA; K. T. Ramesh, Johns Hopkins University, USA

The Materials in Extreme Dynamic Environments CRA was established to create the capability to design materials for use in specific dynamic environments, especially high strain-rate applications. In order to accomplish this goal, the Army Research Laboratory (ARL) began a major basic research program to address the requisite grand challenges required for more revolutionary advances. This CRA recognizes that significant advances in fundamental multi-scale materials research can be enabled by improving collaborations among academia, industry and government. The CRA focuses on the following five areas 1) Modeling and Simulation, 2) Bridging the Scales, 3) Advanced Experimental Techniques, 4)Multiscale Material Metrics and Characterization, and 5) Processing and Synthesis. The cooperative agreement was awarded to the Johns Hopkins University, and consortium members include the California Institute of Technology, Rutgers University, and the University of Delaware. This talk will describe the overall CRA program, its origins, and the collaboration plans with the Army Research Laboratory.

10:40 AM

(ICACC-S4-018-2013) Armor Ceramics in Extreme Dynamic Environments (Invited)

K. T. Ramesh*, Johns Hopkins Univ, USA

We examine the fundamental science issues associated with the response of armor ceramics in extreme dynamic environments. The presentation describes ongoing efforts, and focuses on the development of experimental methods, modeling and simulation approaches, and techniques for scale bridging as applied to a model armor ceramic. The primary issues are discussed in the framework of mechanism-based approaches to describing the response of the material within extreme dynamic environments, with particular attention to the influence of very high strain rates, high pressures and short times at a variety of length scales. We present an approach to these complex problems that is based on fundamental real-time and in situ observations coupled with multiscale modeling approaches over the full range of length scales and timescales of interest.

11:10 AM

(ICACC-S4-019-2013) Materials in Extreme Dynamic Environments (MEDE)– The Opportunities for Boron Carbide as the Next Generation Armor Material (Invited)

R. Haber*, Rutgers University, USA

Boron carbide is a unique material with a low density and outstanding mechanical properties. However, dense boron carbide has demonstrated a deleterious amorphization at high pressures which has limited its use as the next generation armor material. The new Cooperative Research Alliance – MEDE, will examine the potential of eliminating amorphization by a bottom up approach. This presentation will be an overview of boron carbide outlining the atomistic to micro to mesoscale modeling, synthesis and processing that will be employed to gain a better understanding of this material.

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

Li-ion Battery Technology - Design and Interface

Room: Coquina Salon G
Session Chairs: Sehee Lee, University of Colorado; Kevin Jones, University of Florida

8:00 AM

(ICACC-S6-011-2013) The research on all-solid-state battery with hole-array structure (Invited)

K. Kanamura*, T. Nishioka, S. Naoto, J. Wakasugi, R. Osone, H. Munakata, Tokyo Metropolitan University, Japan

Lithium-ion batteries (LIBs) are utilized in many kinds of mobile devices due to their high energy density. In these years, the developments for plug-in hybrid vehicles (PHEVs) and elecrtic vehicles (EVs) have been promoted. The energy dendity of 500-700 Wh/kg is needed for the utilization for PHEVs and EVs, but conventional construction of LIBs does not achieve such energy density. Graphite anode limits energy density to 300 Wh/kg even if high capacitive cathode was used. Li-metal is one of cadidates but the safety of LIBs is a big problem. All-solid-state batteries are ones of near future batteries because nonflammable solid electrolyte is used. But the low capacity is a problem due to large interface resistance. So, three-dimensional construction of interface between electrode and electrolyte is required for the diminishment of interface resistance. Hole-array structure on the surface of solid electrolyte increases interface area between electrode and electrolyte, and is able to make the capacity larger. In the presentation, fabrication of solid electrolyte with hole-array structure and evaluation of the all-solid-state battery with the electrolyte will be reported.

8:30 AM

(ICACC-S6-012-2013) Understanding Li diffusion and interface stability in garnet structured solid electrolyte materials (Invited)

M. Johannes*, Naval Research Laboratory, USA; K. Hoang, George Mason University, USA; N. Bernstein, Naval Research Laboratory, USA; J. Sakamoto, Michigan State University, USA

Garnet-type Li7La3Zr2O12 (LLZO) is considered as a promising candidate for Li-ion battery solid electrolytes because of its high ionic conductivity and electrochemical and chemical stability. We use first-principles density-functional theory calculations and molecular dynamics simulations to reveal the underlying mechanism that drives a tetragonal to cubic transition at elevated temperatures, and also to explain why the cubic phase can be stabilized with the incorporation of a certain amount of supervalent impurities. We show that the relationship between the observance of a cubic phase and the measurement of a substantially higher ionic conductivity is a secondary effect not directly attributable to the presence of Al in the crystal structure and that, in fact, Al has a slight blocking effect that decreases Li mobility. We discuss strategies for improving the Li mobility via targeted doping at non-Li sites. We also show the results of a very large simulation of the electrolyte/electrode (anode) interface to understand why this material is stable vs. Li metal, while the majority of other solid electrolytes degrade.

9:00 AM

(ICACC-S6-013-2013) Tailoring Active Material and Electrode Design for High Capacity Battery Performance

S. Hariharan*, P. Balaya, National University of Singapore, Singapore

Lithium storage by conversion mechanism enables storage of more than one mole of lithium per formula unit, leading to very high storage capacities atleast 2-3 times more than classical insertion electrodes. However, severe volume change induced during this reaction leads to rapid capacity fade and poor reversibility. To address this, we report a set of design attributes for the active material and electrode architecture and show its applicability for a family of transition metal oxides undergoing conversion reaction. The attributes incorporated in the active material design include (i) well-connected particles (ii) adequate surface area (iii) highly uniform electronic wiring (iv) strong adhesion between particles and current collector (v) superior electrode drying. The storage performances of electrode materials incorporating above features have been investigated. For instance, the first cycle reversibility of tailored hematite α-Fe2O3 increases to 90% compared to commercial samples which exhibits only 70% reversibility. Similarly, magnetite, Fe3O4 demonstrates outstanding cyclability over 3000 cycles and rate performance with 600 mAh.g-1 at 10C (6 min. for charge/discharge) with distinct plateaus. Above design principles were further employed on other metal oxides viz., MoO3, NiO and MnO to evaluate their storage performance.

Materials for Energy Storage - Supercapacitors

Room: Coquina Salon G
Session Chairs: Sehee Lee, University of Colorado; Kevin Jones, University of Florida

10:00 AM

(ICACC-S6-015-2013) Carbide-Derived Carbon Films for Integrated Electrochemical Energy Storage (Invited)

M. Heon, M. Beidaghi, Y. Gogotsi*, Drexel University, USA

This presentation will provide an overview of our research activities in the area of nanostructured carbon films for supercapacitors and other energy-related applications. Supercapacitors are devices that store electrical energy electrostatically and are used in applications where batteries cannot provide sufficient power, lifetime or charge-discharge rates. Extraction of metals from carbides can generate a broad range of carbon nanostructures, which are known as Carbide-Derived Carbons (CDCs). The structure of CDCs depends on the crystal structure of the carbide precursor as well as process parameters including temperature, time and environment. Powder-based micro- and mesoporous CDCs have already shown to be promising materials for supercapacitor applications. Monolithic CDC films can be fabricated by extraction of metal from thin carbide films and have a great potential for fabrication of on-chip micro-supercapacitors. The fabrication process of CDC films starts with magnetron sputtering of carbide films followed by chlorination to form a porous carbon film. The CDC films showed an outstanding performance as supercapacitor electrodes when tested in an organic electrolyte. Moreover, micro-supercapacitors with interdigitated electrodes were fabricated by pattering of the CDC films through standard microfabrication methods and showed a great potential for integrated electronics.

10:30 AM

(ICACC-S6-016-2013) Nanostructured MnO2/composites for supercapacitors (Invited)

L. Lu*, National University of Singapore, Singapore

Supercapacitors are alternative energy storage systems. Although they have relatively lower energy density, they can provide high power density and long cyclic life. Due to its high power density, an energy storage system with both high power density and high energy density can be achieved by hybridizing supercapacitors with rechargeable batteires. Different from the traditional capacitors, one of key factors in controlling capacitance of the supercapacitors is surface area of electrodes. In this research several methods have been used in the fabrication of nanostructured MnO2 films, including electrodepositions, composites prepared using hydrothermal growth, and lithiation of MnO2 thin films. It is found that the morphologies of the nanostructure materials and composites, and hence surface areas are dependent on deposition current density, temperature and concentration of solvent, and lithiation cycles. Although carbon nanoture (CNT) shows the best capacitance shape, CNT-MnO2 composite possesses high capacitance due to contributions from high conductivity of CNT and from high capacitance of MnO2.1-5 This research also provides an evidence of formation of nanostructured and porous MnO2 through lithiation of MnO2 thin film.

11:00 AM

(ICACC-S6-017-2013) Metal oxide-carbon composite nanofibers with enhanced electrochemical energy storage performance (Invited)

Y. Mao*, Q. Li, University of Texas-Pan American, USA

Hierarchical oxide/carbon nanofiber (NF) composites with nano-sized oxide (i.e. MnO and V2O5) particles, rods or flakes encased by carbon were fabricated through a novel ForceSpinning technique followed by a calcinations process. The control of morphology and composition of the nanocomposites is achieved. Especially for MnO, the combination of anodic and cyclic voltammetric oxidations causes the phase transformations and results in formation of MnO2. It enhances the electrochemical performance of the binder-free electrodes carrying the nanocomposite electrodes. The electrochemical performances of these NFs were systematically investigated by cyclic voltammetry, galvanostatic charge-discharge and electrochemical impedance spectroscopy. The hierarchical architecture of the nanocomposite fibers combined with the carbon coating enables the improved electron and ion transportation. For manganese oxide system, it exhibits a maximum specific capacitance of ~450 F/g in 1 M Na2SO4 electrolyte solution, at a current density of 0.2A/g, a couple of orders of magnitude larger than the capacitance prior oxidations. The above synergic characteristics enable these NFs to be a promising electrode material for supercapacitors and Li-ion batteries.

11:30 AM

(ICACC-S6-018-2013) Combined in-situ TEM-EELS and Synchrotron X-ray Techniques for Tracking Lithium Transport and Electrochemical Reactions (Invited)

F. Wang*, S. Kim, L. Wu, Y. Zhu, J. Graetz, Brookhaven National Laboratory, USA

Lithium-ion batteries are the preferred energy storage devices for portable electronics and may become the main power sources for electrical vehicles and grid storage. The development of high-energy electrodes for a new generation of batteries requires a better understanding of how electrode materials function by tracking lithium reactions with individual components in a working electrode. However, this type of characterization requires high sensitivity to lithium and other constituents at relevant spatial and temporal resolution. Ex-situ and in-situ transmission electron microscopy and energy-loss spectroscopy (TEM-EELS), in combination with synchrotron x-ray diffraction and absorption spectroscopy (XRD, XAS), and first principle calculations were used to track lithium transport and local structural changes of electrodes upon lithiation and delithiation. Recent results from studies of several different types of electrodes will be presented, including intercalation (Li4Ti5O12, LiMn1.5Ni0.5O4), alloying (Si, Sn), conversion (FeF2, CuF2), and displacement (CuV2O5) Compounds.

S7: 7th International Symposium on Nanostructured Materials and Nanocomposites

Nanomaterials for Energy Applications I

Room: Coquina Salon B
Session Chairs: Vladimir Sivakov, Institute of Photonic Technology; Mark Hersam, Northwestern University

8:00 AM

(ICACC-S7-011-2013) Piezoelectric Nanogenerators and Piezotronics for Energy and Optoelectronic Device Applications (Invited)

S. Kim*, Sungkyunkwan University, Republic of Korea

I will present a novel approach that greatly enhances piezoelectric power generation by introducing a p-type polymer layer on a piezoelectric semiconducting thin film. Holes at the film surface greatly reduce the piezoelectric potential screening effect caused by free electrons in a piezoelectric semiconducting material. P3HT was used as a p-type polymer on piezoelectric semiconducting ZnO thin film, and PCBM was added to P3HT to improve carrier transport. The ZnO/P3HT:PCBM-assembled piezoelectric power generator demonstrated 18-fold enhancement in the output voltage, and tripled the current, relative to a power generator with ZnO only at a strain of 0.068 %. The overall output power density exceeded 0.88 W/cm3, and the average power conversion efficiency was up to 18 %. Additionally, I will present a flexible hybrid architecture designed to harvest mechanical and solar energies, either separately or simultaneously. By using ZnO with intrinsically coupled piezoelectric and n-type conductive properties, a flexible hybrid energy scavenger is naturally created without any crosstalk and an additional assembling process, thus totally differing from a simple integration of two different energy generators.

8:30 AM

(ICACC-S7-012-2013) Oxide Nanowires for Opto-electronics

G. Faglia*, C. Baratto, E. Comini, I. Concina, M. Ferroni, A. Ponzoni, G. Vardan, D. Zappa, G. Sberveglieri, Universita' degli Studi di Brescia, Italy

Oxides represent the most diverse class of materials, with properties covering almost all aspects of material science and physics in areas including oxide electronics, superconductivity, ferroelectricity, magnetism, and more. Recent achievements at SENSOR Lab in preparation of Metal Oxide Nanowires NWs for for Opto-electronics applications will be reviewed: ZnO NWs on p-GaN for Light Emission; Thermo-electical properties of ZnO(n) and CuO(p) NWs for micropower generation; and Metal oxide NWs and TiO2 nanotubes as n- and p-type semiconductor chemical sensors.

9:00 AM

(ICACC-S7-013-2013) Electrospinning of TiO2 Nanofibers and Hydrogen Plasma Treatment for Solar Water Splitting

A. Lepcha*, A. P. Singh, A. Mettenbörger, S. Mathur, University of Cologne, Germany

Photoelectrochemical (PEC) splitting of water appears to be the most promising, economically viable and sustainable way for the production of hydrogen. In this regard, nanostructured metal oxide semiconductors are promising materials for application in photoelectrochemical cell as an anode material for solar energy harvesting. This report deals with the synthesis of one dimensional TiO2 nanofiber mats by electrospinning which open a new area to solve the problem of integration of aligned nanomaterials. The prepared TiO2 nanofiber mats were further modified by hydrogen plasma treatment at different temperatures for creating the disorder zone on the surface which provide the effective carrier-trapping sites for suppressing rapid recombination to enhance the photoelectrochemical response. The concept of surface disordering opens a new direction for altering optical absorption and carrier transport in semiconductor nanostructures. By combining these two methods, fabrication and modification, we are able to design visible light active substrate free 1D TiO2 nanofibers mats which show 20 times higher photoelectrochemical response as compared to untreated fibres.

9:20 AM

(ICACC-S7-014-2013) Effect of Doping on In-Situ Crystallization and Crystal Growth in Electrospun TiO2 Nanofibres

H. Albetran, H. Haroosh, R. Dong, J. Low*, Curtin University, Australia

In this paper, we report on the structural characterization and morphology of titanium dioxide (TiO2) nanofibers prepared by electrospinning using a solution that contained poly(vinyl pyrrolidone)

(PVP), titanium isoproproxide, acetic acid and ethanol. The as-spun TiO2/PVP composite nanofibers were characterized by in-situ synchrotron radiation diffraction (SRD) to study the kinetics of crystallisation and crystal growth in the temperature range of 25-1000C. The morphology of as-spun and calcined nanofibres were examined using SEM and TEM. The effect of doping by ion-implantation on the crystallisation and phase stability of electrospun TiO2 nanofibres at elevated temperature was also investigated using SRD. The resultant microstructures, phase changes and composition depth profiles are discussed in terms of SRD, SEM, TEM and Rutherford backscattering spectrometry (RBS).

Nanomaterials for Energy Applications II

Room: Coquina Salon B
Session Chairs: Peter Notten, Eindhoven University of Technology; Guido Faglia, Universita' degli Studi di Brescia

10:00 AM

(ICACC-S7-015-2013) Novel Discovery of Silicon (Invited)

V. Sivakov*, Institute of Photonic Technology, Germany

In spite of almost 15 years of intense research on the formation and studies of semiconductor nanowires (NWs), several of the expected, significant, breakthroughs have been reached due to the influence of the NWs structure. Semiconductor NWs have been attracting large interest as a very promising approach toward post CMOS nano-electronics, for photonic, for energy and life science, as well as for fundamental materials science and physics studies. This is because NWs offer bottom-up or top-down self-assembly of ordered 1D nanostructures, creation of new combinations of hetero-junctions with sharp interfaces, including materials with large lattice mismatch, and the ability to grow semiconductor NWs on silicon and further integration in silicon technology. The silicon based technologies are certainly favored because of material abundance and non-toxicity at a high level of materials control and understanding together with a huge industrial infrastructure to account for low production/processing costs and high production yields. This paper comprises a comprehensive review of new observation in silicon material grown by top-down or bottom-up technologies which can be useful for the future optoelectronic applications, especially in energy and biotechnology sector.

10:30 AM

(ICACC-S7-016-2013) Design and integration of Q1D metal oxide heterostructures

R. Fiz*, S. Mathur, Universität zu Köln, Germany

Quasi-one-dimensional (1D) metal oxide nanostructures are considered ideal building blocks for nanodevice fabrication. The 1D geometry entails great advantages concerning charge carrier transport properties due to the 1D confinement and high aspect ratio. Moreover, metal oxide nanostructures exhibit high thermal and mechanical stability as well as low cost fabrication with the possible modulation of their morphological and structural properties. Heterostructures represent an innovating step in the development of novel device nanostructures, enabling the design of materials with unique properties and functionalities, showing great advantages over their single component counterparts. SnO2-based heterostructures have been fabricated by sequential chemical vapor deposition. Multistep CVD processes enable the control over branching and composition of the metal oxide shell deposited on the SnO2 core. Structural distortions at the heterointerface such as defects and strain formation influence the electronic and physical properties of the final material. Understanding the effects at the heterojunction is therefore essential to design multifunctional materials with the desired properties. Finally, the integration of multicomponent metal oxide nanowires such heterostructures in devices of larger dimensions allows the upscaling of 3D networks of interconnected 1D components leading to novel collective transport properties.

10:50 AM

(ICACC-S7-017-2013) Monodisperse Carbon Nanomaterial Coatings and Composites in Electronic and Energy Conversion Devices (Invited)

M. C. Hersam*, Northwestern University, USA

Recent years have seen substantial improvements in the structural, chemical, and electronic monodispersity of carbon nanomaterials, leading to improved performance in a variety of device applications. This talk will highlight our latest efforts to exploit monodisperse carbon nanomaterials in electronic and energy conversion devices. For example, high purity semiconducting single-walled carbon nanotubes (SWCNTs) allow the fabrication of thin-film field-effect transistors with concurrently high on-state conductance and on/off ratio and/or high frequency operation exceeding 150 GHz. Using dielectrophoretic assembly, arrays of individual SWCNT transistors can also be realized with high yield. Similarly, high performance digital circuits can be fabricated from semiconducting SWCNT inks via aerosol jet printing. Beyond transistors, semiconducting SWCNTs have been utilized for light-emitting optoelectronic devices or chemical sensors, while metallic SWNCTs are well-suited as transparent conductors in organic photovoltaics. This talk will also explore the utility of solution-processed graphene for high-frequency transistors, charge blocking layers in organic photovoltaics, and supports for photocatalytic production of solar fuels.

11:20 AM

(ICACC-S7-018-2013) Microwave assisted synthesis of Graphene/Metal Oxide Nanocomposites for Lithium-Ion Battery Anodes

R. Mueller*, S. Mathur, University of Cologne, Germany

Graphene/metal oxide nanocomposites can be obtained by means of a simple microwave assisted reduction of graphene oxide (GO) with M2+ ions (M = Sn, Fe, Co). This direct conversion reaction offers the advantage of an effective separation of single and few layered graphene by in situ formed oxide nanoparticles, whereby the graphene sheets can further act as a buffer material compensating the tremendous structural changes of the oxide phase involved during battery cycling. By this approach graphene/SnO2 nanocomposites could be obtained showing stable discharge capacities of about 500 mAh/g after 50 cycles as well as significantly enhanced cycle stabilities, compared to bare SnO2 particles. The concept could further be extended to Fe2+ and Co2+ systems showing high potential for the fabrication of future lithium-ion battery materials.

11:40 AM

(ICACC-S7-019-2013) From materials research to integrated Li-ion micro-batteries (Invited)

P. H. Notten*, Eindhoven University of Technology, Netherlands

Planar thin-film lithium ion batteries nowadays reveal excellent reversible electrochemical performance. To increase the energy density of these thin-film batteries, novel approaches have been proposed. One of the new concepts is based on the etching of deep 3D-structures into a silicon substrate, increasing the effective surface area significantly. In combination with advanced materials new opportunities are obtained to increase the energy density further. Silicon and Germanium turned out to be excellent candidates for Li-storage electrode materials. About 4 Lithium atoms can be stored per Si/Ge atom. The volume expansion is, however, tremendous inducing material deterioration. In order to cope with this various approaches has been adopted. Nano-wires were found to be too mechanically sensitive to be applied in all-solid-state battery stacks. Honeycomb structure has recently also been proposed. Striking reversible materials deformation has been reported upon (de)lithiation. Finally, thin films turned out to extremely stable.

S8: 7th International Symposium on Advanced Processing and Manufacturing Technologies for Structural and Multifunctional Materials and Systems (APMT)

Advanced Composite Manufacturing

Room: Coquina Salon A
Session Chairs: Yury Gogotsi, Drexel University; Tatsuki Ohji, National Institute of Advanced Industrial Science and Technology (AIST)

8:00 AM

(ICACC-S8-011-2013) Carbon nanotubes in silicon nitride (Invited)

C. Balazsi*, Hungarian Academy of Sciences, Hungary

This research explores the use of a variety of nanoparticles to impart electrical, thermal conductivity, good frictional properties to ceramic matrices. We have chosen highly promising families of carbon materials: multiwall, singlewall carbon nanotubes (MWCNTs, SWCNTs), graphene, carbon black nanograins and graphite micrograins for use as fillers. These materials were dispersed in silicon nitride matrix with different percentages in the range 1-10wt%. A high efficiency attritor mill has also been used for proper dispersion of second phases in the matrix. In order to get the full use of the benefits provided by CNTs it is crucial to retain CNTs un-reacted in the composites and to optimize the interfacial bonding between CNT and matrix. The silicon nitride nanocomposites systems retained the mechanical robustness of the original systems. Bending strength as high as 700 MPa was maintained and an electrical conductivity of 10 S/m was achieved in the case of 3wt% MWCNT addition. Electrically conductive silicon nitride ceramics have also been realized using carbon black (in order of 1000 S/m) and graphite additions in comparison. Examples of these systems, methods of fabrication, electrical percolation, mechanical, thermal and tribological properties and potential uses will be discussed.

8:30 AM

(ICACC-S8-012-2013) Manufacturing and Properties of 2-Dimensional Carbides and Carbonitrides (MXenes) (Invited)

M. Naguib, O. Mashtalir, M. Kurtoglu, M. W. Barsoum, Y. Gogotsi*, Drexel University, USA

The 2-D materials world is limited to graphene, BN, oxides and hydroxides - clays, and chalcogenides. Herein, we report on the fabrication of a new family of 2-D Mn+1Xn sheets from MAX phases. MAX phases are a large family of ternary carbides and nitrides, where M stands for an early transition metal, A stands for a group 13 to 16 element and X is C and/or N. The exfoliation process was carried out by immersing selected MAX phase powders in hydrofluoric acid, at room temperature. It results in etching the A layer from MAX phases and exfoliation of 2-D layers, so called MXenes. Not only are individual layers formed, but also multi-layer particles and conical scrolls of radius less than 20nm have been demonstrated. Several examples are discussed, such as Ti_2C, $(Ti_{0.5}Nb_{0.5})_2C$, Nb_2C, Ti_3C_2, Ta_4C_3, and $Ti_3(C_{0.5}N_{0.5})_2$. DFT simulation showed that MXenes band gap can be tuned by varying the surface termination. The large elastic moduli predicted by ab initio simulation and the possibility of varying MXene's surface chemistry render these nanosheets attractive as composite fillers. Cold pressed discs of MXenes showed hydrophilic behavior and electrical conductivity compared to multilayer graphene. This makes them attractive for electrochemical energy storage applications. Since there are over 60 MAX phases known to date, this discovery opens the door to synthesis a large number of other 2-D materials.

9:00 AM

(ICACC-S8-013-2013) Fractals in Ceramic Structure and Properties Higher Integrations

V. Mitic*, V. Paunovic, University of Nis, Serbia; S. Jankovic, Mathematical institute, SASA, Serbia; L. Kocic, University of Nis, Serbia; V. Pavlovic, University of Belgrade, Serbia

In this study, in order to establish grain shapes of sintered ceramics, new approach on correlation between microstructure-nanostructure and properties of rare-earth (Er, Yb and Ho) and other additives doped BaTiO3 and all electronics ceramics based on fractal geometry, related to intergranular contact surfaces and mathematical statistics calculations, have been developed. Fractal geometry has been used to describe complexity of the spatial distribution of BaTiO3-grains. The model of impedances, between clusters of ceramics grains, has been presented and calculations of microcapacitance generated in grains contacts of doped BaTiO3 have been performed. By the control of shapes and number of contact surfaces on the level of the entire BaTiO3-ceramic sample, the control over structural properties of these ceramics can be done, with the aim of correlation between material electronic properties and corresponding microstructure. The fractal nature for the ceramics structure analysis of the providing a new approach for modeling and prognosing the grain shape and relations between the BaTiO3-ceramic structure, micro- and nano-, and dielectrical, ferroelectrics and all other electronic properties in the light of new frontier for higher level electronic circuits integration.

9:20 AM

(ICACC-S8-016-2013) Development and Applications of Ceramic Bonded Carbon Composites

W. Chen, Y. Miyamoto*, Joining and Welding Research Institute, Osaka University, Japan

New carbon composites named Ceramic Bonded Carbon (CBC) are made of carbon particles sintered with thin ceramic boundaries of SiC and AlN. They are produced by sintering the green bodies of specially mixed carbon and ceramic powders at temperatures of 2073-2273 K using SPS or HP. Because various kinds of carbon and the content of ceramics can be chosen besides each carbon particle is covered and tightly bonded with thin continuous phase of ceramics with several μm thick, we can provide wide excellent performances to CBCs comparing to conventional graphite and carbon materials. For instance, CBCs made of meso-phase pitch carbon and 20~30 vol.%SiC or AlN with sintering additives have right weight (2.3~2.4 Mg/m3), low porosity (2%), isotropic properties of excellent strength (100~220Pa), thermal conductivity (90~170W/cmK), low shore hardness (45~70), low particles emission, easy and precise machining abilities. Moreover, they can be joined with ceramics or metals such as W and Mo. CBCs and their joints can be applied to heat dissipative and radiation resistant materials, low friction and wear parts, and other robust devices.

10:00 AM

(ICACC-S8-017-2013) Composite metal oxide particles from chemical vapor synthesis

A. K. Sternig, A. Gheisi, O. Diwald*, University of Erlangen Nürnberg, Germany; S. Klacar, H. Groenbeck, Chalmers University of Technology, Sweden

Chemical vapor synthesis allows for nonequilibrium mixtures of metal oxide particles. After combustion of Ba or Zn in the MgO flame and quenching these are characterized by a statistical distribution of the components. Differences in ionic radii drive the annealing induced segregation of the admixed cations into the particle surface. These effects can be utilized to generate composite surface structures with altered chemical and optical properties. On Ba-Mg-O particle systems high resolution TEM and XRD reveal MgO-based support particles with hemispherical BaO phases.[1] Structural and energetic properties of BaO dissolved inside the MgO host and adsorbed on MgO surface were investigated by DFT calculations. Ab initio thermodynamics revealed that the segregate shape results from the growth process and become stabilized by surface hydroxylation. Zn-Mg-O particles were synthesized in the range from solid solutions of Zn(2+) ions in MgO to phase separated particle mixtures.[2,3] In composite particles, admixed ZnO produces bulk PL emission and suppresses MgO specific surface excitons. Obtained insights are relevant for composite metal oxide nanoparticles where the impact of the interface composition on their properties is usually neglected. [1] Sternig et al. J. Phys. Chem. C 115 (2011) 15853 [2] Stankic et al. Nanotechn. 21 (2010) 355603 [3] Zhang et al. ACS Appl. Mater. & Interfaces 4 (2012) 2490.

10:20 AM

(ICACC-S8-018-2013) Fabrication and Properties of High Thermal Conductivity Silicon Nitride

Y. Zhou, H. Hyuga, T. Ohji*, K. Hirao, National Institute of Advanced Industrial Science and Technology (AIST), Japan

Amongst a variety of fabrication procedures for silicon nitride and related ceramics, reaction bonded processing has some advantages, such as low environmental impact, low sintering shrinkage and low raw material cost. In this study, silicon nitrides with high thermal conductivities over 80 Wm-1K-1 were prepared via nitridation of Si powder compacts followed by post-sintering (sintered reaction bonded Si3N4, SRBSN) . The thermal conductivities of SRBSN specimens were increased with increasing holding time. For example thermal conductivities of SRBSNs fabricated under reducing nitridation atmosphere followed by post-sintering of 3, 6, 12 and 24 hrs were 109, 125, 146, and 154 Wm-1K-1, respectively. Lattice oxygen contents were measured by the hot-gas extraction method. It was confirmed that thermal conductivity was increased with decreasing lattice oxygen regardless of additives, processing routes, indicating that the lattice oxygen is a decisive factor for fabricating high thermal conductivity Si3N4. Fracture resistance behaviors of high thermal conductivity Si3N4 weres also investigated by chevron-notched beam tests.

10:40 AM

(ICACC-S8-019-2013) Structure-Property Relationship of Polymer-Derived Amorphous SiBCN Ceramics

Y. Chen*, L. An, University of Central Florida, USA

Amorphous SiBCN ceramics are synthesized by pyrolysis of polyborosilazanes with various boron concentration at 1000 to 1600 °C. The microstructures of the resultant ceramics are characterized using FT-IR, XPS, NMR and EPR. The electric and dielectric properties of the SiBCN ceramics are measured. The properties are correlated with the structures to illustrate the structure-property relationships for this new class of ceramics.

11:00 AM

(ICACC-S8-020-2013) Processing and properties of zirconia toughened WC-based cermets

I. Hussainova*, N. Voltsihhin, Tallinn University of Technology, Estonia; S. Hannula, E. Cura, Aalto University Foundation, Finland

The outstanding toughening capability exhibited by zirconia-based ceramics has raised considerable attention in materials doped by tetragonal zirconia. To obtain materials of desired microstructure and provide properties required for the different applications manufacturing process should be considered in details. Different milling techniques as well as a wide choice of sintering technologies make the task extremely complicated. The main aim of this work was to prototype the composite characterized by the uniformly dispersed zirconia grains of the sub-critical size throughout the matrix of WC-Ni and to retain tetragonal polymorphs of ZrO2 during sintering. Transformation depends upon zirconia particle size. Basing on the interaction energy and taking into account interface surface energy as well as elastic moduli and thermal expansion coefficients of matrix and inclusions the proper range of particle sizes needed for considerable increase in fracture toughness in WC-based cermets is estimated. Hot isostatic pressing, spark plasma sintering and vacuum sintering were used to find the best parameters and conditions to produce a reliable composite. The WC-Ni-ZrO2 composites are described as synergistically toughened ones due to anticipated interactions between crack bridging and stress-induced phase transformation.

11:20 AM

(ICACC-S8-015-2013) Evaluation of High Fiber Volume Fraction Fiber Reinforced Polymer Composites Fabricated in an Out-of-Autoclave Resing Infusion Process

L. R. Holmes*, US Army Research Labs, USA

The U.S. Army Research Laboratory (ARL) has a long history in the fabrication of fiber reinforced polymer composite materials for both lightweight structures and vehicular armor. Throughout the years, ARL research has focused on cost efficient materials and processes with Army specific goals in mind. While retaining the Army perspective, we focus on the basic scientific fundamentals that lead to high quality, cost effective composite systems for uses across the scientific spectrum. In our research, we have been increasing the fiber-volume fraction by Vacuum Assisted Resin Transfer Molding (VARTM) in order to produce composite structures with aerospace grade qualities. Of specific focus is the control of processing parameters during resin infusion to obtain fiber-volume fractions like those of autoclave processed composites. Using a combination of viscosity control, ARL based VARTM techniques, and a pressure control system, we have shown an increase in fiber-volume content from 50 % (ARLs normal processing range for a particular material system and VARTM process) to over 60 %. The increase in fiber-volume fraction provides for higher strength to weight ratios in composite parts while cutting the cost of fabrication. Mechanical Characterization and processing characteristics are presented, and evaluations are discussed.

S9: Porous Ceramics: Novel Developments and Applications

Membranes and High SSA Ceramics

Room: Coquina Salon C
Session Chair: Gian Domenico Soraru, University of Trento

8:00 AM

(ICACC-S9-011-2013) Structuring of Porous Powders into Hierarchically Porous Macroscopic Adsorbents for Gas separation (Invited)

F. Akhtar*, A. Ojuva, N. Keshavarzi, L. Bergström, Stockholm University, Sweden

The use of porous materials in industrially important applications, e.g. gas separation and purification, require that the porous material is assembled into mechanically strong and hierarchically porous macroscopic structures such as structured monoliths and laminates. Zeolites possess well-defined micropores, high surface area, high thermal stability, making them a preferred material for a number of important gas separation processes, e.g. in the purification of biogas and CO2 separation from flue gas. We will demonstrate a versatile binder-less approach to structure zeolite monoliths with high CO2 uptake capacity, high CO2 selectivity and rapid uptake and release kinetics and high mechanical strength. A figure of merit will be defined to evaluate the performance of such structured adsorbents and comparisons with recently published porous carbons and metal organic frameworks will be made. In addition, we will show how the zeolite material can be structured in to a membrane support for zeolite films. The pore architecture of membrane supports can be designed to ensure high mass transfer through the support, mechanical stability and a thin porous layer on top to facilitate the silicalite-1 film growth. Finally, the concepts of adsorption and diffusion, mass and heat transfer will be combined in a discussion of the optimal porous architecture and geometry of structured adsorbents.

8:30 AM

(ICACC-S9-012-2013) Pore size control of amorphous silica membrane synthesized by chemical vapor deposition

T. Nagano*, K. Sato, Japan Fine Ceramics Center, Japan

Pore size control of amorphous silica membranes on γ-Al2O3-coated α-Al2O3 porous supports was performed by changing source gas, flow rate difference between source gas and reaction gas, thickness and pore size distribution of intermediate layer, porosity of porous support were investigated. Herium and H2 permeance was depended on the porosity of porous supports. The permeance of He and H2 also increased with increasing pore size at intermediate layer. The permeance of CO2, Ar and N2 decreased with increasing thickness of intermediate layer and pore size of γ-Al2O3 intermediate layer. Hydrogen permselectivity to N2 was depended on the thickness of γ-Al2O3 intermediate layer. The relationship between source gas size and pore size distribution in intermediate layer was very important for H2/N2 permselectivity.

8:50 AM

(ICACC-S9-013-2013) Gas permeation properties of microporous amorphous silica-based membranes

Y. Iwamoto*, Graduate School of Engineering, Nagoya Institute of Technology, Japan; A. Mori, Graduate School of Engineering, Nagoya Institute of Technology, Japan; H. Mizuno, Graduate School of Engineering, Nagoya Institute of Technology, Japan; A. Kimura, Graduate School of Engineering, Nagoya Institute of Technology, Japan; K. Hataya, Graduate School of Engineering, Nagoya Institute of Technology, Japan; S. Honda, Graduate School of Engineering, Nagoya Institute of Technology, Japan

Amorphous silica-based multicomponent [Si-M1-M2-O, (M1, M2= hetero element)] membranes were synthesized from liquid metal-organic precursors. The precursor solution was dip-coated on a fine and asymmetric alumina porous support, and subsequently heat treated at 873 K in air. The gas permeation properties of the membranes were found to strongly depend on the chemical composition of the Si-M1-M2-O membrane material system, and some transition metal cation-doped membranes exhibited unique high-temperature H2 permeation properties which were apparently different from those explained by the activated diffusion often observed for the metal-organic precursors-derived microporous amorphous silica membranes. To clarify the dominant mechanism for the H2 permeation, powered samples, and layered thin film samples on quartz substrates were prepared using the same metal-organic precursor solution for membrane syntheses and boehmite sol, then characterized by the X-ray photoelectron spectroscopy (XPS), FT-IR by using DRIFTS technique and the TPR/TPD analysis. From the results of these analyses, the reactivity toward hydrogen at high temperature was found to be significantly higher than that of the dopant-free amorphous silica These experimental results will be discussed from a viewpoint of application of the ceramic membranes for developing novel highly efficient hydrogen production, storage and transportation systems.

9:10 AM

(ICACC-S9-014-2013) Permeability and Fracture Properties of Porous Alumina for Support Substrates of Ceramic Membranes

S. Honda*, N. Nishihara, S. Hashimoto, Nagoya Institute of Technology, Japan; T. Eda, Noritake Corpolation Limited, Japan; H. Watanabe, Noritake Corpolation Limited, Japan; K. Miyajima, Noritake Corpolation Limited, Japan; Y. Iwamoto, Nagoya Institute of Technology, Japan

The permeability and fracture properties of alumina porous structures, the support substrates for permselective microporous ceramic membranes were studied. To study the influence of porosity and pore sizes on the various properties systematically, porous alumina with different porous structure were fabricated. The mechanical and thermal properties related to the thermal shock resistance were also measured and the influence of porosity and pore size on the properties was estimated. Gas permeability of porous alumina were increased with increase in porosity and pore size. To estimate the long term stability of the porous alumina support substrate, the fatigue test were examined by the bending test. The fracture strength, Young's modulus values and thermal conductivity were decreased with increase in porosity of the samples with same pore size. However, the sample with well-growing necking of alumina grain was higher properties in spite of having the large pore size. Porous structure was clarified that combined with high gas permeability and excellent fracture properties.

9:30 AM

(ICACC-S9-015-2013) Hydrogen permeation properties of sol-gel derived amorphous silica membranes fabricated at high temperatures

M. Kanezashi*, T. Sasaki, Hiroshima University, Japan; H. Tawarayama, Sumitomo Electric Industries Ltd, Japan; T. Yoshioka, T. Tsuru, Hiroshima University, Japan

The sol-gel method was applied for the fabrication of amorphous silica membranes for hydrogen separation. Hydrogen permeation properties in a wide temperature range of 300-700 °C for amorphous silica membranes with different calcination temperatures were evaluated. Hydrothermal stability was also evaluated by determination of the time-course of gas permeance under a steam atmosphere (500 oC, steam: 70 kPa). An amorphous silica membrane just after fabrication at 550 oC showed He and H2 permeances of 1.3 x 10-6 and 6.0 x 10-7 mol m-2 s-1 Pa-1 with He/N2 and H2/N2 permeance ratio of 230 and 80, respectively. However, the permeances of He and H2 decreased with an increase of heat treatment especially above 650 oC, while that of N2 increased with an increase of heat treatment temperature, resulting in drastic decrease of He/N2 (= 30) and H2/N2 (= 10) permeance ratio after heat treatment at 800 oC. The permeance ratios of H2/H2O for membranes fired at 700 oC increased drastically over the range of He/H2 permeance ratio of approximately 3-4 and showed approximately 25, much higher than those fired at 500 oC. When amorphous silica membranes were fabricated at higher temperatures that can lead to elimination of silanol groups, the pore size distribution of amorphous silica structure seems to be densified probably because of condensation reaction of silanol groups

Processing Methods for Porous Ceramics III

Room: Coquina Salon C
Session Chair: Yuji Iwamoto, Graduate School of Engineering,Nagoya Institute of Technology

10:10 AM

(ICACC-S9-016-2013) Microstructure evaluation and simulation of micro cellular ceramics (Invited)

T. Fey*, University of Erlangen-Nuremberg, Germany; P. Greil, University of Erlangen-Nuremberg, Germany; M. Stumpf, University of Erlangen-Nuremberg, Germany

Micro cellular oxide ceramics were processed using different mixtures of alumina and different amount of sacrificial pore templates and shapes. Sintering is applied at 1700° C for 3 hrs after debinding and pore template removal at least for 45 h in air (600°C). A wide porosity range (10-60%) with a bending strength between 15 to 170 MPa, thermal conductivity between (2,7 – 14.4 W/mK) can be adjusted. Due to wide mechanical and thermal property variations possible applications can be found as refractory or isolation material. Microstructure evaluation is done by SEM and μCT-measurements. The formation of the interpenetrating perculation network of pores depending on amount, shape and combination of sacrificial pore templates is determined, analyzed and characterized based on μCT-data. The preculation network connectivity increases with the amount of spherical pore templates using a bimodal distribution instead of monomodal. The highest pore connectivity was reached using a three modal pore template distribution with adding additional fibre pore templates with an 1:10 (length:diameter) aspect ratio. The effect of the microstructure on mechanical and thermal properties was calculated with FE-simulations.

10:40 AM

(ICACC-S9-017-2013) Colloidal processing of advanced ceramics for applications in purification technology

K. Rezwan*, Advanced Ceramics, University of Bremen, Germany

An ionotropic gelation route is presented for obtaining porous alumina/silica microbeads (MBs) with tailorable morphology, specific surface area (SBET) and pore size which can directly be sintered into porous, monolithic adsorbents (MAds). After sintering SBETs from 20 m2/g up to 70 m2/g with open porosities up to 90 % could be achieved, depending on the silica nanoparticle addition. The significantly increased SBET resulted in a several hundredfold faster uptake of model dye molecules. Depending on silica content and sintering temperature the MBs were also found to be chemically stable in technologically relevant solvents such as water, acetone, acetonitrile, hydrochloric acid and methanol for at least one week except for sodium hydroxide. By adjusting the processing parameters spherical, fibrous or irregular microbead morphologies could be obtained. The same route was also successfully applied for obtaining calcium phosphate, titania and zirconia microbeads. The presented straight-forward ionotropic gelation route is basically applicable to any other ceramic material and therefore extremely versatile. The obtained MBs and MAds can be further adapted to any type of environmental or biotechnological purification process by additional functionalisation steps.

11:00 AM

(ICACC-S9-018-2013) SiC aerogels from preceramic polymers

G. Soraru*, E. Zera, R. Campostrini, University of Trento, Italy; Y. Blum, SRI International, USA

Due to its exceptional chemical and thermal stability micro/mesoporous SiC can find applications in a variety of different fields such as catalyst support for chemical reactions, membranes/ultrafilters for chemical separations, high temperature thermal insulations etc. On the other hand synthesis of highly porous SiC is not easy: it can be obtained from organic modified silica xerogels via high temperature carbothermal reduction or by casting liquid polycarbosilane into a sacrificial templates. Here we report a novel and simple process which starts from the synthesis of a polycarbosilane aerogel and its pyrolythic conversion into the corresponding SiC aerogel. The crosslinking of the starting polycarbosilane is performed through hydrosilylation reaction in a highly diluted solution. The wet polycarbosilane network is supercritically dried using CO2. Finally, the polymeric aerogel is fired in controlled atmosphere up to 1500°C. SiC aerogels having a density as low as 0.17 g/cm3, a porosity of 90 vol% and SSA of 500 m2/g have been obtained.

11:20 AM

(ICACC-S9-019-2013) Processing of microporous membranes for H_2/CO_2 and CO_2/N_2 separation

T. Van Gestel*, J. Hoffmann, J. Eiberger, M. Bram, W. Meulenberg, H. Buchkremer, Forschungszentrum Jülich, Germany

This paper reports the synthesis and characterization of graded microporous membranes which are under investigation for H_2/CO_2 and CO_2/N_2 separation in next generation fossil power plants. Each membrane type consists of a macroporous α-Al_2O_3 support and mesoporous intermediate layers, which are made by dip-coating Al_2O_3 and/or ZrO_2 nano-suspensions and sols. The active top layer of the membrane can be a SiO_2 or modified SiO_2 thin film, with an improved steam resistance or CO_2 affinity. Sols of these materials are prepared by precipitate-free hydrolysis-condensation synthesis methods, starting from metal-organic precursors. Three different thin film deposition techniques are considered: dip-coating, spin-coating and ink-jet printing. An important observation is that each method delivers a homogeneous thin film with the required microporous structure (pore size < 1 nm) and thickness of approximately 100 nm. Our membranes achieve an average H_2/CO_2 selectivity over 30 reproducibly using a dip-coating process on planar samples. Also stainless-steel supported membranes have been successfully synthesized. Upscaling to tubular substrates with a size up to 25 cm is ongoing. In this study, we also introduce novel functional ink-jet printed microporous membranes. For rapid production, the coating processes are combined with a rapid thermal process (RTP).

11:40 AM

(ICACC-S9-020-2013) Synthesis of Cubic-shaped ZnO Particles through Controlling Crystal Growth of Metal-Organic Frameworks

Y. Kimitsuka*, Keio University, Japan; E. Hosono, National Institute of Advanced Industrial Science and Technology, Japan; S. Ueno, Keio University, Japan; H. Zhou, National Institute of Advanced Industrial Science and Technology, Japan; S. Fujihara, Keio University, Japan

Metal-organic frameworks (MOFs) are a new class of crystalline hybrid materials which can be derived from an assembly of organic linkers with metal ions. Generally MOFs have high-specific surface areas and many well-ordered micropores in crystals. Furthermore, it is possible to design crystal structure and control the size and characteristics of micropores by selecting organic ligands and metal ions appropriately. Thus, MOFs have great potential for many applications in molecular adsorption and separation, ion and molecular recognition, ion-exchange, gas storage, specific reactions, and so on. However, despite many investigations for designing crystal structures of MOFs, the mechanism of crystal growth of MOFs is still unclear. We have synthesized porous nanosheets of metal oxides by using metal hydroxide nanosheets as self-templates. In this work, we succeeded in synthesizing porous metal oxides particles using MOFs as self-template instead of metal hydroxide nanosheets. That is, we synthesized cubic-shaped MOF-5 particles constructed by Zn2+ ions and terephthalic acid by the solvothermal method. The calcination of the MOF-5 particles led to the formation of porous ZnO particles. This ZnO particles had a cubic-shaped morphology 10 - 30 μm in size. Additionally, we focused on investigating the influence of synthesis conditions for crystal growth of MOF-5.

S10: Virtual Materials (Computational) Design and Ceramic Genome

Prediction and Modeling of Properties of Ceramics and Composites

Room: Oceanview
Session Chairs: Hans Seifert, Karlsruhe Institute of Technology; Yanwen Zhang, Oak Ridge National Laboratory

8:00 AM

(ICACC-S10-001-2013) First Principles Calculatin of Electronic, Optical, and Mechanical Properties of a Large Random Network model of a-SiO2 Glass (Invited)

W. Ching*, N. Li, University of Missouri-Kansas City, USA

The electronic structure, network bonding, electron localization, optical properties, elastic constants and mechanical properties of a larger continuous random network (CRN) model of amorphous SiO2 (a-SiO2) with 432 SiO2 molecules and no broken bonds were studied by first principles methods. The initial structure was first relaxed by using VASP to high accuracy and the final model with density of 2.194 gm./c.c. and very small bond length and bond angle distortions. The fully relaxed periodic and non-cubic model is used as input for the calculation of electronic structure and optical properties using the OLCAO method. It is shown that the calculated physical properties including reflective index and elastic properties of this ideal a-SiO2 structure are very close to the experimentally measured data. Also studied are the variations of these properties under hydrostatic pressure. Comparison of the same properties with crystalline counterpart a-quartz yields much insight on the subtle differences and the nature of non-crystalline solids with no long range order as compared with crystalline solids. This CRN model can serve as the standard model for an amorphous inorganic glass.

8:30 AM

(ICACC-S10-002-2013) Genome Approach for Advanced Ceramics with Extremely Low Thermal Conductivity (Invited)

J. Wang*, Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, China

Searching novel ceramic with low thermal conductivity is the great challenge in the field of thermal barrier protection. However, the task is very difficult to be realized because there are intractable choices among countless possible candidates, and there is still absence of rigorous theoretical method for predicting high-temperature thermal conductivity. The present work shows that searching advanced ceramic with extremely low thermal conductivity can be guided by the genome approach based on theoretical prediction of minimum lattice thermal conductivity at high temperature. Based on the theoretical calculations, we developed some ternary RE-Si-O silicates and quaternary RE-Si-O-N oxynitrides, which have extremely low thermal conductivity from room to high temperature. The theoretical predictions are validated by experimental measurements of thermal conductivity after breakthroughs in synthesizing the dense and bulk samples of these novel ceramics.

9:00 AM

(ICACC-S10-003-2013) A numerical method for the simulation of coupled radiative/conductive heat transfer

G. L. Vignoles*, University Bordeaux, France

Numerous materials intended to work at high temperatures, like thermal protection system materials, heat exchangers, gas burners, etc … are porous and involve heat transfer both by conduction through the solid phase and radiation through the pores. Addressing simultaneously both types of heat transfer is a rather tricky task; previously developed techniques usually involve distinct solving procedures for conduction and radiation. Here, we present a numerical tool allowing simulation of heat transfer by these modalities in a fully coupled fashion, based on a mixed random walk algorithm. The code is intended to work on 3D images produced either from CMT or any other similar technique or from image synthesis; moreover, it can account for the heterogeneous and anisotropic nature of the solid phase (fiber bundles). Validation on test cases and some preliminary results on X-ray CT images are shown.

9:20 AM

(ICACC-S10-004-2013) Structure, Phonon, Bonding, and Hardness of a series of TMB4, TMB6 and TMB12 (TM = transition metal)

P. Liu*, X. Cheng, H. Niu, X. Chen, D. Li, Y. Li, Institute of Metal Research, China

Covalent networks with high densities and three-dimensional (3D) morphologies are basic features of most of the known superhard materials. Inspired by the 3D boron network in the CrB4 compound which shares the same framework with the rigid carbon sp3 network proposed recently for the high-pressure superhard carbon allotrope of bct-C4, we have investigated the structure, bonding and hardness of a series of TMB4 and TMB6 and TMB12 in detail through first-principles calculations with structural search techniques and experimental measurements. The evolutions of covalent boron frameworks associated with optimized mechanical properties and superhardness will be represented, in combination with the electronic structure analysis.

10:00 AM

(ICACC-S10-005-2013) Kinetic Monte Carlo Simulation of Cation Diffusion in Low-K Ceramics (Invited)

B. Good*, NASA Glenn Research Center, USA

Low thermal conductivity ceramic materials are potentially of interest to the aerospace community for use as the thermal barrier component of coating systems for turbine engine components. In particular, zirconia based materials exhibit both low thermal conductivity and structural stability at high temperature, making them suitable for such applications. Because creep is one of the potential failure modes, and because diffusion is involved in a number of creep mechanisms, we have performed computer simulations of cation diffusion in a variety of zirconia-based low-K materials. The kinetic Monte Carlo (kMC) simulation method is an alternative to the more widely known molecular dynamics method. It is designed to study “infrequent-event” processes, such as diffusion, for which molecular dynamics simulation can be highly inefficient. We describe the results of kinetic Monte Carlo computer simulations of cation diffusion in several zirconia-based materials,specifically, zirconia doped with Y, Gd and Yb. Diffusion paths are identified, and diffusive energy barriers are obtained from density functional calculations and from the literature. We present results on the temperature dependence of the diffusivity, and on the effects of the presence of oxygen vacancies as well.

10:30 AM

(ICACC-S10-006-2013) Elastic, Electronic Structure and Optical Properties Change with Increasing Alumina Content in Mullite (Invited)

S. R. Aryal*, P. Rulis, W. Ching, University of Missouri Kansas City, USA

Alumino-silicate series ($Al_{4+2x}Si_{2-2x}O_{10-x}$, x=0 to 1), is an important class of structural ceramics. When x = 0, the series leads to perfect crystal sillimanite and when x = 1 to silica-free mullite-like phase, known as iota-alumina (ι-Al_2O_3). All other phases in between these two end members are called mullite. Mullite phases have partial occupied sites, which makes theoretical study a formidable task. We used supercell approach to model the structure of four stoichiometric mullite phases $3Al_2O_3{\bullet}2SiO_2$, $2Al_2O_3{\bullet}SiO_2$, $4Al_2O_3{\bullet}SiO_2$, $9Al_2O_3{\bullet}SiO_2$, with x=0.25, 0.40, 0.67 and 0.842 respectively. *Ab initio* calculations, using Vienna *ab initio* simulation package (VASP) and orthogonalised linear combination of atomic orbitals (OLCAO), show how the elastic, electronic structure and optical properties in mullite change with increasing alumina content. Mullite phases are stiffer along the crystallographic c-axis in consistent with mullite structural configuration but stiffness decreases rapidly with increasing alumina content. Increasing alumina makes mullite structure more disordered leading decrease in band gap and refractive index.

11:00 AM

(ICACC-S10-007-2013) First-principles calculation of temperature dependent thermal and mechanical properties of layered ternary carbides, Ti2AlC and Cr2AlC

J. Wang*, J. Wang, Institute of Metal Research, China; Y. Zhou, Aerospace Research Institute of Material & Processing Technology, China

Mn+1AXn phases (where M is an early transition metal, A is an A group element, and X is carbon or nitrogen) are good candidate materials for the high temperature structural applications due to the combination of merits of both ceramics and metals. Considering the high temperature application of MAX phases, the temperature dependant mechanical and thermal properties are important and need to be clarified. In recent years, prediction of properties of MAX phases based on first-principles method has made great achievements. However, most of these works are considered properties in ground state without the effect of temperature. In this work, we try to explore a reliable method to calculate the temperature dependent properties of MAX phases. The temperature dependences of thermal expansion, heat capacity, bulk modulus and Grüneisen parameters of two representative MAX phases, Ti2AlC and Cr2AlC, were studied theoretically. The present calculated thermal and mechanical properties agree well with the experimental data. The calculated results show that although the two compounds have isotypic structures, Ti2AlC and Cr2AlC show different trends in mechanical and thermal properties with respect to temperature changes. The different trends can be explained by the different lattice dynamic behaviors of the two compounds.

11:20 AM

(ICACC-S10-008-2013) Theoretical investigations of the ferroelectric domain walls in LiNbO3 by first-principles calculations

E. Tochigi*, Lawrence Berkeley National Laboratory, USA; A. Nakamura, Nagoya University, Japan; T. Mizoguchi, The University of Tokyo, Japan

LiNbO3 is a ferroelectric material which has spontaneous polarization along the <0001> axis at room temperature. Antiparallel ferroelectric domain walls can form between regions having different polarization directions in this crystal. Recently, ferroelectric domain walls attract much attention because they often have characteristic functional properties. However, the atomic and electronic structures of the ferroelectric domain walls in LiNbO3 are not well understood. In this study, we performed first-principles projector augmented wave calculations in order to investigate the atomic and electronic structures of two types of the ferroelectric domain walls in LiNbO3. Our results showed that characteristic electronic structures appear for both the domain walls. This would be due to off-stoichiometry and structural relaxation of the domain walls. In the presentation we will discuss the atomic and electronic structures and the expected functional properties at the domain walls in detail.

11:40 AM

(ICACC-S10-009-2013) The Effective Elastic Properties of the C/C Composites calculated Using 3D Unit Cell Presentation of the Microstructure

R. Piat*, G. Stasiuk, Karlsruhe Inst of Technology, Germany

Both micro constituents of C/C composites, carbon fibers and pyrolytic carbon are orthotropic and for this reason, the effective properties of these composites are strongly dependent on the fiber distributions in the preform. For better understanding of the relationship between fiber orientations and corresponding elastic properties, the 3D unit cell models for different fibers distributions are created. These cells are numerically generated and reproduce 3D fibers arrangements in the real preform. The numerical procedure for microstructure generation consists in creation of a set of non-intersecting cylinders. It is considered that fibers are straight and there is no "packing problem" due to their low volume fraction. The distribution of the cylinders is random and it statistically corresponds to the distribution of the fibers studied with the micro computer tomography (μCT). Then the growing algorithm is used for reproduction of the PyC coating on the fiber interfaces. After that, generated geometry of the microstructure is meshed and utilized for calculation of the effective mechanical properties by FE method. Calculated elastic and thermal properties are closed to obtained using homogenization procedure and to experimental ones.

2nd Global Young Investigators Forum

Ceramic Hybrid Materials and Composites: Ceramic Matrix Composites, Biological and Medical Applications

Room: Coquina Salon F
Session Chairs: Bonex Mwakikunga, Council for Scientific and Industrial Research; Martin Seifert, University of Bayreuth

8:00 AM

(ICACC-GYIF-012-2013) Calculation of the Interlaminar Mode I Crack Growth Energy Release Rate of Carbon/Carbon Composites

T. Krause*, K. Tushtev, University of Bremen, Germany; D. Krause, German Aerospace Center, Germany; G. Grathwohl, University of Bremen, Germany

The Double Cantilever Beam test was used to investigate interlaminar crack propagation in mode I in a carbon fibre /carbon matrix composite. The main fracture mechanism was debonding at the inter-ply fibre-matrix interface which was accompanied by multiple small delaminations apart from the main crack. Six different methods for the calculation of the critical energy release rate were then evaluated in terms of their suitability to account for the specific fracture mechanisms present in carbon/carbon. A conservative estimation of the energy release rates for specimens with one main crack can be achieved by the modified compliance calibration method which considers the change of compliance in the cantilever arms. The occurrence of secondary cracks can only be taken into account by the integration of the load-displacement curve, but this method delivers less conservative values.

8:20 AM

(ICACC-GYIF-013-2013) Eosinophil peroxidase-mediated biodegradation of single-walled carbon nanotubes

F. Torres Andon*, Karolinska Institutet, Sweden; A. A. Kapralov, N. Yanamala, W. Feng, University of Pittsburgh, USA; A. Baygan, B. J. Chambers, K. Hultenby, Karolinska Institutet, Sweden; F. Ye, M. S. Toprak, Royal Institute of Technology, Sweden; B. D. Brander, A. Fornara, Institute for Surface Chemistry, Sweden; J. Klein-Seetharaman, G. P. Kotchey, A. Star, University of Pittsburgh, USA; A. A. Shvedova, NIOSH/CDC and West Virginia University, USA; B. Fadeel, Karolinska Institutet, Sweden; V. E. Kagan, University of Pittsburgh, USA

Single-walled carbon nanotubes (SWCNT) have high potential for applications in nanotechnology, electronics and medicine but may also exert adverse effects on human health and the environment. We aimed to study the biodegradation of SWCNT by eosinophil peroxidase (EPO), a mammalian peroxidase exocytosed by eosinophils, which is known to be actively involved in increased oxidant production during lung inflammation after exposure to pollutants and cigarette smoke. Incubation with recombinant EPO and H_2O_2 caused degradation of SWCNT over time. Biodegradation of SWCNT was higher in the presence of NaBr, but neither EPO alone nor H_2O_2 alone caused nanotube degradation. Computer modeling was used to structurally characterize possible SWCNT interaction sites with EPO. An ex vivo culture system was employed to generate large numbers of primary eosinophils at high purity from mouse bone marrow progenitors. Eosinophil degranulation was stimulated by lyso-PAF (platelet-activating factor) and cytochalasin B every 6 h. Biodegradation was evidenced by a range of methods including transmission electron microscopy (TEM), ultraviolet-visible-near-infrared (UV-vis-NIR) spectroscopy, and Raman spectroscopy (in vitro) or confocal Raman imaging (ex vivo). This is the first evidence of carbon nanotube biodegradation by eosinophil peroxidase.

8:40 AM

(ICACC-GYIF-014-2013) Controlled synthesis of SPIONs for biomedical applications

G. Salas*, iMdea Nanoscience, Spain; M. Calero, Universidad Autónoma de Madrid, Spain; C. Casado, F. J. Teran, iMdea Nanoscience, Spain; A. Villanueva, J. Camarero, Universidad Autónoma de Madrid, Spain; R. Miranda, iMdea Nanoscience, Spain; M. Morales, ICMM-CSIC, Spain

The synthesis of superparamagnetic iron oxide nanoparticles (SPIONs) has been intensively developed in the last years because of its many technological applications in biomedicine and other fields.[1] Properties of these nanomaterials strongly depend on their size and shape. The high-temperature decomposition of an iron precursor in organic media is one of the best methods to produce monodisperse particles, with good size control between 4 and 15 nm. Seed-growth methods are often employed to increase the size, although with some drawbacks related to structural defects in detriment of the magnetic properties of the particles. Here we present a modified thermal decomposition procedure that allow preparing monodisperse SPIONs with tuned sizes over 20 nm with good magnetic properties.[2] The relationship between magnetic and magneto-thermal properties with the size and size distribution of the SPIONs will be discussed. Current studies on cell internalization, toxicity and calorific power for hyperthermia treatment of tumors will be presented. [1] Tartaj, P. et al Adv. Mater. 2011, 23, 5243-5249. [2] Salas, G. et al J. Mater. Chem.DOI: 10.1039/C2JM34402E.

9:00 AM

(ICACC-GYIF-015-2013) Controlled Growth of Selectively Doped ZnO Nanocrystals on Calcium Aluminum Silicate Beads Support under Hydrothermal and Solvothermal Conditions for Enhancing Photocatalytic Activity

K. Byrappa, K. Namratha*, University of Mysore, India

ZnO is an attractive material for a wide range of applications owing to its multi-functional capabilities as electronics, photonics, acoustics, UV sensing, UV laser, gas sensor, etc. In recent years, ZnO finds extensive applications in the biomedical fields. In optical emitters, its high exciton binding energy (60 meV) gives ZnO an edge over the other semiconductors such as GaN, if reproducible and reliable p-type doping in ZnO were to be achieved, which currently remains to be the main obstacle for realization of bipolar devices. In this context extensive research work is being carried out on the synthesis of ZnO nanocrystals worldwide using a wide range of dopant metals to achieve the required p-type semiconductor properties. The authors have grown ZnO nanocrystals under mild hydrothermal and solvothermal conditions using a variety of solvents – both aqueous and non-aqueous in nature. Gluconic acid has been used as the surface modifier in order to control the size and morphology of the ZnO nanocrystals.

Ceramic Processing and Application: Novel Processing and Synthesis Routes

Room: Coquina Salon F
Session Chairs: Federico Miguel, Saarland University; Gorka Salas Hernandez, Ciudad Universitaria de Cantoblanco

9:40 AM

(ICACC-GYIF-017-2013) Brazing of Silicon Carbide (SiC) to Kovar for the Integration of Metallic Fuel Tubes into a Ceramic Lean Direct Fuel Injector

K. Alsup*, Case Western Reserve University, USA; M. C. Halbig, NASA Glenn Research Center, USA; M. Singh, Ohio Aerospace Institute, USA

With the increasing cost of fuel, a priority in the aviation industry is to develop more fuel efficient engines with reduced emissions. There is growing interest in the development of advanced fuel injection and control systems using the Micro-Electro-Mechanical System-based Lean Direct Injector (MEMS LDI). Silicon carbide has been chosen because of its capability to be integrated with high temperature fuel actuators and sensors for flow control and monitoring. However, for the implementation of silicon carbide into fuel injectors, ceramic to ceramic bonding for injector fabrication and ceramic to metal bonding for injector-fuel tubes integration have to be developed. Active metal brazing technology was developed for bonding of silicon carbide to Kovar (53Fe-29Ni-17Co-alloy) plates and tubes using a Ag-Cu-Ti alloy (63.0Ag-35.25Cu-1.75Ti) and copper interlayers. Various simple and complex shape joints were fabricated and evaluated using optical microscopy, scanning electron microscopy, energy dispersive spectroscopy, and Knoop hardness testing to determine the quality of the bond. Effect of joint configuration (tubes vs plates) on the braze penetration and spreading was also evaluated.

10:00 AM

(ICACC-GYIF-019-2013) SiCN/Nb-ceramic composite derived by precursor reaction

M. Seifert*, W. Krenkel, G. Motz, chair of ceramic materials engineering, Germany

A SiCN/Nb composite containing niobium silicides, nitrides and carbides was developed by a powder processing route, using a poly(carbo)silazane as reactive preceremic polymer and niobium powder as active filler. The starting composition was adjusted by a polymer/filler to generate on the one hand the NbN, NbC and NbxSiy phases and on the other hand to obtain zero shrinkage. The powder mixtures were uniaxial pressed and the polymer network was catalytically and thermally crosslinked. Pyrolysis in flowing argon at 1000 °C, 1400 °C and 1600 °C led to the formation of porous pellets. Qualitative and quantitative X-ray analysis proved the existence of Nb5Si3 and depending on the polymer/filler ratio different Nb(C,N) phases in the composites. Thermogravimetry was used to investigate the weight changes and dilatometer measurements were used to follow dimensional changes during the pyrolysis process. Pyrolysed samples were characterized by SEM, EDS and EBSD. Residual porosity was investigated with He pycnometry and BET. First results show an improvement of oxidation resistance and the ability to control phase formation, porosity and density by varying the polymer/filler ratio as well as the pyrolysis consitions.

10:20 AM

(ICACC-GYIF-020-2013) Ink-Jet Printing: An Efficient Way for Digitally Controlled Device Fabrication

M. Vaseem*, A. Hong, Y. Hahn, Chonbuk National University, Republic of Korea

Recently, inkjet-printing technique to fabricate semiconductor as well as conductive devices is considered as a most promising technology by which device fabrication can be possible via direct and simple steps without wasting processing materials. In ink-jet printing technology, only the requirement is to formulate ink using nanoparticles, which must be well suited for ink-jet printer heads (nozzles). Accordingly, based on various ink-formulations, until now polymer based photovoltaic, light emitting device, thin film transistors and organic semiconductor based thin film transistors, have been extensively studied. However, ink formulation and inkjet printed metal oxide based ink have been seldom reported. In this regards, we have successfully synthesized well dispersed uniform CuO and doped-ZnO nanoparticles formulated as an ink using mixed solvents of water, ethanol, isopropanol and diethylene. As-formulated inks samples were further Ink-jetted to make uniform pattern lines on various substrates. It is observed that wt % of CuO nanoparticles and types of dopant in ZnO, separately, in as-formulated inks were very important to produce uniform pattern line with smooth edge definition and controlled electrical behavior. In this paper, we present the first results of inkjet printed CuO and doped-ZnO field effect transistors (FET) on Si/SiO2 (gate material) substrate.

10:40 AM

(ICACC-GYIF-021-2013) Progress in Ultrasonic Spray Pyrolysis for Ceramic Materials Sciences Developed From Ultrasonic Nebulization Theories Since Michael Faraday

B. W. Mwakikunga*, Council for Scientific and Industrial Research, South Africa

This review presentation outlines, in great detail, the history of the phenomenon of ultrasonic nebulization of liquids since the discovery of such an effect by Michael Faraday and the explanation of the phenomenon by capillary wave mechanism and “cavitation” hypothesis. Ultrasonic spray pyrolysis for materials processing (especially ceramics) and the theories that predict the final particle size and particle size distribution are discussed. The popularity of the technique is shown by the rising number of research groups in the world processing various materials by this method due to its cost-effectiveness, purity of its products and controllability of particle size as well final properties

11:00 AM

(ICACC-GYIF-022-2013) Morphology Evolution and Phase Evaluation in MAX Phase – Shape Memory Alloy Interpenetrating Composites

L. Hu*, A. Kothalkar, I. Karaman, M. Radovic, Texas A&M University, USA

Herein we report on the fabrication of MAX phase – shape memory alloy (SMA) interpenetrating composites by spark plasma sintering

(SPS) from Ti3SiC2 or Ti2AlC powders and Ni50Ti50 or Ni50.4Ti49.6 prealloyed powders at temperatures in 960 – 1100 oC temperature range under 100 MPa uniaxial pressure. The microstructure and phase composition along the interfaces of these two-phase composites were studied using Scanning Electron Microscopy (SEM) and Energy-Dispersive Spectroscopy (EDS). The morphology and phases near the interfaces depend significantly on starting powders, sintering temperature and holding time. Differential Scanning Calorimetry (DSC) has been carried out to confirm the martensitic phase transformation, and estimate the fraction of transformable NiTi phase in the SPSed composite samples. Reactivity between equiatomic NiTi or Ni rich NiTi and Ti3SiC2 or Ti2AlC is also discussed, along with practical implications of optimized conditions for fabricating MAX phase –SMA interpenetrating composites with thin interface and high fraction of transformable NiTi phase.

S1: Mechanical Behavior and Performance of Ceramics & Composites

Processing, Microstructure and Mechanical Properties Correlation II

Room: Coquina Salon D
Session Chairs: Shaoming Dong, Shanghai Institute of Ceramics, CAS; Sivakumar Ramasamy, The University of Akron

1:30 PM

(ICACC-S1-023-2013) High Fracture Toughness-High Strengthe Ceramics for Welding Applications

V. D. Krstic*, Queen's University, Canada

A new generation of partially stabilized zirconia and silicon nitride ceramics possessing combination of high fracture toughness and strength are presented. In the case of zirconia, the role of stabilizing agents on the level of tetragonal phase and grain size is discussed. In the case of silicon nitride, the effect of sintering aids on microstructure and mechanical properties is discussed. The result of this study is the material with fracture toughness of over 15 MPa.m1/2 and fracture strength of over 1150 MPa. This new class of structural ceramics finds applications as weld/guide pins in resistant welding where the life of the pins have been increased by a factor of 5-10 compared to ceramic coated metal pins.

1:50 PM

(ICACC-S1-024-2013) Scientific Fundamentals and Industrial Applications of Superhard Nanocomposite Coatings

S. Veprek*, Technical University Munich, Germany

The recent search for super- and ultrahard materials conducted by many groups has concentrated on those with high elastic moduli. However, plastic deformation occurs in shear upon a large strain at atomic level, where the electronic structure may undergo instabilities. Therefore many solids with a high value of elastic moduli undergo structural transformations to a softer phase. Therefore I shall concentrate on the recent progress in the understanding of the origin of the superhardness in nc-TmN/a-Si3N4 nanocomposites (Tm = Ti, V, Mo, …, in which 3-4 nm size TmN nanocrystals are "glued" together by about 1 monolayer (1 ML) thick SiNx interface. Simple calculation shows that these materials can reach hardness in the range of diamond when correctly prepared and essentially free of defects. I shall also briefly discuss some recent criticism of our earlier results and show that the hardness of 80 to ≥ 100 GPa reported by us in quasi-ternary nc-TiN/a-Si3N4/TiSi2 nanocomposites has been correctly measured. Finally, I shall briefly summarize the present industrial applications of the nanocomposite coatings on tools for machining, forming and the like, and discuss the possibilities of further improvement of the presently available nanocomposites, in particularly the issue of impurities.

2:10 PM

(ICACC-S1-025-2013) Fabrication of cBN reinforced Y-α-SiAlON composites through the SPS technique

J. C. Garrett*, I. Sigalas, M. Herrmann, University of the Witwatersrand, South Africa

Dense α-Sialon-cBN composites were produced by FAST/SPS – sintering at 1575-1625°C. The hardness of the materials increases only up to 21 GPa for materials with 10 vol.% cBN. On the other hand the fracture toughness increases up to nearly 8MPam^{½} with 30 vol.% cBN. The reason for the increase in fracture toughness is attributed to crack deflection at cBN grains due to the weak bonding of the grains in the matrix. The weak interfaces are also responsible for the moderate increase in the hardness of α-Sialon-cBN composites. The produced composites have superior hardness (by as much 5 GPa) to that of reported β-Sialon-cBN composites.

2:30 PM

(ICACC-S1-026-2013) Processing, structure and mechanical behavior of (Si)-B-C ceramics

F. Teyssandier*, C. Pallier, G. Chollon, W. Patrick, J. Leyssale, CNRS-LCTS, France; C. Gervais, LCMCP Paris 6 Collège de France, France; H. Fischer, F. Sirroti, Synchrotron SOLEIL, France

Amorphous B-C and Si-B-C ceramics were deposited by CVD from BCl3-CH4-H2 and BCl3-CH3SiCl3-H2 mixtures, respectively, at temperatures around 1000°C and reduced pressure. All the as-deposited (Si)-B-C ceramic coatings are nearly amorphous and consist of a common very disordered boron carbide phase (BxC) and, in the Si-B-C coatings, sub-nanometric SiC crystals. The structure and crystallization behavior in inert atmosphere of the (Si)-B-C ceramics were investigated as a function of the elemental composition and the annealing temperature and time. Ex-situ analyses were conducted by heat-treating the specimens under high vacuum at different temperatures/durations. The structure was characterized at short and long range, by solid MAS-NMR, Raman microspectroscopy, neutron diffraction, X-ray absorption, X-ray diffraction and transmission electron microscopy. The structural model was confirmed by liquid quench molecular dynamics simulation. High temperature tensile tests were performed on model 1D composites consisting of (Si)-B-C coatings deposited on soft carbon monofilaments. These micro tensile tests allow the evaluation of the changes of (i) the volume (or density), (ii) the Young's modulus, (iii) the creep rate and (iv) the thermal expansion of the coatings. The results obtained on the various materials are discussed on the basis of their elemental composition, initial structure and processing conditions.

2:50 PM

(ICACC-S1-027-2013) Non-Reactive Processing Methods for Producing Biomorphic Graphite/Copper Composites

A. E. Childers*, K. T. Faber, Northwestern University, USA

Scientific interest has increased in copper/graphite composites for use in thermal management applications and energy devices. By using a biomorphic ceramic graphite scaffold produced from wood, it is possible to create anisotropically porous graphite with relative ease of processing as compared to traditional porous ceramic-processing methods. However, molten copper does not readily wet to graphite and the compounds used in reactive wetting solutions are detrimental to the thermal properties of the system. Therefore, two non-reactive methods have been investigated – pressure-assisted melt infiltration and electrodepositon, with the latter having the added bonus of being a low-temperature process. This talk will compare the effect of processing method on the composite properties, including the extent of copper infiltration, microstructure of the constituent phases, and resulting structural integrity of the ceramic scaffold.

3:30 PM

(ICACC-S1-028-2013) Towards a Multiscale Model of Thermally-Induced Microcracking in Porous Ceramics

R. S. Fertig*, University of Wyoming, USA; S. Nickerson, Corning Incorporated, USA

The tendency for ceramic materials with high thermal expansion anisotropy to crack at domain boundaries during thermal cycling has been extensively documented. However, much work still remains to develop a model that can predict this behavior as a function of thermal history. Here we present the development of a mechanism-based model that accurately predicts the temperature history-dependent behavior observed during thermal cycling of a porous ceramic, including elastic modulus hysteresis, microcrack formation, and microcrack healing. The functional forms describing the mechanisms in this model were developed from detailed study of a microscale finite element model, which will also be discussed. Excellent agreement between experimental results and model predictions are shown.

3:50 PM

(ICACC-S1-029-2013) Investigation on reliability of high alumina refractories

W. Yuan*, Q. Zhu, C. Deng, H. Zhu, Wuhan University of Science and Technology, China

Refractories are key materials in high temperature industry including steel making, cement and glass manufacturing. Because of its poor plasticity, refractories are sensitive to several parameters including pores and phase compositions, and the random of the parameters leads to great scatter of strength data. In this study, the flexural strength of high alumina refractories has been statistically analyzed by Weibull distribution based on the data of thirty-five bending tests for every kind of samples. The reliability of the flexural strength of high alumina refractories was evaluated. The phase composition and fracture surface morphology of samples was characterized by X-ray diffraction and scanning electron microscope respectively. The results demonstrated that the difference of Weibull modulus value of high alumina bricks is obvious because of the different chemical and phase composition. The ranges of failure probability were determined using the Weibull estimates. The mullite particles have been close bonded in high alumina refractories with appropriate amorphous phase, which has higher Weibull modulus and scale parameter.

4:10 PM

(ICACC-S1-030-2013) Porous oxide ceramic matrix composites produced by the lamination of thermoplastic prepregs

P. O. Guglielmi*, Technische Universität Hamburg-Harburg, Germany; D. Blaese, M. P. Hablitzel, D. P. Goulart, M. C. Fredel, D. Hotza, Universidade Federal de Santa Catarina, Brazil; R. Janssen, Technische Universität Hamburg-Harburg, Germany

A new concept for the production of porous oxide ceramic matrix composites (OCMCs) was developed and used to produce alumina fiber reinforced samples. This new route is based on the lamination of thermoplastic prepregs produced with paraffin-based suspensions of the matrix powder (in this work a mixture of 80 vol% Al_2O_3 and 20 vol% ZrO_2). For a better infiltration of fiber bundles, fiber textiles were infiltrated with a liquid slurry of the matrix prior to lamination. The advantage of using prepregs laminated with paraffin-based suspensions is the possibility of joining different OCMC parts in the green state to form complex-shaped composites. Additionally, the shelf life of these prepregs is much longer than those produced with conventional liquid slurry infiltration. 3M™ Nextel™ 610 woven fabrics were used as reinforcement and the prepregs were laid up in a cross-ply configuration, followed by warm-pressing, debinding and sintering. Microstructural analysis of the sintered OCMC samples showed very good adhesion of the different prepregs. No delamination or joining lines were detected. Matrix porosity was about 38 vol% after sintering the OCMCs at 1200°C. Fiber volume fractions of about 33 vol% were achieved. First mechanical characterization showed strength values of approximately 350 MPa in 4-point bending tests and 7 MPa interlaminar shear strength in short beam shear experiments.

4:30 PM

(ICACC-S1-032-2013) Microstructure and Mechanical properties of In-situ processed B4C-HfB2 Composites

S. Kannan, T. Murthy*, J. Sonber, C. Subramanian, R. Hubli, A. Suri, Bhabha Atomic Research Centre, India

Fully dense B4C-HfB2 ceramic composites were fabricated by in-situ processing using B4C, HfO2 and CNT, as starting materials. The effect of HfO2 content on microstructure and mechanical properties of B4C composite has been investigated. Additions of 2.5 – 30 wt% HfO2 resulted in improvement in density and mechanical properties. On increasing HfO2 content, the fracture toughness of the composite increased more than twice that of monolithic B4C, whereas hardness decreased by about 12%. Elastic Modulus of the composites was measured to be in the range of 570-615 GPa. Crack deflection observed in the composites was found to be the major toughening mechanism due to the existence of residual thermal stress. The maximum values of hardness, fracture toughness and elastic modulus were 35 GPa, 6.7 MPa m1/2, and 615 GPa, respectively.

4:50 PM

(ICACC-S1-033-2013) Densification of SiC with AlN- Nd2O3 sintering additives

L. Wu*, Y. Jiang, W. Sun, Y. Chen, Z. Huang, Beifang University of Nationalities, China

Rare earth oxides are used as sintering additives of silicon carbide frequently. Together with AlN, the rare earth oxides (Y2O3, La2O3, Nd2O3 and so on) forms sintering additive systems of AlN-R2O3, which enhance the densification of the SiC. Solid solution of R2AlO3N are also found with some of the rare earth additives. The present research concerned with AlN-Nd2O3 sintered SiC. The sintered samples were analyzed by X-Ray diffraction, Electron Probe Microscopic Analyzer and Scanning Electron Microscope. Base on the experiments results, it indicates that the particle size of Nd2O3 plays an important role in the microstructure and the properties of the sintered bodies. Coarse Nd2O3 particles(more than 10 microns) are hardly reacted completely during the sintering. The grains did not participate in the thermal chemical reaction caused the samples pulverizing in a few days because Nd2O3 is easy to be hydrated. Fine particles react thoroughly during the sintering with no residues of Nd2O3 left in the ceramics. It helps the sintered materials to gain stability and better properties.

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

Thermal Barrier Coatings II

Room: Ponce DeLeon
Session Chair: Kevin Plucknett, Dalhousie University

1:30 PM

(ICACC-S2-021-2013) Materials R&D Within DOE's Advanced Turbine Program

B. White, P. Burke*, Dept. of Energy, USA

Development of an electric power generation technology that efficiently and economically utilizes coal and natural gas while meeting current and projected environmental conservation requirements is of crucial importance to the United States. With that objective, 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 turbine technology. Material research and development is a key part of FE's Advanced Turbine Program, which is focused on increasing turbine output and efficiency, while maintaining low capital costs and viable service lifetimes. Enabling the increase in firing temperatures remains a central theme and this is being accomplished through developments in substrate alloys, bond coats, and thermal barrier coatings. In addition to more traditional advancements of the state of the art, the project portfolio also covers novel manufacturing routes to internally-cooled airfoils and ceramic matrix composites. An effort on materials for supercritical CO2 cycles has also just begun. Materials development highlights will be presented within the context of DOE's Advanced Turbine Program.

2:00 PM

(ICACC-S2-022-2013) Effect of microstructure on the fracture toughness of plasma sprayed thermal barrier coatings

G. Dwivedi, V. Viswanathan*, Stony Brook University, USA; A. Shyam, E. Lara-Curzio, Oak Ridge National Lab, USA; S. Sampath, Stony Brook University, USA

Recent studies have suggested that interfacial fracture toughness of the thermal barrier oxides is a key parameter affecting coating durability. Double torsion technique was used to determine the fracture toughness of plasma sprayed yttria stabilized zirconia (YSZ) and Gd_2ZrO_7 coatings deposited at different processing conditions in order to assess the role of chemistry and microstructure. The results indicated that the fracture toughness of coatings depends on starting microstructures for both the coating materials. Coatings with higher overall porosity and interfacial defects showed lower fracture toughness than those with lower defect content. In addition, the Gd_2ZrO_7 coatings showed significantly lower fracture toughness values than YSZ coatings. Furthermore, measurements on YSZ coatings exposed to different thermal aging durations (10, 25 and 50 hours) at 1200^{o}C revealed an increase in fracture toughness with initial aging followed by limited changes for extended durations. These results indicate the critical role of processing on the durability of thermal barrier coatings.

2:20 PM

(ICACC-S2-023-2013) Thermal Barrier Coatings Degradation Mechanisms in Land Based Gas Turbines

G. Witz*, B. Bordenet, H. Bossmann, Alstom Power, Switzerland

It is important to understand the degradation mechanisms of thermal barrier coating that can occur during engine operation such to develop accurate lifing models and coating lifetime improvement. A careful study of the coating degradation mechanisms has shown that the failure mechanisms of thermal barrier coating systems thicker than ~1mm is different than the one of thinner thermal barrier coating systems. In thick coatings systems, cracks grow in the thermal barrier coating far from the bondcoat interface, whereas in thin coating system, the dominant degradation mechanism is linked to bondcoat oxidation. This required the development of two independent thermal barrier coating lifing models. Some engine operation factors can lead to the occurrence of accelerated degradation mechanisms. For instance, bondcoat corrosion can lead to early coating loss due to a reaction between the bondcoat corrosion products and the thermal barrier coating. In such cases, understanding of the bondcoat corrosion kinetic is not sufficient to describe and predict the thermal barrier coating life and more complex experiments have to be developed for laboratory testing. Various coating degradation mechanisms and the associated laboratory testing strategies for coating lifing or ranking will be discussed.

2:40 PM

(ICACC-S2-024-2013) Evaluation of Thermal Degradation of Thermal Barrier Coatings

J. Sun*, Argonne National Laboratory, USA

Thermal barrier coatings (TBCs) are widely used to improve the performance and extend the life of combustor and gas turbine components. TBC degradation occurs during the high-temperature applications. Under a simplified model, a TBC undergoes an initial sintering process with a continued increase in stiffness. This, combined with the increased stress at the interface due to the growth of thermally growing oxide, causes TBC cracking near the interface and eventual TBC delamination and spalling. The material degradation, sintering and cracking, also affects TBC's optical and thermal properties, so can be monitored by optical and thermal methods. In this study, we evaluated TBC samples exposed in thermal cycling tests using nondestructive (NDE) and destructive examination methods. The NDE methods included laser backscatter, mid-IR reflectance, and thermal imaging based on a multilayer analysis method. The TBC degradation was characterized by the change of TBC's optical and thermal properties as a function of the exposure level represented by the Larson-Miller parameter. It was identified that contamination may affect the results of these NDE methods. The detected damages are being verified by sectioning microstructural analysis. This paper presents the NDE methods, experimental results, and TBC degradation modeling.

Coating for Tribological Applications

Room: Ponce DeLeon
Session Chair: Shanghua Wu, Guangdong University of Technology

3:20 PM

(ICACC-S2-025-2013) Innovative ceramic like coatings for tooling, machining, aerospace, energy and automotive industry (Invited)

P. H. Mayrhofer*, Vienna University of Technology, Austria

This work summarizes recent developments on applying thin film structure and architecture concepts to hard coatings for optimized performance in various application fields. Hard coatings deposited by plasma-assisted vapour deposition are widely used to reduce friction and wear of tools and engineering components in energy, automotive and aerospace industry. We will look in more detail into the correlation between microstructure and mechanical and thermal properties of hard ceramic coatings. This is done for single-phase coatings and composition or phase modulated layers. In the latter case, the microstructure can be designed by choice of the deposition technique, understanding the growth processes taking place on a film surface, either by sequential deposition of layers or by taking advantage of self-organization processes including segregation effects of the elements. Consequently, the effects of individual microstructural features like grain size, defect density, phase arrangements in an one-, two- or three-dimensional manner on the mechanical properties are treated. The microstructural changes of hard ceramic coatings during a post-deposition annealing treatment are discussed in detail. The various thin film structure and architecture concepts allow the utilization of multifunctional properties facilitating the development of next generation's hard coatings.

3:50 PM

(ICACC-S2-026-2013) Zirconia Coating on Stainless Steel with Growing Integration Layer [GIL] Oxides (Invited)

M. Yoshimura*, K. Chen, Y. Lin, C. Hwang, National Cheng Kung University, Taiwan

Zirconia coating on stainless steel(SS) is important in various applications like thermal barrier, anti-corrosion, energy, solid oxide fuel cell, bio-medical, etc. In those applications, the adhesion is the most serious problem. We have succeeded well adhered zirconia coating on SS304 with a novel "Growing Integration Layer"[GIL] concept, where grown oxide film(s) from SS304 would prepare intermediate layer(s) between zirconia and SS substrate. The intermediate oxide layer of FeCr2O4 –rich with 50-400 nm thickness could be fabricated by the anodization of SS plate in a H2SO4 + HNO3 solution at 70 C by a square wave pulses(E =1.2 V,E = 0.8 V, and 0.3 Sec interval). Pure and CeO2-doped Zirconia films were fabricated on those GIL substrates by Dip-Coating from precursor solutions, where Polyvinyl

Alcohol (PVA) was used as Complex- and Gel-formation agent . After calcined at 300 C in air zirconia coating films with 100-500 nm thick were obtained. Improved adhesion by scratch tests and increased corrosion potentials by 0.1-0.5 Volts were confirmed by Tafel-plot. The effects of anodization condition and Dip-Coating have been optimized.

4:10 PM

(ICACC-S2-028-2013) Structure and properties of some PVD coatings on ceramic cutting inserts for dry and high speed cutting processes (Invited)

Y. Long, Q. Wang, S. Wu*, Guangdong University of Technology, China

Ceramic tools have high resistance to heat and to wear and can be used to machine metals that are extremely hard. These attributes allow them to be used to machine metals at high cutting speeds and in dry machining conditions. Hard coatings have been widely applied on high-speed steel tools and cemented carbide cutting tools. The coatings can provide high hardness, anti-friction, chemically inertness and thermal isolating properties. As such, coated tools compared to uncoated ones, offer better protection against mechanical and thermal loads, diminish friction and interactions between tool and chip and improve wear resistance in a wide cutting temperature range. However, up to now, relatively less research has been conducted on coated ceramics cutting tools than those on coated cutting tools of high-speed steel and cemented carbide. In the present work, CrTiAlN, AlCrN, and Al2O3 coatings were deposited on Al2O3+TiC and Si3N4 inserts using reactive unbalanced magnetron sputtering. Coated cemented carbide inserts were used for comparison. The surface morphology, microstructures, chemical composition, hardness, interfacial adhesion and wear properties of the coatings were investigated. The evaluation of these inserts for turning hardened steels was also conducted. The related wear performance of the coatings were recorded and analyzed.

4:30 PM

(ICACC-S2-029-2013) Surface Boriding of Titanium Alloys

T. Sarkar, B. Blakney, P. Bishop, K. P. Plucknett*, Dalhousie University, Canada

The effects of a simple thermochemical surface treatment process, known as pack boriding, have been assessed for both Grade 2 commercially pure titanium and the Grade 5 alloy Ti-6Al-4V. Boriding was achieved by vacuum heat treatment of alloy samples, held within a proprietary B4C-based powder bed, at temperatures between 950 and 1150C, for up to 24 h. After boriding, the surface diffusion layers were assessed using x-ray diffraction, together with both optical and scanning electron microscopy. Dual layer, ceramic coatings (comprising of TiB and TiB2) were formed using this approach, with the coating thickness increasing with both boriding temperature and time. TiB formed in a 'whisker-like' morphology, penetrating into the substrate material (with whiskers up to 25-30 μm long), while TiB2 comprised the outer layer (up to 7-8 μm thick after heat-treatment at 1150C for 24 hours). Under the most extreme conditions (i.e. 1150C for 24 hours), Al2O3 was also observed to form on the outer boride surface layer. Vickers hardness measurements, showed a consistent increase with temperature and/or time. Tensile testing demonstrated that the ultimate tensile strength was consistently reduced in comparison to the as-received extruded titanium (typically by 5-10 %).

4:50 PM

(ICACC-S2-030-2013) Characterization and Performance of TiB2 Coatings on SiAlON Ceramic Cutting Tools

S. Turan*, Anadolu University, Turkey; H. Alagoz, E. Uzun, Bilkent University, Turkey; S. Ulukut, Anadolu University, Turkey; E. Bengu, Bilkent University, Turkey

In this study, influence of titanium diboride (TiB2) coatings on the performance of SiAlON ceramic cutting tools was investigated. TiB2 coatings were initially deposited and optimized on 100Cr6 steel discs. Coatings were sputter deposited from two TiB2 compound targets using an industrial scale DC Magnetron Sputtering system. We used x-ray diffraction technique to find out the phase composition present in the films. The hardness values of the films were measured using the nano-indentation technique and we used a high-temperature tribometer (up to 800°C) to investigate the wear-rates of the coatings. Our results indicated that cubic TiB phase was the dominant phase in the coatings. Hardness values up to 30 GPa at RT was measured. Surprisingly, hardness was improved after treatment at 500oC. Wear performances of the coatings were considerably good at both RT and 500oC performed against an alumina ball of 6 mm diameter. Wear rates were ~7.0x10-6 mm3/Nm at RT and ~9.0x10-6 mm3/Nm at 500oC. The microstructure of the coatings were characterized by using analytical scanning electron microscopy and transmission electron microscopy techniques such as energy dispersive x-ray spectrometer and electron energy loss spectrometer. Finally, we have used same deposition parameters to deposit TiB2 coatings on ceramic tools made out of SiAlON to investigate the cutting performance of the coated tools.

S3: 10th International Symposium on Solid Oxide Fuel Cells (SOFC): Materials, Science and Technology

Electrodes I

Room: Coquina Salon H

Session Chairs: Meilin Liu, Georgia Tech; Fanglin (Frank) Chen, University of South Carolina

1:30 PM

(ICACC-S3-009-2013) Recent Progress in Modeling and In Situ Characterization of SOFC Electrode Processes (Invited)

M. Liu*, Georgia Tech, USA; K. Blinn, X. Li, S. Lai, M. Lynch, Georgia Institute of Technology, USA

The performance of solid oxide fuel cells (SOFC) are often limited by the charge and mass transfer along surfaces and across interfaces. Fundamental understanding of the rate-limiting steps is vital to achieving rational design of new electrode materials or structures with dramatically enhanced functionality. This presentation will highlight some recent advances in multi-scale modeling and in situ characterization of electrode processes in order to optimize electrode performance through surface modifications. Raman spectroscopy has been used for probing and mapping new phases and reaction intermediates on electrode surfaces under operating conditions. Further, synchrotron-based XRD and XAS have been used to characterize the atomistic structure, composition, and electronic structure of electrode surfaces and interfaces. These studies, together with multiscale modeling and simulation, have helped us to develop new surfaces and interfaces with unique functionalities. For example, we have demonstrated that the electrocatalytic activity and durability of widely-used electrodes can be enhanced by the introduction of a catalytic coating.

2:00 PM

(ICACC-S3-010-2013) Electronic Property of Mn and Fe doped CeO_2 as an Oxide Anode for Solid Oxide Fuel Cell using $LaGaO_3$ base Electrolyte Film (Invited)

T. Ishihara*, J. Ju, S. Ida, Kyushu University, Japan

Nonstoichiometry and mixed electronic-oxide ionic conductivity of Mn and Fe doped CeO_2 (CMF) was studied for oxide anode of SOFC. It was found that CMF shows superior property of anode for SOFC using $LaGaO_3$ base electrolyte. In this study, application of Fe and Mn doped CeO_2 film with nano size thickness for dense anode of SOFC using thin film of LaGaO3 prepared with PLD method and it was found that CMF is highly active for anode reaction in spite of dense shape. In addition, doped CeO_2 is also effective for preventing Ni diffusion into $LaGaO_3$ electrolyte film and so Mn. Fe co-doped CeO_2 shows bi-functional role for solid oxide fuel cells using $LaGaO_3$ perovskite electrolyte film. Mixed electronic and oxide ionic conductivity in CeO_2 is much improved by doping both Mn and Fe. Although solid solubility limit of Mn exists around 20 mol%, no impurity phase was observed by addition of Fe suggesting the solubility limit of Mn is much expanded by addition of Fe. By inserting CMF dense nano film between Ni-Fe substrate and LSGM electrolyte, the power density of the cell was much improved, in particular, at intermediate temperatures. The maximum power density became higher than 3 W/cm^2 at 973 K and ca.0.2W/cm^2 was achieved at 673 K.

2:30 PM

(ICACC-S3-011-2013) Heterogeneous Functional Ceramic Anodes for Solid Oxide Fuel Cells (Invited)

G. Xiao, C. Yang, University of South Carolina, USA; Z. Yang, China University of Mining & Technology, China; X. Dong, Q. Liu, L. Zhang, F. Chen*, University of South Carolina, USA; M. Han, China University of Mining & Technology, China

Solid oxide fuel cells (SOFCs) can convert chemical energy to electrical energy with high efficiency and fuel flexibility. The conventional Ni-based anode has low tolerance to sulfur-contamination, is vulnerable to deactivation by carbon build-up (coking) from direct oxidation of hydrocarbon fuels, and suffers volume instability on redox cycling. The objective of this study is to explore ceramic-based heterogeneous functional materials as SOFC anodes that possess a combined property of good sulfur tolerance, coking resistance and redox cyclability. The general philosophy to design SOFC ceramic anodes applied in this work is to develop ceramic materials that are redox-stable, possess mixed ionic and electronic mixed conductivity, and have catalytic activities for fuel oxidation. Four different types of ceramic anode materials have been explored and characterized as SOFC anodes, including LaGaO3-based materials, LaCrO3-based materials, Sr2FeMoO6-based materials, and SrFeO3-based materials. The phase formation, redox-stability, electrical conductivity, electrochemical performance, and tolerance to sulfur contaminants have been systematically evaluated. By judicious design of ceramic-based heterogeneous functional materials, high performance sulfur-tolerant redox-flexible ceramic anodes have been achieved for direct oxidation of hydrocarbon fuels.

3:20 PM

(ICACC-S3-012-2013) Structural and Electrochemical Characterization of Fe-Substituted Perovskite Anodes for Solid Oxide Fuel Cells

D. Fowler*, S. Cho, J. Haag, S. A. Barnett, K. R. Poeppelmeier, Northwestern University, USA

Two Fe-substituted perovskite compounds with different Fe concentrations — $La_{1-x}Sr_xFe_xCr_{1-x}O_{3-\delta}$ (LSFeCr) and $SrTi_{1-y}Fe_yO_{3-\gamma}$ (STF) — were synthesized by solid state reaction and tested as solid oxide fuel cell (SOFC) anodes. The $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\varepsilon}$ electrolyte-supported cells consisted of $La_{0.4}Ce_{0.6}O_2$ barrier layers, LSFeCr-$Gd_{0.1}Ce_{0.9}O_{2-\beta}$ (GDC) or STF-GDC composite anodes, and $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\alpha}$ cathodes. Oxygen deficiencies up to $\delta = 0.08$ for LSFeCr and $\gamma = 0.16$ for STF were observed under reducing conditions at 800 °C by thermogravimetric analysis. Unit cell sizes decreased as Fe content increased for both air-synthesized compounds and increased upon reduction of STF in 5% H_2 / 95% Ar, as determined by powder X-ray diffraction. Anodes with higher Fe contents (up to $x = 0.67$ and $y = 0.7$) yielded lower polarization resistance for both compounds. They were stable against decomposition in typical fuel conditions. Cells tested in humidified H_2 at 800 °C achieved anode polarization resistances of 0.32 $\Omega{\bullet}cm^2$ for LSFeCr and 0.17 $\Omega{\bullet}cm^2$ for STF. Peak power densities were 255 mW/cm^2 for LSFeCr and 337 mW/cm^2 for STF, limited largely by the thick electrolyte. The improved anode performance with increasing Fe content may be attributed to the oxygen loss, which should introduce significant ionic conductivity to these predominantly electronically conducting perovskites.

3:40 PM

(ICACC-S3-013-2013) Promising anode material for medium temperature SOFCs based on SDC electrolyte

K. Tamm*, University of Tartu, Estonia; R. Küngas, University of Pennsylvania, USA; E. Lust, University of Tartu, Estonia; R. J. Gorte, University of Pennsylvania, USA

Ceramic materials with the perovskite structure are considered as promising alternatives to Ni-based SOFC anodes. Highly conductive doped rare earth vanadates, such as $La_{0.8}Sr_{0.2}VO_3$, are particularly interesting materials for SOFCs anode application operating within the temperature range 773-973 K. $La_{0.8}Sr_{0.2}VO_3$-SDC anode and $La_{0.8}Sr_{0.2}CoO_3$-SDC cathode investigated in this study were fabricated by infiltrating the porous scaffold of $Ce_{0.8}Sm_{0.2}O_2$ (SDC) with an aqueous solution of nitrates. To enchase catalytic activity, CeO_2 and Pd were added into the anode composite. In some experiments bulk anode SDC scaffold microstructure was modified using wet HF etching for 1h. Electrochemical measurements were carried out with the cathode exposed to air and the anode exposed to humidified (3% H_2O) H_2 or CH_4. Very low total polarization resistance values, 0.28 $\Omega\ cm^2$, were obtained from impedance spectra already at 873 K in humidified H_2, decreased to 0.10 $\Omega\ cm^2$, if an anode SDC bulk electrode scaffold surface area increased from 0.32 m^2/g to 0.53 m^2/g by HF treatment. Good performance has been established if humidified CH_4 was used as a fuel. The resistance values at 873 K being 0.57 $\Omega\ cm^2$ and 0.45 $\Omega\ cm^2$ for untreated and HF-treated single cell, respectively. The HF-treated single cell showed low degradation in performance during 38 h in humidified H_2 or CH_4 working at 873 K and cell potential value 0.7 V.

4:00 PM

(ICACC-S3-014-2013) Nickel Pattern anodes for studying SOFC electrochemistry

H. Patel*, V. Venkatraman, P. Aravind, Technical University of Delft, Netherlands

The SOFC anode is a complex 3D structure where the gas phase, ionic phase and electronic phases are intermingled heterogeneously. This not only makes it difficult to quantify the triple phase boundary (TPB) length exactly, but also makes individual processes like charge transfer, diffusion, surface diffusion etc, difficult to localise and study. Pattern electrodes offer the advantage of having a well defined TPB length, so that reactions are localised. Impedance spectroscopy on pattern electrodes can provide mechanistic information in addition to identifying rate limiting steps. In this work nickel is sputtered on YSZ with DC magnetron sputtering using a Nickel target and a metallic mask on YSZ substrate in a specific pattern to give a well-defined TPB length. A TPB length of 0.2027 m/cm2 was achieved. This method is much easier and is less expensive than the photolithographic techniques used earlier (Bieberle et al ETH Zurich, Mizuzaki et al Yokohama National University and Boer de et al University of Twente). Impedance spectroscopy is carried out on symmetrical cells in pure hydrogen with 4.3 % water vapour. Preliminary results from equivalent circuit fitting of the impedance spectra indicate that the results are comparable to results available in literature and the rate limiting mechanisms can be identified. A detailed analysis of the results will be presented subsequently in the manuscript.

4:20 PM

(ICACC-S3-015-2013) Infiltrated Y-doped SrTiO3-based Anodes for Solid Oxide Fuel Cells

A. Torabi*, T. R. Etsell, University of Alberta, Canada

The purpose of this work is to study the electrochemical behavior of infiltrated YST-based sulfur tolerant anodes. 0.3 mm thick YSZ discs were used as the electrolyte as well as the mechanical support. A thin porous YSZ scaffold was used as a support for the anode and cathode electrodes. Solution impregnation was used to incorporate YST precursor into the YSZ scaffold as an anode, and LSM precursor into the scaffold as a cathode. The perovskite phases were to be prepared in-situ. It was found that both the purity and crystal size of the titanate depend on the in-situ treatment procedure. This also affects the electrochemical performance to a great extent. Both V-i characteristics and ac impedance studies showed that under hydrogen fuel with different H2S contents, the more H2S in the fuel, the better the performance. Such performance improvement upon H¬2S introduction was much stronger with methane fuel. While the cell performed very poorly under humidified methane (power density <5 mW/cm2), it showed a large performance increase when 5000 ppm H2S was introduced into the fuel (power density >35 mW/cm2). The V-i behavior under methane was, however, abnormal as a decrease in current density was observed at lower cell voltages (typically <0.5 V). This study shows that H2S can highly promote the methane conversion reactions on YST-based anodes.

4:40 PM

(ICACC-S3-016-2013) Ni Modified WC-based Anode Materials for Direct Methane Solid Oxide Fuel Cells

A. Torabi*, T. R. Etsell, University of Alberta, Canada

The purpose of this work is to investigate the performance of solid oxide fuel cells based on Ni-CeO2-WC-YSZ (NCWZ) composite anodes under humidified methane fuel. 0.3 mm thick YSZ discs were used as the electrolyte as well as the mechanical support. A thin porous YSZ scaffold was used as a support for the anode and cathode electrodes. WC, Ni and CeO2 were incorporated into the YSZ scaffold to prepare the anode and LSM was incorporated into the YSZ scaffold to prepare the cathode by solution impregnation. Ac impedance analysis under open circuit potential showed no carbon formation at 850°C with humidified CH4. Also, no degradation was observed during a stability test under a constant voltage of 0.7 V at 850°C for a period of 24 h under humidified CH4 neither because of instability of the carbide phase nor due to carbon formation on the Ni modified WC-based anode. Furthermore, the cell successfully survived an oxidation-reduction-recarburization cycle. It was found that when a WC-based anode is modified with Ni, not only can the attributes of nickel be taken advantage of, but its tendency toward catalyzing the build-up of carbon could be beneficial. These results suggest that a Ni modified WC-based anode is compatible with methane fuel, with reasonable and stable performance.

5:00 PM

(ICACC-S3-017-2013) Tailoring the shrinking upon co-sintering in Metal Supported Solid Oxide Fuel Cells by the addition of doping elements to NiO-anode producing powder

P. Satardekar*, University of Trento, Italy; D. Montinaro, Viale Trento, Italy; V. Sglavo, University of Trento, Italy

Co-sintering of multilayers for Metal Supported Solid Oxide Fuel Cell (MS-SOFC) fabrication leads to interdiffusion of Ni and Cr and RedOx reactions involving volume changes at interface between Ni-based anode and the substrate. Such effects result in cracking and delamination of the multilayer laminate. In the present work, metal substrates based on ferritic stainless steels were considered for MS-SOFC production. Ni/YSZ cermet and 8YSZ were used for the anode and the electrolyte, respectively. In order to limit the steel-induced NiO reduction and, consequently, the sudden volume change associated to this reaction, NiO RedOx kinetic was modified by the addition of reactive doping elements, like Ce, Mg and Al, to NiO powder. From dilatometric and TG-DTA measurements it was observed that pure NiO-YSZ-Steel composite expands rapidly above 400°C and then shows a substantial shrinkage above 1000°C. Such expansion causing delamination was significantly limited by the addition of the cited doping elements. Moreover, SEM observations of NiO-YSZ composite sintered at 1350°C in Ar revealed that doped NiO was more homogenously dispersed in YSZ matrix, this accounting for a limitation of Ni coarsening. It was found that NiO-YSZ composites containing doped-Ni, facilitate co-sintering of MS-SOFC by maintaining a suitable shrinking profile.

S4: Armor Ceramics

Boron-Icosahedral Based Ceramics I

Room: Coquina Salon E
Session Chair: Jerry LaSalvia, U.S. Army Research Laboratory

1:20 PM

(ICACC-S4-020-2013) Electronic Structures of Boron Crystals (Invited)

K. Shirai*, ISIR, Osaka University, Japan

Solid boron has many polymorphic modifications, while all of them belong to semiconductor. The basic character of boron crystals is the flexibility in structure, which makes theoretical study more complicated. In this paper, I will review the recent theoretical achievements on this class of materials. A big problem about boron crystals is a discrepancy between band calculation and experiment as to whether the crystal is insulating or metallic. All predictions by band theory show metallic, while experimentally semiconducting. The key issue is the presence of defects. For boron crystals, the defects are intrinsic properties of the crystals. The second issue is prediction of phase diagram of boron. I will discuss a recent progress in both of theory and experiment. The third issue is the valence control of boron, which is important for practical applications. We have studied superconductivity search on a-boron by using both of high-pressure and doping methods. In both methods, we have succeeded to observe superconductivity. The mechanism will be discussed.

1:50 PM

(ICACC-S4-021-2013) Failure and Phase Transformation in Boron Carbide from a Shock Physics Perspective (Invited)

D. Grady*, Applied Research Associates, USA

Boron carbide ceramics have been particularly problematic in attempts to develop adequate constitutive model descriptions for purposes of computational simulation of dynamic response in the ballistic environment. Dynamic strength properties of boron carbide ceramic differ uniquely from comparable ceramics, and are difficult to characterize. Further, boron carbide is suspected of undergoing polymorphic phase transformation within the impact shock event. Phase transformation features of boron carbide have been particularly elusive under experimental investigation, and consequently are also difficult to capture within appropriate constitutive models. The experimental methods of shock physics including, Hugoniot state, structured waves, novel loading waves and spall waves offer unique perspectives on the equation of state, strength and failure properties of ceramics. This presentation examines the distinctive equation of state, failure and phase transformation properties of boron carbide ceramic from the perspective of experimental shock physics methods.

2:30 PM

(ICACC-S4-022-2013) A brief review of deformation induced amorphization of boron carbide (Invited)

M. Chen*, Tohoku University, Japan

It has been 10 years since the discovery of amorphous shear bands in boron carbide fragments produced by ballistic tests in 2003. The deformation-induced localized amorphization has been widely observed in boron carbide subjected to indentation, mechanical scratching, non-hydrostatic diamond anvil cell experiments, plate impact tests, etc. Coupling with high applied stresses and/or high loading rates, the formation of the weak amorphous phase well explains the anomalous ballistic performance and fragmentation of boron carbide, which has been an important failure mode of the super-hard and lightweight material. In this talk I will briefly review recent progress in the development of a comprehensive understanding of the amorphization mechanisms and the intrinsic correlation between the amorphization and high-pressure mechanics of boron carbide, focusing on the outstanding questions and critical issues that appear to warrant future research. The recent advances in the effect of amorphization on the enhanced mechanical properties of nanocrystalline boron carbide will also be introduced.

3:20 PM

(ICACC-S4-023-2013) Stoichiometry effects on the mechanical properties of icosahedral boron carbide under load (Invited)

D. Taylor*, J. W. McCauley, Army Research Laboratory, USA

The effects of stoichiometry and atomic structure on the mechanical properties of boron carbide (B4C) have been studied using density functional theory and quantum molecular dynamics simulations. Computational cells of boron carbide containing up to 960 atoms and spanning compositions ranging from 6.7% to 26.7% carbon were used to determine stoichiometry effects on the atomic structure, elastic properties, and stress-strain response as a function of hydrostatic, uniaxial, and shear loading paths. Effects of variable stoichiometry, as well as different atomic arrangements within a fixed stoichiometry, will be discussed and the significantly reduced strength of boron carbide under shear loading will be demonstrated.

3:50 PM

(ICACC-S4-024-2013) Can We Truly Measure the Hardness of Crystalline Boron Carbide? - New Insights into the Spatial Distribution of Amorphized Zone

G. Subhash*, University of Florida, USA

Boron carbide ceramic is known to undergo a solid-state phase transformation from crystalline to amorphous state under high-pressure loads. Because of this phenomenon, as soon as a sharp indenter comes in contact with the ceramic surface, amorphization is induced and the indenter subsequently penetrates into the amorphized material rather than the crystalline boron carbide. Thus, we argue that the true hardness of crystalline boron carbide is never measured. The amorphized material is substantially weaker than the crystalline phase and hence it is argued that in the absence of amorphization, boron carbide would have exhibited significantly higher hardness than that is currently being measured. To substantiate this argument, the spatial distribution in the intensity of amorphization beneath static and dynamic indentations are measured using micro-Raman spectroscopy. It is found that the depth of amorphization zone increases with load but the maximum severity of amorphization occurs at a depth slightly beneath the indented surface. These findings are consistent with the Hertzian contact theory. It was also determined that the size of the amorphized zone is smaller than the radius of the estimated plastic zone size. Finally, the study revealed the existence of a highly comminuted Mescal zone beneath the indentation.

4:10 PM

(ICACC-S4-025-2013) Indentation Size Effect in Boron Carbide

E. Shanholtz*, J. C. LaSalvia, K. D. Behler, U.S. Army Research Lab, USA; V. Domnich, Rutgers University, USA

Boron carbide has been previously shown to undergo stress-induced solid-state amorphization (SSA) under both quasi-static and dynamic loading conditions. The possible relationships between SSA, cracking, and the indentation size effect (ISE) are explored in the present study by conducting Knoop indentation on a hot pressed boron carbide (B4C) between loads of 0.1 – 20 kgf. Residual indentations and cross-sections were examined using scanning electron microscopy (SEM) to reveal inelastic deformation mechanisms present at various loads. Evidence for SSA and characterization of its spatial extent as a function of load was determined by Raman spectroscopy. The load dependence of hardness was analyzed using a multi-fractal scaling (MFS) model. SEM and Raman observations are discussed with reference to the hardness-load curve and MFS model results.

4:30 PM

(ICACC-S4-026-2013) Characterization of the Hardness-Load Dependence of Boron Suboxide

J. C. LaSalvia, U.S. Army Research Laboratory, USA; V. Domnich, Rutgers, The State University of New Jersey, USA; R. Pavlacka*, E. R. Shanholtz, K. D. Behler, U.S. Army Research Laboratory, USA

Boron suboxide is a boron-icosahedral based compound that is attractive for armor applications due to its low density and high hardness. Isostructural with boron carbide, boron suboxide may be prone to stress-induced solid-state amorphization (SSA) and deformation-induced shear localization. In the present study, scanning electron microscopy (SEM) and Raman spectroscopy were used to examine surface and sub-surface features of Knoop indents in a boron suboxide in an effort to find evidence for SSA, and more generally, identify deformation mechanisms possibly responsible for the exhibited indentation-size effect (ISE). Boron suboxide specimens were prepared from disks that were densified by the spark-plasma sintering technique. Knoop indentation was conducted on the polished specimens in the load range 0.1 – 20 kgf. The observed ISE was analyzed by a multi-fractal scaling (MFS) model to identify load regimes which exhibit different behaviors. Specimens from these load regimes were carefully sectioned and polished to examine sub-surface features. SEM and Raman observations are presented in reference to the MFS model results.

4:50 PM

(ICACC-S4-027-2013) Structural Instability of Boron Carbide Under High-Velocity Impact

V. Domnich*, Rutgers University, USA; J. C. LaSalvia, E. R. Shanholtz, U.S. Army Research Laboratory, USA; R. A. Haber, Rutgers University, USA

Scanning electron microscopy and Raman microspectroscopy were used to characterize the structure of commercial boron carbide impacted at high velocity with a cemented carbide sphere. Band-like microstructural features, consistent with shear bands, were observed near the impact region, varying approximately 1 – 10 μm in thickness and 100 – 1000 μm in length. Brittle fracture and classic fragmentation were also observed. Clear evidence was found for structural instability under high velocity impact, similar to earlier observations of amorphization in boron carbide under indentation and scratching. Further, Raman spectra from selected areas in the vicinity of the impact region were found to be consistent with spectra of annealed amorphized boron carbide, suggesting localized heating in excess of 600 °C. Using Raman imaging of the impact region, the correlation between the amorphization pattern and the deformation features formed during loading was demonstrated.

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

Materials for Clean Energy Technologies

Room: Coquina Salon G
Session Chairs: Kuan-Zong Fung, National Cheng Kung University; Pavol Sajgalík, Slovak Academy of Sciences

1:30 PM

(ICACC-S6-019-2013) A binder-free process for making all plastic substrate flexible dye-sensitized solar cells having gel electrolyte (Invited)

J. Ting*, National Cheng Kung University, Taiwan

Binder-free electrophoretic deposition (EPD) and mechanical compression were employed to fabricate TiO2 photoanodes for use in all plastic substrate flexible dye-sensitized solar cells having a gel electrolyte. The photoanodes were composed of commercial 20-nm TiO2 powders with and without the addition of 160-nm TiO2 powders. The EPD was performed under different DC powers and deposition times to obtained photoanodes having different thicknesses. Depending on the thickness, various electron diffusion times, ranging from 8.08 to 12.40 ms, and electron lifetimes, ranging from 16.79 to 32.05 ms, were obtained for the photoanodes consisting of only commercial 20-nm TiO2. The electron diffusion time was reduced and the electron lifetime remained the same as a result of the addition of another commercial 160-nm TiO2 powders. The added 160-nm TiO2 powders enhanced the light absorptance by serving as light scattering centers. All plastic flexible dye-sensitized solar cells were made and evaluated. Compared to the 20-nm TiO2 only cells, the cells containing mixed powders exhibit enhanced efficiencies and the enhancement can be as much as 22%.

2:00 PM

(ICACC-S6-021-2013) Europium and Cerium-Doped MgSiN2 and LaSi3N5 - Electronic Structure and Luminescent Properties

Z. Lences*, L. Benco, M. Hrabalová, A. Czímerová, I. Ibrahim, P. Šajgalík, Slovak Academy of Sciences, Slovakia

Europium and cerium-doped MgSiN2 and LaSi3N5 have been synthesized from Si/Mg2Si/Si3N4 or LaSi/Si/Si3N4 mixtures by direct nitridation. The dopants were added in a form of Eu2O3 and CeO2. Stepwise heat treatment schedule up to 1400°C has been adopted for the reaction synthesis of both ternary nitrides doped with Eu or Ce. After nitridation the doped ternary nitrides were annealed at 1530°C (MgSiN2:Eu) and 1650°C (LaSi3N5:Eu) under nitrogen overpressure (2 MPa). The emission band of LaSi3N5:Eu phosphor was in the green light region, while MgSiN2:Eu emitted red light. The influence of Ce addition on the luminescent properties of LaSi3N5:Eu and MgSiN2:Eu 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 and N/O substituted ternary nitrides. To mimic the realistic concentration of Eu and O the cell volume was expanded to the 2×1×2 super-cell with 144 atoms. Electronic structure and band gaps were calculated using both the plain DFT and the hybrid functional (HSE). The La3+/Eu3+ substitution did not lead to a significant change of the gap, while La3+/Eu2+ substitution introduced a narrow band of Eu 4f-states in the gap thus narrowing the band-gap.

2:20 PM

(ICACC-S6-022-2013) Functionalization of nitride engineering ceramics by polymer derived sintering aids

P. Sajgalík*, Z. Lences, T. Plachky, Slovak Academy of Sciences, Slovakia; R. Riedel, H. J. Kleebe, Technische Universität Darmstadt, Germany

Densification of Si3N4 and SiC ceramics is usually reached by liquid phase sintering at temperatures above 1750°C. The major part of liquid phase is formed from the used oxide additives and SiO2 as a main impurity in nonoxide ceramics powders. The selection of particular oxides affects not only the sintering conditions, but also the highest temperature limit of their application. It seems to be beneficial to replace the binary oxide sintering additives by other more viscous systems. In this work SiOC and SiAlOC sintering additives were used, which were prepared from organometalic precursors by cross-linking and subsequent pyrolysis. The hot-pressed ceramic composites consist of the major crystalline phases (sialon, Si3N4), SiC nano-inclusions and residual glassy phase. Room temperature hardness and fracture toughness of composites are similar to those for the liquid phase sintered Si3N4. Moreover, the thermal conductivity of composites increased up to 80 W/m•K. From the same starting mixture (Si3N4+SiAlOC) and doping with europium O-sialon based phosphor was prepared, which emitted green-yellowish light.

Energy Storage Technology

Room: Coquina Salon G

Session Chairs: Kuan-Zong Fung, National Cheng Kung University; Pavol Sajgalík, Slovak Academy of Sciences

3:20 PM

(ICACC-S6-024-2013) Sodium iron phosphate Na2FeP2O7 glass-ceramics for sodium ion battery

T. Honma*, T. Togashi, N. Ito, T. Komatsu, Nagaoka Univeristy of Technology, Japan

New cathode candidate Na2FeP2O7 for rechargeable sodium ion second battery was successfully prepared by glass-ceramics method. The precursor glass, which is same composition in Na2FeP2O7, was prepared by melt-quenching method. Na2FeP2O7 was obtained by heat treatment of precursor glass powder with 10% glucose addition as reduction agent of Fe3+ in electric furnace. By means of electrochemical charge-discharge testing, Na2FeP2O7 exhibits 2.9V, 88mAh/g, in which is 90% for the theoretical capacity during 2.0-3.8V cut-off voltages. Na2FeP2O7 ceramics has the potential for the safety cathode candidate for the sodium ion battery with a low materials cost.

3:50 PM

(ICACC-S6-025-2013) The Effect of Geometric Factors on Sodium Conduction: A Comparison of β- and β”-Alumina

E. Kennedy*, D. Birnie, Rutgers University, USA

β”-alumina has been shown to have superior sodium conduction compared with β-alumina, and therefore is used more often as the solid electrolyte in sodium battery systems. The β”-alumina structure is composed of layers of (111) oriented spinel-structure units separated by conduction planes that are comparably more open allowing for sodium diffusion. The β-alumina structure is similar except that the spinel units are aligned differently creating a smaller and less flexible conduction plane. In this paper we analyze the differences in these structures that affect sodium conduction. In addition to being more flexible, β”-alumina is able to absorb stabilizing ions into the spinel unit, whereas β-alumina does not appear to have that capability. This comparison will assist in understanding the β”-alumina structure and enhancing its capacity for greater conduction of sodium.

4:10 PM

(ICACC-S6-026-2013) New energy storage with high power and low cost: A combination of computational and experimental study of cathode materials for Na-ion batteries

J. Xu*, D. Lee, S. Meng, Univeristy of California, San Diego, USA

The wide availability and low cost of sodium resource attract more and more attention to ambient temperature sodium-based batteries, which is believed to have the potential for providing reliable, low-cost, and long life energy storage. In this talk, we report our work on layered phases of sodium transition metal (TM) oxides with and without Li doped, NaxNi1/3Mn2/3O2 (0<x<2/3) and NaxLiyNi0.25Mn0.75O2 (0<x,y<1), working as cathode materials in Na ion batteries. In these layered TM oxides, two-dimensional transport or intercalation of sodium ions in/between the transition metal slabs occurs concomitant with transition metal redox changes during cycling. To evaluate those redox potentials, ion motilities, and defects stabilities in the material system, both experiments and first principles calculations are implemented at the same time. By identifying and controlling the interplay among structural changes, electronic configurations, and electrochemical reactions, the battery performance is improved dramatically, indicating a bright future for Na-ion batteries.

S7: 7th International Symposium on Nanostructured Materials and Nanocomposites

Chemical Processing of Nanomaterials I

Room: Coquina Salon B
Session Chairs: Dunwei Wang, Boston College; An Hardy, Hasselt University - imomec

1:30 PM

(ICACC-S7-023-2013) Nanostructured metal oxides from aqueous solution deposition (Invited)

A. Hardy*, M. Van Bael, Hasselt University - imomec, Belgium

Metal oxides find applications in various fields including oxide electronics and data storage, energy generation storage, etc. The evolution of these technologies has resulted in a constant renewal of the demands imposed upon the materials involved as well as their processing window.In many fields, nanoscaling of the oxides applied, has been found of interest as it evokes improved functionality. Research has shown, however, that there is a tremendous effect of the material's morphology and (nano)structure on the final device performance. This has been an incentive for research of both the consequences of nanosizing, as well as new synthesis routes that enable optimal nanostructures in view of the desired properties. Chemical synthesis and deposition routes are interesting in many cases due to their ease, strong control over the nanostructure obtained and applicability to a wide range of materials. Here, recent research results will be presented concerning chemical solution deposition of monometal oxides (ZnO, TiO2, VOx) as well as multi-metal oxides (high-k oxides, multiferroics, ferroelectrics) with possible applications in hybrid organic-inorganic and other solar cells, data storage devices, etc. Experimental strategies for nanoscale patterning based on templates, self assembly or a combination thereof will be discussed, while touching in-depth understanding of the (physico)chemical mechanisms behind.

2:00 PM

(ICACC-S7-061-2013) Rheology of Alumina Nano Powder Suspensions in the Presence of Organic Acids

S. Cinar*, M. Akinc, Iowa State University, USA

The control over the viscosity of ceramic suspensions is critical for evolution of the cast and the microstructure by colloidal processing. Nano powders with high surface area reduce the fraction of "available" water which is reflected in high viscosity for these suspensions. The viscosity aqueous alumina powder suspensions are studied by rheometry and low temperature DSC (LT-DSC) as a function of pH, ionic strength, and processing additives. The roles of fructose, several mono- and multi-protonic carboxylic acids on the viscosity of nano powder suspensions were investigated. LT-DSC of suspensions shows two or more water melting events. Lower melting event represents with "bound" water that is strongly coupled with the solid particle surface. The LT-DSC results are correlated with rheological behavior of the suspensions. Reduction in shear thinning with additives related to changes in pH and adsorption capacity of the additives. This study is in part funded by NSF, CBET Particulate and Multiphase Processes, Grant # CBET - 0931038.

2:20 PM

(ICACC-S7-070-2013) Synthesis and Characterisation of Nanostructured Copper Oxide

D. Dodoo-Arhin*, University of Ghana, Ghana; M. Leoni, P. Scardi, University of Trento, Italy

Nanostructured copper oxide has attracted several research interests over the years due to their interesting optical properties and their potential use in several electronic applications such as solar cells and gas sensors. In this work, reverse micelle microemulsions and high energy milling have been employed for the production of defect-free and highly defective nanocrystals. The defect-free nanocrystals show good crystallinity with the nanometric nature of the primary domains (20 nm – 4 nm) leading to quantum confinement phenomena observed by photoluminescence measurements. Models have been proposed for the nanocrystal formation and growth validated by means of several techniques such as XRD,SEM,TEM, UV-Vis and FTIR. The effect of high energy milling on the microstructure evolution was investigated using synchrotron radiation XRD line profile analysis supported by High Resolution TEM and SEM. The reduction in the average size of coherently scattering domains - and simultaneous narrowing of the size distribution - occurs in the first minutes. A proper nanocrystalline microstructure is obtained for a milling of ca. 20 min with asymptotic limit of ca. 10 nm. The reduction in size occurs at the expenses of introducing a massive quantity of dislocations in the system, reaching a limit of ca. 4×10-16 m-2.

Functional Nanocomposites

Room: Coquina Salon B
Session Chair: David Kisailus, UC Riverside

3:30 PM

(ICACC-S7-024-2013) Innovating hematite-based materials for improved solar water splitting (Invited)

D. Wang*, Boston College, USA

Photosynthesis harvests solar energy and stores it in chemical forms. When used to produce fuels, this process promises a solution to challenges associated with the intermittent nature of sunlight. Theoretical studies show that photosynthesis can be efficient and inexpensive. To achieve this goal, we need materials with suitable properties of light absorption, charge separation, chemical stability, and catalytic activity. For large-scale implementations, the materials should also be made of earth abundant elements. Due to the intricacy of these considerations, a material that meets all requirements simultaneously is absent and, as a result, existing photosynthesis is either inefficient or costly or both, creating a critical challenge in solar energy research. Using inorganic semiconductors as model systems, here we present our strategies to combat this challenge through rational material design and precise synthesis control. Guided by an insight that complex functionalities may be obtained by combining multiple material components through homo- or hetero-junctions, we have produced a number of material combinations aimed at solving fundamental challenges common in inorganic semiconductors such as poor charge collection, mismatch of energy levels, and weak light absorption. Most of these results will be presented within the context of solar water splitting.

4:00 PM

(ICACC-S7-025-2013) Heteroepitaxial Branched TiO2 Nanorods on Sb:SnO2 Nanobelt backbones for Phtoelectrochemical Hydrogen Production

S. Park*, S. Seo, C. Lee, S. Kim, Seoul National University, Republic of Korea; S. Lee, University of California at Berkeley, USA; D. Kim, Ajou University, Republic of Korea; K. Hong, Seoul National University, Republic of Korea

We report a novel heteroepitaxial branched nanoarchitecture composed of Sb-doped SnO2 (ATO) nanobelt (NB) stem and TiO2 rutile nanorod (NR) branches for high-performance photoelectrochemical (PEC) electrodes as it simultaneously provides a long optical path for excellent light-trapping characteristics and high-quality one-dimensional (1D) conducting pathway for charge carrier collection, as well as a large contact area with the electrolyte for fast interfacial charge transfer. ATO NBs covered with TiO2 NRs were synthesized by combining a thermal evaporation and a chemical bath deposition. Interestingly, the single-crystalline TiO2 rutile NRs can be epitaxially grown on the ATO NBs, which was clearly demonstrated based on a crystallographic approach through high-resolution transmission electron microscopy analysis. Furthermore, under AM 1.5 solar simulator illumination, a heteronanostructure consisting of 20-μm-long

ATO NBs and 130-nm-long TiO2 NRs yields a photocurrent density of 1.6 mA/cm2 at 0.8 V versus reversible hydrogen electrode (RHE), which were better than TiO2-based electrodes with various morphologies or heterostructures reported previously. These improved PEC performance were attributed to (i) enhanced charge collection properties due to the highly conductive 1D ATO NBs and (ii) low TiO2/ATO interface resistance due to their epitaxial relationship.

4:20 PM

(ICACC-S7-026-2013) Plasma-enhanced Chemical Vapour Deposition of Surface Disordered Metal Oxide Nanostructures: Growth and PEC Applications

A. P. Singh, A. Mettenboerger*, S. Mathur, University of Cologne, Germany

Efficient solar-to-hydrogen conversion in photoelectrochemical (PEC) cell is a ultimate goal for scientific community in the field of energy generation. Surface disor¬dering at nano-level is a promissing tool for altering optical absorption and carrier transport in metal oxide semiconductors which canbe used an efficient photoelectrode in PEC cell for solar energy harvesting. Plasma-enhanced chemical vapour deposition (PE-CVD) technique offers a viable solution for overcoming thermodynamic impediments involved in thin film growth and disorder-engineering through in-suit molecule precursor-based plasma coatings of metal oxides and anisotropic hydrogen plasma treatment. The novelty of PE-CVD is deposition and hydrogen treatment in a single rector at various temperatures which allows the formation of homogeneous films with relatively low surface roughness. This talk will present how PE-CVD processed nanostructured films of different metal oxides open up new vistas of material properties, which can be transformed into advanced material technologies. Further, the effect of surface disordering of metal oxide nanostructures created by reducing hydrogen plasma treatment on optical, electrical and photoelectrochemical will be discussed.

4:40 PM

(ICACC-S7-027-2013) Modelling of optical and electrical properties of WO3 photoanode with use of plasmonic nanostructures in photoelectrochemical systems

R. Solarska*, University of Warsaw, Poland; K. Bienkowski, Institute of Technology of Electronic Materials, Poland; J. Augustynski, University of Warsaw, Poland

Following earlier attempts to enhance light harvesting in photovoltaic, PV, solar cells the plasmonic metallic nanostructures were implemented in various photo-electrochemical systems including both semiconductor suspensions and thin film semiconductor photo-electrodes. Although very large enhancements in photoconversion efficiency have been observed in some cases, they frequently do not translate into large net photocurrents. Even if the use of metallic nanostructures, consisting typically of silver or gold, results indeed in the enhancement of optical absorption by semiconductor films, it is frequently accompanied by substantial photocurrent losses due to increased e- - h+ recombination. Efforts to control the charge recombination involve deposition of barrier layers between the semiconductor and the metal nanoparticles and/or the use of bimetallic (either alloyed or core-shell) plasmonic nanostructures. Recent advances in implementation of plasmonic metallic nanostructures into tungsten trioxide, WO3, based photoanodes for visible light water splitting will be discussed with special focus on the film architecture. Acknowledgement: This work is supported by the Polish-Swiss Research Program. R.S. acknowledges the support from the Polish Science Foundation through the “homing grant”

5:00 PM

(ICACC-S7-028-2013) Eclipse Transparent Electrode and Applications

H. Demiryont, K. C. Shannon*, Eclipse Energy Systems, Inc., USA; M. Bratcher, U. S. Army Research Laboratory, USA

Indium tin oxide (ITO) has long been the standard material for transparent electrical conductors. While the performance of ITO has been acceptable, engineers require improvements in the conductivity, transparency, and durability so that advances in devices, such as photovoltaics, can be realized. Additionally, mediocre conductivity on flexible substrates and high costs of ITO are other issues that need to be addressed. To that end, we describe here an innovative transparent electrical conductor (TEC) coating technology that can serve as an alternative to ITO. With conductivities that can be tailored from 2-10 Ohms/square at 80-90% transparent, these inorganic coatings are more conductive and more transparent than indium tin oxide (ITO). Another feature of TEC coatings is that the spectral properties in the ultraviolet and infrared spectral regions can be customized as for various applications. The coating fabrication involves a room temperature vacuum deposition process, that is ideal for flexible polymeric substrates, such as poly(ethylene terepthalate). Testing and evaluation of packaged TEC devices against MIL STD 810G has demonstrated the robust nature of the coatings under mechanical and environmental stress. If successful, development of TEC would lead to next-generation OLEDs/LEDs, dynamic windows, LC and photovoltaic devices.

5:20 PM

(ICACC-S7-029-2013) Atomic Layer Deposition and Plasma-enhanced CVD of Nanometric Metal Oxide thin films for Functional Applications

T. Singh*, T. Fischer, S. Mathur, University of Cologne, Germany

Application of tailor-made molecular precursors in low pressure or plasma-enhanced chemical vapor deposition techniques offers a viable solution for overcoming thermodynamic impediments involved in thin film growth. The use of atomic layer deposition and cold plasmas enables the realization of various functional coatings whose application spectrum spans from transparent conductive coatings, scratch-proof films to anti-bacterial materials. Over the past decade, we have developed several new precursor systems in order to demonstrate the competitive edge of molecule-based plasma coatings. Our work on a large number of metal oxide systems and their characterization towards microstructure, compositional and functional properties supports the advantages of chemical design in simplifying deposition processes and optimizing functional behaviour. This talk will present ALD and PECVD processed nanometric thin films of different metal oxides and functionalized nanometric thin films by chemically and physically grown nanoparticles. This 3D nanoparticle covering of nanometric thin films open up new aspect of material properties, which can lead to advanced material technologies. The presentation will include application of nanometeric thin films of metal oxides and heterostructures for photoelectrochemical (PEC) applications.

S8: 7th International Symposium on Advanced Processing and Manufacturing Technologies for Structural and Multifunctional Materials and Systems (APMT)

Integration and Joining

Room: Coquina Salon A
Session Chairs: Walter Krenkel, University of Bayreuth; Eugene Medvedovski, Consultant

1:30 PM

(ICACC-S8-021-2013) Lifetime Extension of Metal Pipes by Ceramic Jackets (Invited)

W. Krenkel*, N. Langhof, University of Bayreuth, Germany; C. Spatz, Fraunhofer Center for High Temperature Materials and Design, Germany

In order to reach the requirements of future 700°C steam power plants, the creep resistance of metal pipes transporting the hot steam must be improved. The described concept involves a hybrid metal/ceramic construction consisting of an inner metal pipe and an outer CMC jacket. Different oxide CMCs have been investigated with respect to a maximum pyrolysis temperature (800 °C) which is required for an on-site manufacture of the pipes in the power plant. The chosen material system comprises alumina fibers embedded in a siloxane matrix with BN particles. In addition, FE modeling was used to calculate the induced stresses in the outer ceramic reinforcement which occur due to the higher coefficient of thermal expansion of the steel pipe. The FE model examines the influence of geometry factors as well as material parameters and the gap between steel and ceramic pipe. Different material systems, the FE analyses and prototype tests are discussed with respect to mentioned specifications.

2:00 PM

(ICACC-S8-022-2013) Interfacial Characterization of Diffusion Bonded Monolithic and Fiber Bonded Silicon Carbide Ceramics

H. Tsuda*, S. Mori, M. C. Halbig, Osaka Prefecture University, Japan; M. Singh, NASA Glenn Research Center, USA

Advanced silicon carbide-based ceramics and ceramic matrix composite materials are currently undergoing significant development for aerospace and energy applications. Robust ceramic joining and integration technologies are critically needed for the successful implementation of these systems. We have utilized diffusion bonding using metallic interlayers since it can meet the application requirements and yield uniform bonds that have high strength, high temperature capability, and chemical stability. However, some key challenges have to be overcome including the CTE mismatch, microcracking, and phase instability. In this work, pure Ti foils and physical vapor deposited (PVD) Ti coatings were used as joining interlayers and the effect of interlayer thickness (10 and 20 micron) was investigated. Two types of substrate materials were used: chemically vapor deposited (CVD) SiC and SA-Tyrannohex, which has a dense and highly ordered structure consisting of SiC with a carbon interlayer. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were conducted on polished cross-sections and on specimens prepared by focused ion beam (FIB), respectively. Results from the detailed analysis of the various reaction formed phases in the bonded regions will be presented and observed trends will be discussed.

2:20 PM

(ICACC-S8-023-2013) Development of Graphite/AlN Joints with Al-Y-O Phase Penetration

T. Okuni*, Y. Miyamoto, Toyo Tanso Co., Ltd., Japan; H. Abe, M. Naito, Joining and Welding Research Institute, Japan

Isotropic graphite is widely used as industrial materials for many applications. However, graphite easily reacts with some metals such as iron, cobalt and titanium forming carbides, which limits the usage of graphite materials especially in metal heat treatment industries. In order to solve this problem, joining of graphite and nitride ceramics which can prevent the carbide formation was studied. Graphite and AlN were successfully joined at 1900 °C under 30 MPa, because the molten Al-Y-O phase of the sintering aid for AlN was penetrated into open pores of graphite under loading the pressure and solidified during cooling. Compared with the graphite/AlN joints without Y_2O_3 additives, the joint with 10 mass % Y_2O_3 showed the increasing joining strength from 3 MPa to 19 MPa. The joining interface between graphite and AlN was observed by using SEM-EDX, and the joining mechanism was investigated.

2:40 PM

(ICACC-S8-024-2013) Joining of alumina by polycarbosilane and siloxane including phenyl groups

K. Kita*, N. Kondo, National Institute of Advanced Industrial Science and Technology (AIST), Japan

Polymer blends containing polycarbosilane (PCS) and siloxanes including phenyl groups were prepared, and alumina samples were joined by using the polymer blends and aluminum foil on purpose to achieve the energy reduction in joining of alumina. We consider that the reaction between aluminum and silica layer which can react directly at 1073 K and be made into silicon-alumina oxide would be helpful to the purpose and continue the study of joining of alumina by using of the reaction. In the former investigation, we tried using a polymer blend including polymethylsilsesquioxane (PMSQ) for making silica layer easily. However, because of poor solubility between PCS and PMSQ, the joining layer of alumina by using the polymer blend consisted of metal composite containing aluminum and needle-shaped silicon, and the average bending strength was about 176 MPa. We paid attention to polymethylphenylsiloxane (PMPhS) which is one of siloxane including much silicon and oxygen atoms. The solubility to PCS is very good; therefore, there is the possibility of making uniform silica layer and joining layer after heating. The joining layer would increase strength compared with the case of PMSQ.

Design-Oriented Manufacturing

Room: Coquina Salon A

Session Chairs: Walter Krenkel, University of Bayreuth; Eugene Medvedovski, Consultant

3:20 PM

(ICACC-S8-025-2013) Manufacturing and Application of Ceramic Membranes for Filtration (Invited)

A. Michaelis*, I. Voigt, Fraunhofer IKTS, Germany

Ceramic membranes are well established for micro-, ultra- and nanofiltration applications such as waste water purification. Further innovations require an improved control and reduction of pore size. This allows for new applications in gas separation and pervaporation systems. For this, pores sizes below 1 nm have to be generated using specific structural features of selected materials. Several new methods for preparation of such membranes are presented. In a first example we use the well know crystallographic cage structure of zeolites. Employing a new hydrothermal route allows for synthesis of dense zeolite films on porous substrates. It is shown that these membranes can be used for dewatering of bioethanol. In a further example we use carbon layers with well defined lattice distances of 0,35 nm as a membrane for separation of hydrogen from gas mixtures. By subsequent chemical modification of these carbon layers a well designed adsorption selective behaviour can be achieved as is demonstrated with membranes for purification of biogas. Furthermore, we present perovskite materials showing mixed conducting behaviour. Due to an oxygen vacancy structure in the crystal lattice these materials can be used to generate oxygen which in turn can be used to improve the efficiency of combustion processes.

3:50 PM

(ICACC-S8-026-2013) Intelligent processes enable new products in the field of non-oxide ceramics

J. Eichler*, ESK Ceramics GmbH & Co. KG, Germany

ESK Ceramics, a subsidiary of Ceradyne Inc., develops and manufactures pioneering products in the fields of advanced ceramics, ceramic powders and frictional coatings. For many years ESK is known as a quality supplier of non-oxide ceramics. Our materials portfolio includes borides, nitrides and carbides, like Silicon Carbide (SiC), Titanium Diboride (TiB2), and Boron Nitride (BN). In recent years we developed new materials and applications together with our customers. We continually develop innovative product solutions and use a wide range of process technologies. Heat exchangers and flow reactors made from Silicon Carbide enable modern synthesis of valuable fine chemicals and pharmaceuticals under controlled and safe conditions. The production of these apparatuses includes an ESK proprietary knowledge process step to join SiC to complex monolithic shapes. By integrating the ceramic into a system it enables resource and energy efficient processes in the target industries. Following along the process route for heat exchangers a review from a manufacturing standpoint will be given on the current status of an industrial based production for non-oxide ceramics. In an outlook the author will raise some questions from an ESK perspective concerning future trends in processing and manufacturing technology.

4:10 PM

(ICACC-S8-027-2013) Influence of Manufacturing on Corrosion Resistance of Advanced Ceramics

E. Medvedovski*, Consultant, Canada

Advanced oxide ceramics are prospective materials for severe corrosion application conditions, particularly in the oxygen-rich environments, combined with the action of mechanical loads. The corrosion behavior of oxide ceramics, such as alumina, alumina-mullite and zirconia-based ceramics, in the water steam of supercritical conditions (elevated temperatures and pressures) and its influence on mechanical strength, as well as joint action of corrosion and tensile loads, were studied. The influence of processing, including forming methods, and structural defects related to processing on the corrosion resistance and mechanical strength degradation of the ceramics were considered. The oxide ceramics based on the thermodynamically stable crystalline phases (with no glassy phase) and with a microcrystalline structure made through the colloidal processing, when a high homogeneity, minimal internal defects and minimal amounts of the "foreign" impurities are achieved, possess the highest level of reliability and corrosion resistance, e.g. in water steam, and the lower degradation of mechanical properties.

4:30 PM

(ICACC-S8-028-2013) Numerical Analysis of Microstructural Fracture Behavior in Nano Composites under HVEM

H. Serizawa*, Osaka University, Japan; T. Shibayama, Hokkaido University, Japan; H. Murakawa, Osaka University, Japan

As a result of R&D efforts about microstructural evaluation techniques of advanced multifunctional material, an in-situ observation method of fracture behavior on nano structures by using high voltage electron microscope (HVEM) has been developed. By using this method, interfacial fracture behavior of SiC fiber reinforced SiC matrix composite was observed and the inter-laminar shear strength between SiC matrix and coated carbon layer on SiC fiber was also measured. However, the inter-laminar shear strength measured was about thirty times higher than that obtained by fiber push-out test of the standard size specimen. On the other hand, the interface element has been developed as the element for modeling the interfacial behavior directly and various types of fracture behavior have been numerically studied by using the finite element method with interface element. So, in this study, in order to examine the difference between micro and macro size specimen, the finite element analyses were conducted where debonding and sliding at the interface were directly modeled by the interface element. The fracture behavior of miniature sized double notch shear test and one fiber push-out test was successfully demonstrated by using the interface element with the same interfacial potential function and the difference of fracture strength was also studied.

4:50 PM

(ICACC-S8-029-2013) Study of the effects of an unexpected ceramic phase at the head of the pipe on joining and post processing of a ceramic-lined composite pipe

R. Mahmoodian*, University of Malaya, Malaysia; R. Rahbari Ghahnavyeh, University of Toronto, Canada; M. Hamdi, M. Hassan, M. Sparham, University of Malaya, Malaysia

Produced ceramic-lined steel pipe using the self-propagating high-temperature synthesis (SHS) method has found use in many applications. A SHS-centrifugal machine was designed to produce a ceramic-lined steel pipe from ferric oxide and aluminum powder (thermite mixture) under high centrifugal acceleration. The obtained products is expected to be Al2O3 ceramic in the innermost layer, and a Fe layer in a region between the outer steel pipes. In the present work, specific regions of a pipe was particularly observed to investigate the stuck (dead) spaces at the pipe head because of its importance in further processes (joining, welding, etc.) which may affect the quality of the next operations. In the current research paper, the product's composition, phase separation, micro-hardness, and surface finish were studied on three zones of the pipe.

S9: Porous Ceramics: Novel Developments and Applications

Processing Methods for Porous Ceramics IV

Room: Coquina Salon C
Session Chair: Tobias Fey, University of Erlangen-Nuremberg

1:30 PM

(ICACC-S9-021-2013) Structure Control, Processing and Properties of Porous Ceramics with High Porosity and High Strength (Invited)

C. Wang*, Tsinghua University, China

Porous ceramics have been widely used for filtration, separation, heat insulation, sound adsorption, catalyst support, bioceramics and so on due to their special properties including high porosity, high specific surface area, lightweight, refractory, erosion-resistant, heat-insulation and other good properties. The properties of porous ceramics depend on the characteristics of the composition and structure including porosity, pore configuration, pore size and distribution. A lot of processing methods, such as pore form agent, sacrificial template, direct foaming, sol-gel, gelcasting and so on, have been developed for the production of porous ceramics. However, strength of porous ceramics decreases obviously with porosity because of inhomogeneity of porous structure. In our research, some novel processing techniques including modified gelcasting, freeze-casting, fiber reinforcing, aerogel impregnation and so on have been developed to design and control the specific porous structure, therefore, some specific properties including ultra-high porosity, ultra-lightweight, high strength, low thermal conductivity and other physical properties can be achieved for some potential applications.

2:00 PM

(ICACC-S9-022-2013) Controlling the formation of particle-stabilized water-in-oil emulsions

P. N. Sturzenegger*, U. T. Gonzenbach, ETH Zurich, Switzerland; S. Koltzenburg, BASF SE, Germany; L. J. Gauckler, ETH Zurich, Switzerland

We apply the versatile method of in-situ hydrophobization of aluminum oxide particles with short amphiphiles for the stabilization of water-in-toluene emulsions. We found that octyl gallate is an ideal surface modifier to adjust particle wetting properties in toluene. The most important parameters affecting the droplet size were investigated including particle size and wetting properties, particle concentration, emulsion composition, and shear rate. The median droplet size ranged between 2.6 and 80 μm in this study. The results are discussed to shed light on the underlying processes controlling the droplet size. It was found that emulsion formation is either rupture or coalescence controlled, which is in close analogy to the mechanisms reported for surfactant-stabilized emulsions.

2:20 PM

(ICACC-S9-023-2013) Tailoring Network Characteristics of Freeze-Cast Porous Ceramics

S. M. Miller*, Northwestern University, USA; X. Xiao, Argonne National Laboratory, USA; K. Faber, Northwestern University, USA

As the number of uses for porous ceramics increases, it becomes necessary to tailor pore networks to requirements for specific applications. Pore network characteristics include pore size and shape, interconnectivity and tortuosity, and internal specific surface area. Freeze casting is a valuable method of fabricating directionally porous ceramics due to the large number of processing parameters that can be altered within the straightforward process. The pore network can be altered by varying slurry composition (dispersion medium, solids loading, and additives), and altering temperature parameters (thermal gradient and undercooling). In this study the effects of temperature gradients and the magnitude of undercooling for two different dispersion media (water and camphene, separately) on pore network characteristics of freeze-cast aluminum oxide are examined and quantified. Scanning electron microscopy, X-ray computed tomography, and the resulting computational image processing are used to examine and compare differences between samples created under varying fabrication conditions, and the influences of the temperature parameters mentioned are analyzed.

2:40 PM

(ICACC-S9-024-2013) Boron-Modified Polysilylcarbodiimides-Derived Highly Porous Si-B-C-N Ceramics

L. Yang*, L. An, University of Central Florida, USA

In this study, we report on the investigation of a template free method for preparing highly porous Si-B-C-N ceramics by using boron-modified polysilylcarbodiimides gel as the precursor. Boron-modified polysilylcarbodiimides gel was synthesized by the reaction of tris[dichloromethylsilylethyl]borane with bis(trimethylsilyl)carbodiimide. After gelation, Styrene (with 1wt% AIBN as the initiator) was added to substitute trimethylchlorosilane generated in the gel. Styrene was polymerized at 80°C and then decomposed to be pores after pyrolysis at 1000°C. The processing procedure was and the obtained porous ceramics were characterized.

Mechanical Properties of Porous Ceramics

Room: Coquina Salon C
Session Chair: Tom Watkins, ORNL

3:20 PM

(ICACC-S9-025-2013) Uniaxial Tensile Response of Microcracked Porous Ceramics (Invited)

A. Pandey*, A. Shyam, T. R. Watkins, E. Lara-Curzio, ORNL, USA; R. J. Stafford, Cummins Inc., USA

In this presentation, we report the uniaxial tensile stress-strain response of three porous ceramics with varying microcrack densities. Materials investigated were cordierite, aluminum titanate based material, and silicon carbide based material. Tensile load experiments were performed using a microscale testing setup and strains were obtained with full field non-contact 2D digital image correlation (DIC) techniques. The uniaxial tensile responses of these materials reveal strain dependency of Young's modulus and the elastic properties were found to be a function of microcrack density. Results obtained in the present investigation provide a possible solution to the reported discrepancy in Young's modulus of porous microcracked ceramic materials measured from static (flexure testing) and dynamic (RUS, sonic resonance etc.) experimental techniques. Finally, the implications of the presented results will be discussed in the context of lifetime prediction in diesel particulate filters.

3:50 PM

(ICACC-S9-026-2013) Influence of specimen preparation on the double torsion fracture toughness results for two extruded porous microcracked cordierite compositions

K. Hoff*, G. Bruno, T. Montigny, X. Luo, Corning, USA; A. Shyam, T. Watkins, R. Parten, Oak Ridge National Lab, USA

The double torsion test technique is ideally suited to measure the fracture properties of materials made into thin plates due to the simple specimen geometry. Also, precise measurement of the crack length is not required for fracture toughness calculation. In this study, we compare the influence of two different specimen preparation techniques on the recorded fracture toughness values for two cordierite compositions with differing microstructural properties (porosity, microcrack density, and domain size). Preparation techniques include dry versus wet grinding, as well as, vacuum versus wax infiltration fixturing. The double torsion fracture toughness results are statistically compared between cordierite microstructures and specimen preparation techniques. A critical discussion is made on the validity of mode one stress intensity factor versus strain energy release rate as a metric for quantifying fracture of porous microcracked materials.

4:10 PM

(ICACC-S9-027-2013) Non-linear stress-strain relations in porous microcracked ceramics, and their interpretation

G. Bruno*, Y. Kilali, M. L. Kachanov, Corning Incorporated, USA

Some recent results on the behavior of porous microcracked ceramics under uniaxial compression are given, in the examples of cordierite and aluminum titanate. They are compared with non-microcracked ceramics such as silicon carbide. All those materials show non-linear behavior, which can be attributed to the activity of microcracks, closure and/or the generation. The non-linear stress-strain behavior is modeled through the micromechanical "differential scheme". Through this modeling, microstructural features such as the microcrack density parameter can be extracted, and compared with SEM pictures. While it has often been neglected in the literature, we show that microcrack sliding is an important phenomenon in compression, and we give quantitative assessment of its contribution to the non-linear stress-strain curves.

4:30 PM

(ICACC-S9-028-2013) Impact of Biodiesel on the Mechanical Properties of Diesel Particulate Filter Ceramics (Invited)

M. J. Lance*, A. A. Wereszczak, M. K. Ferber, E. E. Fox, T. J. Toops, B. G. Bunting, E. J. Nafziger, A. Williams, Oak Ridge National Laboratory, USA; J. Burton, R. L. McCormick, National Renewable Energy Laboratory, USA

Alkali and alkaline earth impurities found in biodiesel are potential poisons for diesel particulate filters (DPFs) and may impact durability. In order to determine the effects of these impurities on DPF durability, production exhaust systems with SiC DPFs from a 2011 Ford F250 were aged to an equivalent of 150,000 miles with four different fuels; ULSD, 20 vol% biodiesel (B20)+Na, B20+K, and B20+Ca. Mechanical testing of the DPF biaxial flexure tiles showed a slight increase in the apparent strength following aging but no change in the coefficient of thermal expansion. A second aging procedure employed a stationary diesel generator or gen-set to thermally cycle the DPF by a combination of gen-set load and exhaust fuel injection to reach temperatures up to 1200C in a 15 minute cycle. Cylindrical samples were harvested from the tested DPFs and the fracture strength and elastic modulus were measured using a new uniaxial tensile test method by gripping the porous DPF with epoxy and measuring the corresponding tensile elongation using contact extensometry. In addition to contrasting the effects of the impurities on the mechanical responses, a discussion of the benefits of tensile testing of DPFs over other methods will be presented. Research sponsored by the Propulsion Materials Program, DOE Office of Vehicle Technologies, under contract DE-AC05-00OR22725 with UT-Battelle, LLC.

5:00 PM

(ICACC-S9-029-2013) Mechanical properties of highly porous alumina foams investigated with different testing methods

B. S. Seeber*, U. T. Gonzenbach, L. J. Gauckler, ETH Zurich, Switzerland

The mechanical properties of porous ceramics are greatly influenced by their microstructure. Therefore, mechanical behavior of highly porous ceramics is different to that of dense ceramics. Here, we evaluate different mechanical testing methods such as compression, Brazilian disc test and 3-point bending on their suitability for comparison of highly porous ceramic materials. The porous samples used for this study were produced via direct foaming of in-situ hydrophobized alumina particles. It is shown that 3-point bending is more suitable than compression or Brazilian disc testing, as the material exhibits no critical crack propagation under compressive loading. Under cyclic compression the foams exhibit a very high crack tolerance in combination with the preservation of their structural integrity even at high strains of 10%. With 3-point bending tests, a quantitative comparison of the mechanical properties of foams with different microstructures and porosities is possible. Foams of two different porosities are compared and their pore size and pore size distributions are analyzed. The results are compared to data found in literature as well as the beams and bars model by Gibson and Ashby.

5:20 PM

(ICACC-S9-030-2013) Ceramic Foams by Emulsion Templating

E. García-Tuñón*, R. Bell, S. Barg, J. Weaver, E. Saiz, Imperial College London, United Kingdom

This presentation describes the fabrication of ceramic foams with complex shapes by emulsion templating. Ceramic suspensions with solid contents ranging from 25-82wt% (up to 64vol%) were emulsified and their rheological behaviour was evaluated as a function of their composition. This work will describe the morphology and microstructure of the sintered materials with particular emphasis in density, pore size, pore shape and strut thickness. The mechanical properties (flexural and compressive strengths) were also evaluated. Alumina foams with closed porosities ~60 vol% can exhibit compressive strengths of ~140 MPa in the upper range for this type of materials. Our preliminary results show that this procedure is a promising path to fabricate strong, porous ceramics with complex shapes.

S10: Virtual Materials (Computational) Design and Ceramic Genome

Innovative Modeling and Simulation Methods

Room: Oceanview

Session Chairs: Wai-Yim Ching, University of Missouri-Kansas City; John Lawson, NASA Ames Research Center

1:30 PM

(ICACC-S10-010-2013) Grain Boundary "Phase" Diagrams — A Useful Component for "Materials Genome"? (Invited)

N. Zhou, Y. Zhang, J. Luo*, Clemson University, USA

Bulk phase diagrams are one of the most useful tools for materials science. Materials researchers have long recognized that grain boundaries (GBs) can exhibit phase behaviors; for example, the classical Fowler adsorption isotherm already implied the existence of first-order transitions, and Hart used the concept of GB phase transitions to understand the temper embrittlement phenomenon in steels in 1958. Following the seminal Cahn model (for critical-point wetting), various grain boundary (premelting and prewetting types) phase diagrams have been constructed by Straumal, Carter, Mishin, Wynblatt and others. Furthermore, recent studies using advanced microscopy directly observed a series of discrete GB interfacial phases (which were also named as "complexions"). After a briefly review of some historical aspects, this talk will discuss our recent efforts on developing GB (phase) diagrams as a useful tool for materials science, which include both the less rigorous — yet robustly useful — GB lambda diagrams and more rigorous GB phase diagrams with well-defined transition lines and critical points. Recent studies demonstrated that such GB diagrams are useful in solving old scientific mysteries, predicting new phenomena, and designing optimal fabrication recipes. Several recent examples will be discussed. We suggest that GB (phase) diagrams can be a useful component for the Materials Genome project.

2:00 PM

(ICACC-S10-011-2013) Computational ELNES Spectral Imaging Incorporating Signal Contrast

J. Currie*, P. Rulis, University of Missouri - Kansas City, USA

Computational electron energy loss near edge spectroscopy (ELNES) has been developed into a powerful tool for materials characterization. However, it has seen limited use for studying grain boundary, interface, and other defect containing systems due to their large size and the commensurate computational cost. In this presentation we demonstrate an extension of an ab initio computational spectral imaging method that creates a visual representation of the correlation between atomic position and ELNES spectral response. This can be particularly useful for characterizing local structures in defect regions and in particular it is applied to a {113} passive defect model in silicon. Here, based on the wave function and charge density distribution, the signal intensity is predicted and incorporated into the visualization to provide contrast in the computed image. This approach forms an image that is significantly more analogous to the types of images produced experimentally, thus its utility for aiding in image interpretation is substantially enhanced.

2:20 PM

(ICACC-S10-012-2013) Families of Superhard Crystalline Carbon Allotropes Constructed via Cold-compressed Graphite and Nanotubes

H. Niu*, X. Chen, D. Li, Y. Li, Institute of Metal Research, China

Cold compressed graphite (CC-G) and carbon nanotubes (CC-CNTs) represent an important family of carbon allotropes that are composed of mostly σ-bonds in three-dimensional framework, wide-gap insulators, and superhard. Here, we report a general scheme to systematically construct two classes of structural families (S- and B-families) of superhard sp3 carbon allotropes of both CC-G and CC-CNTs through topological analysis of odd 5+7 or even 4+8 membered carbon rings stemmed from the stacking of zigzag and armchair chains. Our results also demonstrate that the actual candidates which can interpret the structural transformation of CC-G and CC-CNTs may be numerous, depending on the different stacking and combinations of their topological carbon rings (5, 7, 4, 8 and ideal 6-membered rings). It has been found that the previously proposed M, bct-C4, W and Z allotropes belong to our currently proposed families. We further propose twelve new carbon allotropes, all exhibiting the transparent wide-gap insulator with Vickers hardness comparable to diamond. Among our proposed families of carbon allotropes, R carbon in S-family and P carbon in B-family are the best candidates for CC-G and CC-CNTs, respectively. Our results shed light on resolving the mysteries of CC-G and CC-CNTs, which will be interesting for the community related with diamond and carbon materials.

2:40 PM

(ICACC-S10-013-2013) A Multi-method Approach to Modeling Amorphous Boron Carbide

R. Cramm Horn*, A. Caruso, M. Paquette, A. Kitahara, P. Rulis, University of Missouri - Kansas City, USA

Amorphous hydrogenated boron carbide ($B_xC:H_y$) is a complex molecular solid with both short and medium range order that presents substantial challenges to traditional amorphous materials modeling techniques. This presentation discusses the application of different modeling approaches including (1) manual construction using experimentally determined guidelines, and (2) a "gas phase condensation" scheme based on the slow accumulation of constituent components into an amorphous mass. Important issues include methods to prevent the build-up of internal stresses, allow for realistic bond development, and maintain periodic boundary conditions. We show that using a multi-method approach (classical molecular dynamics, *ab initio* relaxation, manual intervention, etc.) is essential for producing model systems in line with experimental expectations in terms of density, pair distribution function, and electronic structure properties.

3:20 PM

(ICACC-S10-014-2013) Ab initio MD simulations of the response of ceramics to extreme conditions (Invited)

H. Xiao*, University of Tennessee, USA; Y. Zhang, Oak ridge National Lab, USA; W. J. Weber, University of Tennessee, USA

The application of ab initio MD (AIMD) methods to simulations of high-pressure phase transformations and low energy radiation-damage events in several ceramics will be presented. The simulations have identified the mechanism for the high pressure wurtzite to rocksalt phase transformation in SiC and GaN as inhomogeneous displacements via a tetragonal atomic configuration. The effects of charge transfer on ion-solid interaction in SiC have been explored, and the results reveal that the dynamic evolution is a charge-transfer-assisted process, where the variation of charge on atomic recoils alters the energy barrier for stable defect formation. Through AIMD simulation of low energy recoil events in Y2Ti2O7 pyrochlore, two new and highly-stable cation interstitial defects have been identified, which have a significant impact on the electronic structure of pyrochlores. Density functional calculations have shown that the design of pyrochlore materials with controlled electronic properties can be achieved by ion-implantation doping at these interstitial sites. Overall, these studies have demonstrated that AIMD methods are valuable tools for identifying new phenomena and mechanisms for phase transformation and defect generation that are not predictable from classical MD, for predicting new structural phases in prefect and defective states, as well as for designing materials with specific properties.

3:50 PM

(ICACC-S10-015-2013) A Neural Network Approach to Non Self Consistent Total Energy Calculations for Complex Materials (Invited)

P. Rulis*, University of Missouri - Kansas City, USA

This presentation presents an exploration of an alternate method for calculating accurate total energies of complex defect containing solids that is based on machine learning. Within the ab initio orthogonalized linear combination of atomic orbitals (OLCAO) method for electronic structure calculation the solid state potential function is expanded as a summation of atom centered Gaussian functions. The coefficients of these functions are normally determined through self-consistent field iterations applied to the whole system. However, for large and complex systems where many atoms have substantially different local geometries this approach becomes excessively burdensome. A new approach to obtaining the potential function coefficients and subsequently computing the total energy is under development. Progress of the method as applied to a passive defect model in silicon, a self-interstitial model in silicon, and a model of amorphous silica will be presented.

4:20 PM

(ICACC-S10-016-2013) Multiscale extraction of morphological features in woven CMCs

C. Chapoullié, J. Da Costa, C. Germain, University Bordeaux, France; M. Cataldi, Herakles, France; G. L. Vignoles*, University Bordeaux, France

Woven CMCs are key materials in aeronautic industry. Their characterization is often carried out on two-dimensional microscopy data and very few methods aim at the 3D description of their real inner structure. We propose to explore the structure of woven CMCs in 3D using high resolution tomography. In particular, we present two versions of an algorithm for segmentation and labeling combining differential geometry and mathematical morphology. The first one performs at low resolution. It allows extracting the yarn envelope using the structure tensor to obtain local yarn orientation. The second one allows fiber labeling at a higher resolution. It is based on the extraction of fiber skeletons thanks to the structure tensor too. After this two-scale labeling, various morphological features are estimated like: diameter distribution, diameter variations along fibers, fiber orientation distribution, intra-yarn fiber density. Our algorithms are tested on X-ray tomographs of woven Nicalon fiber preforms at the resolution of 1.4 microns per voxel.

4:40 PM

(ICACC-S10-017-2013) Electronic Structure and Interatomic Bonding in Cement Crystals

C. C. Dharmawardhana*, University Of Missouri - Kansas City, USA; A. Misra, University of Kansas, USA; S. R. Aryal, P. M. Rulis, W. Ching, University Of Missouri - Kansas City, USA

The atomic scale properties of calcium silicate hydrate (CSH), the main binding phase of hardened Portland cement, are not well understood. Over the past century intense research identified almost 50 different crystalline CSH minerals which are mainly categorized by their Ca/Si ratio. The electronic structure and interatomic bonding in four major CSH crystalline phases with structures close to those found in hardened cement are investigated via ab initio methods. Our result reveals the critical role of hydrogen bonding and the importance of specifying precise locations for the water molecules. Quantitative analysis of contributions from different bond types to the overall cohesion show that covalent Si-O covalent bonds dominate; however hydrogen bonding and Ca-O bonding are also very significant. We also show the correlation between bond topology and interlayer cohesion. The overall bond order density is found to be a far more critical parameter than the Ca/Si ratio in classifying different CSH crystals.

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

Materials Design: MAX Phases and UHTCs

Room: Coquina Salon F
Session Chair: Sylvain Dubois, Institut PPRIME

1:30 PM

(ICACC-S12-001-2013) The application of Axial Next-Nearest-Neighbor Ising model to the description of the MAX phases (Invited)

T. Ouisse*, D. Chaussende, Grenoble INP, France

Some important features characterizing the MAX phases can be reproduced by modifying the spin model known as Axial Next Nearest Neighbor Ising Model (ANNNI). To do so we describe these phases in terms of M-A or M-X bi-layer stacking along the c-axis. The description of any MAX phase is reduced to the knowledge of four energy parameters characterizing the interaction between first and second neighbor bi-layers. The possibility of polytypism, which can theoretically happen between conventional and hybrid phases with the same stoichiometry, is determined by the strength of second-neighbor interactions. The fact that the simplest hybrid phase has never been reported seems to be in favor of the existence of such interactions. The ANNNI model could thus explain why hybrid phases remain an exception. Phase stability can be partially discussed: studying the pseudo-decomposition of a MAX phase into the MA and MX compounds explains why for some M-A-X ternary systems the M2AX phase cannot be stable, why for others it is the only possible stable compound (if there is any), and why for a third class of ternary systems, all Mn+1AXn phases are potentially stable, stability progressively reducing as n increases. The belonging of a given MAX system to any of those three families is determined by a set of only three interaction energies, which can be computed using ab initio techniques.

2:00 PM

(ICACC-S12-002-2013) Discovery of the new MAX phase Nb_2GeC by a systematic theoretical-experimental approach

P. Eklund*, M. Dahlqvist, O. Tengstrand, L. Hultman, J. Lu, Linkoping University, Sweden; N. Nedfors, U. Jansson, Uppsala University, Sweden; J. Rosén, Linkoping University, Sweden

Mathematical optimization procedures to determine phase stability can be generally applicable to complex ternary or higher-order materials systems where the phase diagrams of the binary constituents are sufficiently known. Here, we employ a simplex-optimization procedure to predict new compounds in the ternary Nb-Ge-C system. Our theoretical results show that the predicted MAX phase Nb_2GeC is stable, and exclude reasonably conceivable competing hypothetical phases (the MAX phases Nb_3GeC_2 and Nb_4GeC_3). Nevertheless, all three $Nb_{n+1}GeC_n$ phases are intrinsically (dynamically) stable, i.e., stable relative to lattice vibrations. This further underscores the importance of realistic phase stability calculations in any prediction-based approach, rather than only investigating intrinsic stability of hypothetical phases. We verify the existence of Nb_2GeC phase by thin film synthesis using magnetron sputtering and characterize its structure by XRD and high-resolution TEM. The crystal structure of Nb_2GeC is the 211 MAX structure with a and c lattice parameters of 3.24 Å and 12.82 Å, respectively. [Eklund et al, Physical Review Letters, 109 035502 2012]

2:20 PM

(ICACC-S12-003-2013) Thin films of Ga-based MAX phases: Cr_2GaC and $(Cr,Mn)_2GaC$

A. Petruhins*, A. Ingason, A. Mockute, P. Persson, J. Rosen, Linkoping University, Sweden

The Cr_2GaC MAX phase has previously been synthesized as bulk material. We report synthesis of Cr_2GaC thin films by DC magnetron sputtering from three elemental targets, including liquid Ga. The films were deposited on MgO(111) substrates. Structural analysis by X-ray diffraction and transmission electron microscopy reveals epitaxial (0001)-oriented MAX phase. Recent theoretical and experimental studies have shown that Mn, an element previously not associated with MAX phases, can be incorporated in Cr_2AlC and Cr_2GeC through alloying on the *M* site. Corresponding theoretical analysis of Ga-based MAX phases predict high thermodynamic stability also for $(Cr,Mn)_2GaC$. This is here verified through corresponding successful thin film synthesis. The potential magnetic properties of these phases, and effects of choice of *A* element thereof, will be discussed.

2:40 PM

(ICACC-S12-004-2013) Synthesis of epitaxial $(Cr,Mn)_2AlC$ – a potential magnetic MAX phase

A. Mockute*, M. Dahlqvist, Linköping University, Sweden; J. Emmerlich, RWTH-Aachen University, Germany; L. Hultman, Linköping University, Sweden; J. M. Schneider, RWTH-Aachen University, Germany; P. Persson, J. Rosen, Linköping University, Sweden

Thin films of a new MAX phase alloy $(Cr,Mn)_2AlC$ have been synthesized by magnetron sputtering from four elemental targets. Structural characterization by X-ray diffraction and cross-sectional transmission electron microscopy reveals (0001)-oriented epitaxial films. Elemental mapping through electron energy-loss spectroscopy and energy dispersive X-ray spectroscopy analysis shows a homogeneous film composition, revealing a Mn content of at least 8 at.%. Theoretical work predicts that substitution of Cr by Mn in Cr_2AlC should provide MAX phase with a magnetic state depending on the Cr/Mn atomic configuration on the *M* sublattice [1]. Initial vibrating sample magnetometry measurements of samples with a Mn content higher than 8 at.% indicate magnetic response well above room temperature. Magnetic MAX phases would be excellent candidates for inherently laminated magnetic materials with atomic-thin layers.

Materials Design II

Room: Coquina Salon F
Session Chair: Per Eklund, Linkoping University

3:20 PM

(ICACC-S12-005-2013) Design of High Emissivity Coatings for Hypersonic Applications using Plasma Spray

W. Tan*, A. H. Strachan, R. W. Trice, Purdue University, USA

Hypersonic vehicles require sharp-featured nose tips and wing leading edges to reduce aerodynamic drag. However, the geometry of these edges increases heat transfer to the surface. This temperature can be reduced via increasing the radiation heat transfer away from the surface. Ultra-high temperature ceramics (UHTCs) such as ZrB_2 with the addition of SiC are often proposed for use as protection for structural systems in high temperature oxidative environments. In this study, an emissivity modifier is incorporated into the ZrB_2 system to improve its surface radiation heat transfer. Rare earth oxides are added to ZrB_2-SiC plasma spray coatings to improve their high temperature properties by increasing emissivity. During the plasma spray process, ZrB_2-20vol%SiC-RE_2O_3 (RE=Sm, Tm, Gd, Er) coatings are formed. X-ray diffraction data suggests that the dopants have been integrated into the coatings. Study shows the doped rare-earth ions still reside in the coatings after oxidization at 1500°C for an hour. The coefficient of thermal expansion (CTE) mismatch between ZrB_2-30 vol% SiC composite and pure rare-earth oxides at 200°C-1400°C is investigated. Total hemispherical emissivity results of the above coatings will also be presented.

3:40 PM

(ICACC-S12-006-2013) Synthesis of Novel Hafnium-Containing Ultrahigh-Temperature Ceramic Nanocomposites

E. Ionescu*, J. Yuan, B. Mainzer, H. Kleebe, R. Riedel, Technische Universitaet Darmstadt, Germany

Polymer-derived ceramic nanocomposites (PDC-NCs) can be synthesized via thermal conversion of suitable single-source precursors, leading in a first step to amorphous single-phase ceramics, which subsequently undergo phase separation processes to furnish bi- or multiphase ceramic nanocomposites. PDC-NCs have been shown to be excellent candidate materials suitable for applications at ultrahigh-temperatures and under harsh environments. In the present work, amorphous SiHf(B)CN-based PDC-NCs were synthesized via cross-linking and ceramization of a polysilazane which was chemically modified by $Hf(NEt_2)_4$ and borane dimethylsulfide complex ($BH_3.SMe_2$). High-temperature annealing of the obtained amorphous SiHf(B)CN ceramics in nitrogen atmosphere led to HfN/Si(B)CN nanocomposites; whereas HfB_2/Si(B)CN was obtained upon annealing in argon atmosphere. The presented results emphasize a convenient preparative approach to nanostructured ultrahigh-temperature stable materials starting from greatly flexible/compliant single-source precursors.

4:00 PM

(ICACC-S12-007-2013) Graphene NanoPlatelets Reinforced Tantalum Carbide Consolidated by Spark Plasma Sintering

A. Nieto*, D. Lahiri, A. Agarwal, Florida International University, USA

Graphene Nanoplatelets reinforced Tantalum Carbide composites are consolidated by spark plasma sintering (SPS). Tantalum Carbide is an ultra high temperature ceramic (UHTC) with various high temperature applications such as scramjet engines and hypersonic entry vehicles. Graphene is a single sheet of sp^2 bonded carbon atoms with excellent mechanical properties making it an ideal reinforcing second phase. GNP consist of 20 – 30 sheets of graphene and have been used to toughen ceramic composites. TaC-GNP composites are synthesized at extreme conditions of 80 – 100 MPa and 1850 °C. Concentration of GNP in composites varies from 1 vol% GNP to

5 vol% GNP. TaC-GNP composites microstructure is characterized using scanning electron microscopy (SEM), x-ray diffraction (XRD), and micro-raman spectroscopy. SPS processing results in high densification of samples without formation of additional phases. SPS processing shows favorable effects on GNP without damaging the GNP. Mechanical properties are evaluated using micro-indentation, nano-indentation, and 3-pt bend flexural testing. Addition of GNP is expected to enhance mechanical properties of TaC through toughening mechanisms observed in bulk GNP and GNP composites.

4:20 PM

(ICACC-S12-008-2013) First Steps into Near-Net-Shape Manufacture of UHTC components: Colloidal Processing Revolution

C. Tallon*, University of Melbourne, Australia; G. V. Franks, Defence Materials Technology Centre, Australia

Ultra High Temperature Ceramics (UHTC) are the material of choice for hypersonic applications. We have previously shown that the use of colloidal processing techniques aids in reducing the number of defects in the green body and produces higher particle packing, which ultimately enable achieving fully densification at lower temperatures and pressures, even pressureless sintering. In addition, the combination of colloidal processing and pressureless sintering allow the preparation of near-net-shape components as leading edges with reasonable sintered densities and without the formation of secondary phases or significant oxidation. Zirconium diboride (ZrB2) leading edges have been prepared by slip casting and pressureless sintering from powder suspensions. The understanding of the interaction forces of the powder in suspension is the key to produce a low viscosity formulation that lead to a high density defect-free material. The leading edges have been tested with an oxyacetylene torch to simulate the extreme conditions these materials will withstand when in use. The leading edges prepared in this way survived more than 3 min at temperature higher than 3300°C, while keeping the shape. This work comprises a study of the material microstructure after testing to evaluate the final suitability of the colloidal processing approach to manufacture UHTC components. The promising results are the starting point in the development of other compositions and other near-net-shape processes for the manufacture of UHTC components.

Structure-Property Relationships I

Room: Coquina Salon F
Session Chair: Thierry Ouisse, Grenoble INP

4:40 PM

(ICACC-S12-009-2013) Plasmon excitations in MAX phases: evidence of atomic scale superlattice-like behavior

V. Mauchamp*, Institut Pprime, France; M. Bugnet, Mc Master University, Canada; P. Chartier, T. Cabioc'h, M. Jaouen, Institut Pprime, France

Plasmon excitations in metallic systems are collective oscillations of the valence electron gas when screening an electromagnetic perturbation. These modes give information on the intrinsic behavior of the valence electrons and, depending on the material, can be correlated to transport properties, mechanical properties, spatial confinement etc. We use Electron Energy-Loss Spectroscopy in a Transmission Electron Microscope to probe the anisotropy of the plasmon excitation in Cr2AlC single grains for various crystallographic orientations ([100] and [001] zone axes). Experimental results are interpreted on the basis of Density Functional Theory calculations including excited states effects. It is shown that the experimentally observed plasmon anisotropy is driven by the competition between the excited states effects (electron-hole interactions) and the charge transfers between the Cr6C and Al layers. Of special interest, these effects are very small within the basal planes of the structure. As a consequence, we demonstrate that the basal plane dielectric behavior of Cr2AlC can be reproduced using an effective medium approach in which the MAX phase is described as an atomic scale superlattice built from pure Al and Cr6C planes. This result, extended to other 211 and 312 compounds, brings a simple approach for the understanding of MAX phases electronic properties.

5:00 PM

(ICACC-S12-010-2013) Evidence for anisotropic transport properties of Ti2AlC

W. Yu, V. Mauchamp, V. Gauthier-Brunet, T. Cabioc'h, Institut PPRIME, France; L. Gence, L. Piraux, Université catholique de Louvain, Belgium; P. Eklund, Linköping University, Sweden; S. Dubois*, Institut PPRIME, France

The anisotropy of Ti2AlC transport properties are understood from the compared study of both a highly-oriented (000l) Ti2AlC thin film and a Ti2AlC polycrystalline bulk sample. Resistivity and Hall voltage are measured as a function of temperature. For the polycrystalline sample, resistivity versus temperature measurements are in good agreement with previously published data. It is shown that electron-phonon interactions are different in and out of the basal plane. It is also demonstrated that the sign of the Hall voltage depends on the orientation of the crystal; it is negative in the polycrystalline sample and positive along the basal plane of the highly-oriented (000l) Ti2AlC thin film. These results are compared to Density Functional Theory based band structure calculations coupled to transport properties calculations, obtained within a semi-classical framework. In particular, the calculations show that the trace of the Hall tensor is negative, confirming the experimental results obtained on the polycrystalline sample, whereas the sign of the basal plane component of the Hall coefficient is positive. Such results, in very good agreement with experimental data, allow understanding the origin of the observed anisotropy from the different band dispersion between the basal plane and c-axis direction of the structure.

5:20 PM

(ICACC-S12-011-2013) The electronic-structure origin of the anisotropic thermopower of nanolaminated Ti3SiC2 determined by polarized x-ray spectroscopy and Seebeck measurements (Invited)

M. Magnuson*, Department of Physics, Chemistry and Biology (IFM), Sweden; M. Mattesini, , Astronomía y Astrofísica I, Universidad Complutense de Madrid, Spain; N. Nong, Technical University of Denmark, Denmark; P. Eklund, L. Hultman, Department of Physics, Chemistry and Biology (IFM), Sweden

In bulk polycrystalline form, Ti3SiC2 has a zero Seebeck coefficient over a wide temperature range. In contrast, we find that the in-plane (basal ab) Seebeck coefficient of Ti3SiC2, measured on single-crystal films has a substantial and positive value of 4-6 μV/K. By employing a combination of polarized angle-dependent x-ray spectroscopy and density functional theory we show electronic structure anisotropy in inherently nanolaminated Ti3SiC2 single-crystal thin films as a model system. The density of Ti 3d and C 2p states at the Fermi level in the basal ab-plane is about 40 % higher than along the c-axis. Positive contribution to the Seebeck coefficient of the element-specific electronic occupations in the basal plane is compensated by 73 % enhanced Si 3d electronic states across the laminate plane that give rise to a negative Seebeck coefficient in that direction. The strong phonon vibration modes with three to four times higher frequency along the c-axis than along the basal ab-plane also influence the electronic population and the measured spectra by the asymmetric average displacements of the Si atoms. These results constitute experimental evidence explaining why the average Seebeck coefficient of Ti3SiC2 in polycrystals is negligible over a wide temperature range [Magnuson et al. PRB 85 195134 (2012)].

S1: Mechanical Behavior and Performance of Ceramics & Composites

S1 Poster Session

Room: Ocean Center

(ICACC-S1-P002-2013) Rapid fabrication process for C/SiC composites with dispersed SiC slurry infiltration method

T. Hara*, Y. Kogo, M. Ishikawa, Tokyo University of Science, Japan; T. Aoki, T. Ogasawara, Japan Aerospace Exploration Agency (JAXA), Japan

The polymer impregnation and pyrolysis (PIP) method, and silicon melt infiltration (Si-MI) method are conventional processing routes of Carbon-fiber-reinforced SiC matrix (C/SiC) composites. In PIP method, due to the low volume yield of pre-ceramic polymers after pyrolysis, PIP should be repeatedly processed to obtain high-density C/SiC composites. This leads to long manufacturing time and high processing cost. For the purpose of reducing the processing cost, a slurry infiltration process was studied in this paper. In this process, the space between fibers in a 2D carbon fiber preform was impregnated with SiC powder slurry by a pressure-assisted infiltration before the PIP process. The preform achieves high particle packing density with well-dispersed SiC slurries in this way. Then, the powder filled preform was further densified by the PIP method or the melt infiltration (MI) method. Through these experiments, SiC powder infiltration behavior during a pressure assisted slurry infiltration process was discussed, and basic mechanical properties of C/SiC composites fabricated by these processes were evaluated.

(ICACC-S1-P003-2013) The Study on the sinterabilty of SiC powders prepared from solarcell wafer sludge

Y. Kim, D. Chun*, Inocera inc., Republic of Korea

This study is designed to investigate effects of processing conditions on the sinterability of SiC powders prepared from solarcell wafer sludge. The main components of the sludge are SiC and Si powders. The size of SiC powders is about 10um. This sludges were heat treated with carbon-black in vacuum in order to transform Si to SiC. These powders were milled by some methods in various conditions. After the treatment, the α/β ratio was determined by XRD. Granules for sintering experiments were spray-dried with sintering aids of Al2O3 and Y2O3 . Then they are pressed with CIP at 200MPa to make formed bodies. The formed bodies were sintered at 1930°C for 1hr in Ar purging atmosphere. The ramp-up speed, sintering atmosphere and other sintering variables were controlled to get higher physical properties. Phase analysis, particle size distribution, hardness and toughness were measured and the microstructures of sintered specimen were investigated using SEM.

(ICACC-S1-P005-2013) A finite element study on the bending behavior of sandwich structured Si-SiC ceramics

C. D'Angelo*, A. Ortona, SUPSI, Switzerland

Sandwich structured ceramic matrix composites are widely used in thermal protection systems for aerospace applications. This work aims at developing a reusable TPS solution able to withstand repeatedly the extreme conditions of a vehicle entering into an atmosphere. These structures are severely thermo-mechanically loaded and a specific design of the sandwich component is mandatory. Starting from a sandwich X ray computed tomography reconstruction the main morphological characteristic were figured out. On this basis an analytical model reproducing a bending test was developed and validated giving indications on the failure modes and loads. Finally an on-line monitoring technique for ceramic sandwiches was set up based on the electrical resistance variation of the foam given by the progressive strut failure.

(ICACC-S1-P006-2013) Microstructure and Properties of Reaction Bonded Metal Modified Ceramics

S. Salamone*, M. Aghajanian, M Cubed Technologies Inc., USA; S. Horner, J. Zheng, Program Executive Office-Soldier, US Army, USA

As a class of materials, reaction bonded ceramics can be readily tailored to obtain the desired properties. Varying the starting powder (preform) characteristics such as morphology, particle size, and composition is one avenue to achieve the required properties. Another method is to alter the infiltration melt. Typical RB(SiC/B_4C) composites use liquid silicon as the infiltration metal. However, the infiltration metal can be alloyed with other metallic species to change the composition and properties of the solidified phases. Several Si-(Cu, Fe)/SiC/B_4C composites were fabricated using the reaction bonding technique with an alloyed melt infiltration containing as much as 20 wgt% Cu and/or Fe. The infiltrated samples were studied using X-ray diffraction and Scanning Electron Microscopy. Several new phases, including silicides, were formed and the resultant physical properties were measured. Microstructure imaging, along with EDS analysis identified the location of various copper and iron rich regions contained within the composite. As the amount of secondary metal species increases there is a corresponding decrease in the residual free silicon content. The compositional changes also affect the physical properties such as density and Young's modulus as well as the mechanical properties. The following study will correlate the composition and microstructure with the mechanical properties.

(ICACC-S1-P008-2013) Weave and Fiber Volume Effects on Durabilty of Ceramic Matrix Composites

G. Ojard*, R. Naik, E. Prevost, Pratt & Whitney, USA; U. Santhosh, Structural Analystics, Inc., USA; D. Jarmon, United Technologies Research Center, USA

With the increasing interest in ceramic matrix composites (CMCs) for a wide range of applications, research is needed to understand the impact of fiber architecture and fiber volume fraction on material durability. With this in mind, three CMC panels were fabricated via a polymer infiltration and pyrolysis process with different fiber architectures: 8 harness satin (HS) balanced weave, 8 HS bias weave, and angle interlock. The different fiber architectures resulted in different fiber volume fractions in the warp and fill directions. Creep and 30 Hz fatigue testing with samples oriented in both the warp and fill directions was accomplished. The results from this testing will be presented, trends reviewed, and analysis reported.

(ICACC-S1-P009-2013) Fiber, Porosity and Weave Effects on Properties of Ceramic Matrix Composites

G. Ojard*, Pratt & Whitney, USA; J. Cuneo, Southern Research Institute, USA; I. Smyth, E. Prevost, Pratt & Whitney, USA; Y. Gowayed, Auburn University, USA; U. Santhosh, Structural Analytics, Inc., USA; A. Calomino, NASA – Langley Research Center, USA

As insertion opportunities keep increasing for ceramic matrix composites in aerospace and power generation, the understanding of changes in the microstructure needs to be explored. Past efforts have looked at different weave architectures on the mechanical performance of CMCs. This effort is expanded by changing the fiber used in the CMC. This change was also accompanied by a process change that affected porosity distribution in the material. The changes introduced were investigated via micro-structural and property characterization. The property characterization consisted of mechanical and durability testing. The results from this testing will be presented, trends reviewed and analysis done and compared to past testing efforts.

(ICACC-S1-P010-2013) Aqueous Corrosion of Ti(C,N)/Ni3Al Cermets

M. B. Holmes, G. J. Kipouros, Z. N. Farhat, K. P. Plucknett*, Dalhousie University, Canada

Ceramic-metal composites, or cermets, are known to be very strong and wear resistant, and as such are often used as drilling or cutting tools, pump seals, and as protective coatings. Cermets based on titanium carbonitride (Ti(C,N)) have drawn considerable attention. In the current work, TiC and Ti(C,N) cermets have been prepared with a nickel aluminide (Ni3Al) binder; Ti(C,N) samples prepared include TiC0.3N0.7, TiC0.5N0.5 and TiC7N3, with 40 vol% Ni3Al binder, while TiC samples were varied between 10 and 40 vol% binder. A 2 hour open circuit potential test was conducted to establish equilibrium between polished cermet samples and a 3.5 wt% NaCl aqueous solution in an electrochemical cell, using a Pt counter electrode and standard calomel electrode (SCE; -241mV compared with the standard H2 electrode). Potentiodynamic tests were subsequently performed, wherein a current is applied to measure the resistance of the now polarized sample, ranging from -0.5V to 3V. Microstructural assessment was conducted using scanning electron microscopy (SEM), optical microscopy and x-ray diffraction. The potentiodynamic tests revealed that the predicted active-passive transition behaviour is observed. SEM images of the post-corroded samples reveal some evidence of cracking and pitting. Post-test chemical analysis of the aqueous solution highlighted elemental species diffusing from the cermets.

(ICACC-S1-P011-2013) Structural, dielectric and ferroelectric properties of Sr doped BZTN-BCT ceramics

J. Rani*, K. L. Yadav, S. Prakash, Indian Institute of Technology Roorkee, India

Polycrystalline ceramics of $Ba_{(1-x)}Sr_x(Zr_{0.2}Ti_{0.8})_{0.9}Nb_{0.1}O_3$-$50(Ba_{0.7}Ca_{0.3})TiO_3$ (BSZTN-BCT); x=0, 0.1, 0.15 have been prepared for the first time as per literature survey. Ceramics were synthesized by solid state reaction method successfully and calcined at 1200 °C for 2 h. XRD pattern of sintered pellets revealed that ceramics have pure perovskite structure, which indicates that Sr^{2+} has diffused in BZTN-BCT lattice to form a homogeneous solid solution. XRD peak shifted towards higher angle side with the doping of Sr^{2+}. Field emission scanning electron microscopy (FESEM) micrographs indicate that samples have grains of spherical/oval shape. There is no significant variation in the grain size with Sr^{2+} doping. Energy dispersive X-ray spectrometer (EDS) was used to semi-quantitatively analyze the chemical composition of synthesized powders and found in stoichiometry. The variation of dielectric constant with temperature depicts that maximum dielectric constant is observed for x=0.1 at Curie temperature (T_C). T_C shifted towards lower temperature with Sr^{2+} doping. The dielectric constant with frequency is found to decrease which may be due to inability of electric dipoles to be in pace with frequency of applied electric field at higher frequency. The polarization-electric field (P-E) hysteresis loops of samples are observed at room temperature.

(ICACC-S1-P013-2013) Advanced Ceramics Property Measurements

J. Salem, NASA GRC, USA; J. D. Helfinstine*, Corning Inc, USA; G. Quinn, NIST, USA; S. Gonczy, Gateway Materials Technology, Inc, USA

Mechanical and physical properties of ceramic bodies can be difficult to measure correctly and repeatedly, unless the proper techniques are used. To help users and producers find established techniques to measure a particular property of a ceramic monolith, composite, or coating, the Advanced Ceramics Committee of ASTM, C-28, has developed dozens of consensus test standards and practices, that give the "what, how and how not, and why" for mechanical, physical, thermal, and performance properties. Using these standards will provide accurate, reliable, and complete data for rigorous comparisons with other test results in your test lab or somewhere else. The C-28 Committee has involved academics, and producers and users of ceramics to write and continually update more than 45 standards since the committee's inception in 1986. Included in this poster will be a pictogram of the C-28 standards and how to obtain individual copies with full details or the complete collection of all of them in one volume. A listing of other committees that might be of interest will be included.

(ICACC-S1-P014-2013) Acoustic Emission and Electrical Resistivity Monitoring of SiC/SiC Composite Cyclic Behavior

C. R. Baker*, G. N. Morscher, University of Akron, USA

Successful implementation of SiC/SiC composites in rotating components demands an excellent understanding of their cyclic stress and fatigue behavior. Two fiber-reinforced melt-infiltrated composites were tested under several cyclic stress conditions. In situ acoustic emission and electrical resistance was used to monitor damage accumulation and understand time and stress dependant degradation of mechanical properties. Post test microscopy and fractography was then used to observe microstructural anomalies which suggest possible damage progression mechanisms. Electrical resistance measurements were in good agreement with calculated interphase wear and show potential as a monitoring technique for fatigue related damage.

(ICACC-S1-P015-2013) Acoustic Emission and Electrical Resistivity During Tensile Testing of Different Volume Fraction SiC/SiC Composites

A. Almansour*, S. Ramasamy, G. N. Morscher, The University of Akron, USA

Hi Nicalon, Hi Nicalon Type S and Tyranno ZMI reinforced mini-composites with BN interphases were tested with different fiber volume fractions. Tensile tests, acoustic emission and electrical resistivity monitoring were performed to assess damage development during the test. Crack density and spacing were analyzed to determine the exact crack formation and crack location. Microstructural analysis was performed on the fracture surface to relate fiber fracture with acoustic signals. Finally, the mechanical behavior was modeled based on damage progression from health monitoring techniques.

(ICACC-S1-P016-2013) Structural, dielectric and magnetoelectric studies of $Ni_{0.75}Zn_{0.25}Fe_2O_4$-$BiFeO_3$ multiferroic composites

N. Adhlakha*, K. L. Yadav, Indian Institute of technology Roorkee, India

The effect of substitution of $Ni_{0.75}Zn_{0.25}Fe_2O_4$ (NZF) on dielectric, ferroelectric and magnetoelectric properties of $BiFeO_3$ has been investigated. Spinel-perovskite multiferroics $(x)Ni_{0.75}Zn_{0.25}Fe_2O_4$-$(1-x)BiFeO_3$ (x=0, 0.10, 0.20) have been prepared via mixed oxide route. The X-ray diffraction (XRD) and Field emmision scanning electron microscopy (FESEM) were used to analyze the structure and morphology of the composites, which revealed the presence of both the spinel (NZF) and perovskite ($BiFeO_3$) phases respectively. The study of variation of dielectric constant with temperature at different frequencies has been carried out and it is found that the value of dielectric constant is increased with increasing NZF content. The well saturated polarization-electric field (P-E) curves are observed at room temperature, which indicates strong ferroelectric characteristic in the prepared composites The value of remnant polarization (P_r) is found to decrease with addition of NZF content. The evidence of magnetoelectric coupling is found from the magnetic field induced relative change of dielectric constant. The increase of NZF content in $BiFeO_3$ content leads to enhanced magnetoelectric coupling at room temperature.

(ICACC-S1-P017-2013) The effect of thermo-mechanical loading and environmental exposure on creep resistance of EBC/CMC systems

M. P. Appleby*, G. N. Morscher, University of Akron, USA; D. Zhu, NASA Glenn Research Center, USA

Interest in SiC fiber-reinforced SiC ceramic matrix composite (CMC) environmental barrier coating (EBC) systems for use in high temperature structural applications has prompted the need for characterization of material strength and creep performance under complex aerospace turbine engine environments. Stress-rupture tests have been performed on SiC/SiC composites systems, with varying fiber types and coating schemes to demonstrate material behavior under isothermal conditions. Further testing was conducted under exposure to thermal stress gradients, thermal cycling and simulated combustion environments to determine the effect on creep resistance and material durability. In order to understand the associated damage mechanisms, emphasis is placed on experimental techniques as well as implementation of non-destructive evaluation; including modal acoustic emission and electrical resistivity monitoring. The influence of environmental and loading conditions on life-limiting material properties is shown.

(ICACC-S1-P019-2013) Local Damage and Heterogeneous Structure in Discontinuous Carbon Fiber Dispersed SiC Matrix Composites under Stress Concentration Source

R. Inoue*, H. Kakisawa, Y. Kagawa, University of Tokyo, Japan

Discontinuous carbon fiber-dispersed SiC matrix (DCF/SiC) composites fabricated by Si melt infiltration process have quite complicated structure, e.g., DCF/SiC/Si multi-phase, random dispersion of DCF bundles. Fracture toughness of this composite is very poor and the level is close to monolithic engineering ceramics, however, this material behaves tough in service condition. To understand this behavior detailed damage observation behavior has been carried out. The observation result shows that various types of microcracks occur under source of stress concentration. Most of the cracks occur in SiC phase near the long crack tip. To understand this cracking behavior, discussion on the origin of microcracks and their effect on tough behavior of the DCF/SiC will be discussed. Especially, special attention has been played on relation between heterogeneous structure and the cracks stability.

(ICACC-S1-P020-2013) Oxidation behavior and mechanical properties degradation of hot-pressed Al2O3/ZrB2/ZrO2 ceramic composites

A. Goodarzi*, H. Taylor, Harvard University, USA; M. Arslan, Ataturk University, Turkey

Composites of Al2O3/ZrB2/ZrO2 ceramic were fabricated by technology of the hot-pressing sintering. The oxidation kinetics model of Al2O3/ZrB2/ZrO2 composite was established, and the high temperature oxidation behavior of the composite was studied. It was found that oxidation velocity increased as the ZrB2/ZrO2 content was raised at the same oxidation time. Oxidation test and XRD analysis indicated that the composites began to oxidate in 500–700 C. Meanwhile, the effect of oxidation on microstructure was analyzed. The high temperature oxidation behavior of the composite was studied. It was found that the experimental weight gain is obviously greater than the forecast model, the reason was some impurities in the oxidation furnace adhered to the sample. The oxidation velocity increased when the ZrB2/ZrO2 content was raised at the same oxidation time. Oxidation test and XRD analysis indicated that the composites began to oxidate at 500-700 C. Meanwhile, the effect of oxidation on the microstructure was analyzed. Results showed that the oxidation region of surface was not as homogeneous as predicted, and small glassy bubbles were visible on the oxidized fracture surface.

(ICACC-S1-P021-2013) Effect of fiber type on mechanical properties of short carbon fiber reinforced B4C composites

A. Goodarzi*, H. Taylor, Harvard University, USA; M. Arslan, Ataturk University, Turkey

In order to enhance the mechanical properties of B4C without density increase, the short carbon fibers M40, M55J and T700 reinforced B4C ceramic composites were fabricated by hot-pressing process. The addition of the carbon fibers accelerates the densification of the B4C, decreases their densities, and improves their strength and toughness. The enhancement effects of the three kinds of carbon fibers were studied by investigating the density, Vickers hardness and the mechanical properties such as flexural strength, flexural modulus and fracture toughness of the composites. The fiber type has a great influence on the mechanical properties and enhancement of the short carbon fiber reinforced B4C composites. The flexible carbon fiber with high strength and low modulus such as T700 is appropriate to reinforce the B4C matrix ceramic composites.

(ICACC-S1-P022-2013) Low temperature Diffusion bonding of Alumina-Alumina ceramics by Hydride inter-layer nano powders mixtures

N. Hosseinabadi*, R. Sarraf MAmoory, TMU, Islamic Republic of Iran

Low temperature diffusion bonding of Alumina-Alumina ceramics bodies was studied based on using special mixture of nano sized hydride powders. The bonding process was carried out with costume modified hot press. The bonds interlayer characteristics were investigated for crystal structure, morphology, and strength by XRD, FE-SEM, TEM, and 4point bending standard tests. The effect of formulized interlayer mixtures on improving contact area and decrease of bond temperature was considerable.

(ICACC-S1-P024-2013) Compression failure analysis of graphite foam core based sandwich composite constructions

H. Hosseini*, S. Ghaffarian, Amirkabir University of Technology (Tehran Polytechnic), Islamic Republic of Iran; M. Teymouri, A. Moeini, National Iranian Oil Company, Research Institute of Petroleum Industry, Islamic Republic of Iran

Coal tar pitch base graphite foams processed and examined under compression test in order to investigate the relation between microstructure and strength properties of microcellular graphite. Two step pyrolysis of coal tar pitch under pressure has been served to obtain microcellular carbonaceous solid which further carbonization converts it to the porous graphite structure with capability of usage as a core in sandwich structures instead of utilizing traditional honeycombs. After machining the as-obtained foams, compression test performed to investigate the mechanical properties of core. It was shown that by increasing the foaming pressure, the compression strength and modulus increases. Amount of porous and formed microstructure within the solid has dominated effect in resistance to catastrophic failure. Increasing temperature in process will form the uniform open cell structure due to progressing in bubble nucleation and growth, which eventually shows higher ductility behavior during the collapse stage. Also higher softening point of coal tar pitch and mesophase pitch precursors obtaining from first step heat treatment, enhances the compression strength due to increasing the melt strength and reaching higher molecular weight, leading more solidus matrix contains air vacancies. Thus by altering the process parameters, mechanical properties of porous graphite material can be regulated.

(ICACC-S1-P026-2013) Ultra High Temperature Oxidation of ZrB2-SiC-ZrC ceramics up to 1700 °C

Y. Arai*, Y. Kogo, M. Ishikawa, Tokyo University of Science, Japan; S. Guo, National Institute for Material Science (NIMS), Japan; K. Goto, Japan Aerospace Exploration Agency (JAXA), Japan; T. Yasuno, Iwaki Meisei University, Japan

The purpose of this study is to decide the optimal composition of ZrB2-SiC-ZrC (ZSZ), and to clarify its oxidation mechanism. ZSZ ceramics with four different compositions containing 16 vol% SiC were sintered by hot press and spark plasma sintering. Firstly, the ZSZs oxidized continuously up to 1500 °C using thermo gravimetric analysis. The ZSZ containing the highest ZrB2 indicated the lowest weight gain, and that containing the highest ZrC indicated the highest weight gain. After the oxidization, the samples' surface and cross section were studied by X-ray diffraction, optical microscope and scanning electron microscope along with X-ray dispersive spectroscopy. Results of these analyses for the samples revealed that ZSZs have oxidation resistance due to formation of the oxide scale, which act as the barrier for oxygen diffusion into the unoxidized substrate. In the next step, ZSZ ceramics was heated continuously up to 1700 °C in air using ultra high temperature furnace. Oxidation test was also carried out at 1700 °C by IR image furnace. The surface of the specimen after oxidation had a number of bubbles and appeared to be covered with zirconia and silica. These results suggested that the active oxidation of SiC was occurred under the oxide scale. In addition, because the spallation of the scale was not observed, it was suggested that ZSZs showed the resistance to the active oxidation of SiC.

(ICACC-S1-P027-2013) The Effect of Heat Treatment on the Microstructure and Creep Properties of Erbium Oxide containing SiAlON Ceramics

D. Turan*, Y. Deniz, S. Kayhan, A. Uludag, Anadolu University, Turkey

SiAlON ceramics are important materials for high temperature applications and their use at high temperatures depends on their behavior under creep conditions. Creep properties of SiAlON are largely controlled by the amount and type of sintering additives. In this work, we investigate the effect of heat treatment on the microstructure and creep properties of Er containing SiAlON samples. The heat treatment of the sintered samples was carried out at different temperatures (1600-1700oC) and times (2, 6 and 24 hour) under 1 bar nitrogen pressure. The creep tests were carried out at different temperatures (1300, 1350 and 1400oC) under different loads (50, 100, 150 MPa). The microstructures were investigated by using scanning electron microscope attached with an energy dispersive x-ray spectrometer. It is found that heat treatment at higher temperatures and longer times result in better creep performance. The activation energy and creep rate was also calculated for the best heat treatment conditions. In this presentation, the relationship between the microstructure and creep performance will be demonstrated.

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

S2 Poster Session

Room: Ocean Center

(ICACC-S2-P027-2013) Large Transverse Thermoelectric Voltage Effect in Nb-doped $SrTiO_3$ Single and Multi layer Epitaxial Film

Y. Qin*, T. Zhao, J. Yang, State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, China

$SrTi_{0.8}Nb_{0.2}O_3$ single layer and $[(SrTiO_3)_n/(SrTi_{0.8}Nb_{0.2}O_3)_m]_N$ multilayer films were grown on $LaAlO_3$ (001) oriented single crystal substrate tilted by 10° toward the [010] direction using pulsed laser deposition. XRD and HRTEM analyses revealed that epitaxial single-crystalline $SrTi_{0.8}Nb_{0.2}O_3$ single layer film was heteroepitaxially grown with (001) planes inclined by 10° against the substrate surface. The value of modulation periods in $[(SrTiO_3)_n/(SrTi_{0.8}Nb_{0.2}O_3)_m]_N$ multilayes calculated from its high angle satellite peaks of XRD was accordance with the results observed by HRTEM. Transverse thermoelectric voltage signals based on anisotropic Seebeck effect were observed in both single and multilayer films. The max voltage signal appeared in $SrTi_{0.8}Nb_{0.2}O_3$ single layer epitaxial film with cubic structure up to 6.88 V along *y* direction in *xy* plane, and it was about ten times larger than the max voltage signal produced in $[(SrTiO_3)_n/(SrTi_{0.8}Nb_{0.2}O_3)_m]_N$ multilayers. The unexpected results revealed that $SrTi_{0.8}Nb_{0.2}O_3$ single layer film grown on tilted substrate exist a large difference of Seebeck coefficient between the *c* axis direction and in the *ab* plane although it is cubic crystal structure. The study of the transverse thermoelectric voltage effect in $SrTi_{0.8}Nb_{0.2}O_3$ films shall expand the potential applications, such as light detector and microcooler.

(ICACC-S2-P028-2013) The self-healing matrix composites: Numerical approach of dynamic behavior of a self-healing fluid and the composite in a rotational system

L. Benazzouk*, E. Arquis, N. Bertrand, C. Descamps, M. Valat, University of Bordeaux 1, France

Self-healing matrix composites are currently in full development their use in the aerospace field is mainly due to their remarkable physical and chemical properties. Microscopic cracks are however inherent in the process of developing and are aggravated by the conditions of the use of composite parts. The self-healing matrix has a feature to allow the formation of viscous glasses in a crack by chemical reaction between the constituent elements of the matrix and oxygen. This glass by filling out the crack protects the fiber reinforcement and extends the life of the composite. To begin with, we focus on dynamic behavior of glass drops formed in a crack model by studying their growth and coalescence. These cases of coalescence lead, either to the formation of a liquid film or to the formation of a bridge. These phenomena are modeled using Thetis software developed by I2M to track the evolution of the glass in the crack when the composite material is subjected to an oxidizing environment as well as intense external mechanical stresses such as rotation. Then the experimental studies are carried to study the wettability of various glasses on a mixed substrate, representative of the multilayer self-healing matrix. Finally, numerical simulations of these experiments are conceivable to compare simulation results with those obtained experimentally.

(ICACC-S2-P029-2013) First principles simulations of vacancy formation in a Σ31 grain boundary of α-alumina

T. Ogawa*, A. Kuwabara, H. Moriwake, Japan Fine Ceramics Center, Japan; K. Matsunaga, Nagoya University, Japan; S. Kitaoka, Japan Fine Ceramics Center, Japan

In this study, we investigate vacancy formation in a Σ31 grain boundary of α-alumina by first principles simulations. The Σ31 grain boundary is expected to show similar characteristics as general grain boundaries. The vacancy formation energies of oxygen and aluminum atoms as a function of temperature and oxygen potential strongly affect migration of the defects in grain boundaries and hence the durability of thermal barrier coating systems. First principles calculations are useful to interpret the vacancy formation in grain boundaries. The electronic structures are calculated by the quantum simulations based on plane-wave expansions and projected augmented wave methods which are implemented in the VASP code. For relaxed atomic positions, formation energies are calculated. We use the Σ31 grain boundary model corresponding to the atomic arrangement observed by the scanning transmission electron microscope. We calculate ionic charges and relative ionic volumes to characterize the grain boundary. Relatively high deviations of the values compared to bulk cases are seen around the grain boundary. The vacancy sites are selected from the information. The formation energies of the vacancies show different behaviors from the bulk cases and structural and electronic details of the vacancy states are also analyzed.

(ICACC-S2-P031-2013) Development of solid lubricant by nano ceramic composite binder

W. Chung*, K. Yoo, Korea Automotive Technology Institute, Republic of Korea; G. Lee, SAM SAN SLC co., LTD., Republic of Korea; J. Min, Korea Automotive Technology Institute, Republic of Korea

Solid lubricants based on various nano sized compositions were manufactured by coating process. The nano composite binder was produced using several nano sized ceramic powder combined with organic polymer matrix. Experimental results depending on composition of ceramic powder and polymer matrix, and processing conditions will be presented. In addition, SEM morphology and the evaluated friction resistance of solid lubricant coating will be posted. This coating technology will be applied in an automotive parts like moving parts for application requiring wear-resistance.

(ICACC-S2-P032-2013) Formation of microcrystalline 3C-SiC film from Si and graphite sources by using a high-pressure hydrogen plasma

H. Ohmi*, H. Kakiuchi, K. Yasutake, Osaka University, Japan

The formation of microcrystalline 3C-SiC films on glass/Si substrates by the plasma enhanced chemical transport method was carried out using a high pressure hydrogen glow plasma. The precursors of the SiC films are generated by the chemical erosion of graphite and silicon in a hydrogen plasma. Fourier transform infrared (FTIR) absorption gas analysis indicated that the volatile species generated from the graphite and Si source were mainly CH4 and SiH4, respectively. The deposition rate of the SiC film increased monotonically from 14 nm/min to 29 nm/min with increasing substrate temperature (Tsub). All of the film compositions prepared were nearly stoichiometric. Electron diffraction showed that the prepared SiC films were microcrystalline 3C-SiC. Electrical conductivity of the prepared SiC films was found to increase exponentially from 3 x 10-4 S/cm to 1.7 S/cm with increasing Tsub. The prepared SiC films revealed n-type conductivity. By preparing the SiC film as n-type layer on p-type Si(001) substrate, the pn junction diode was fabricated. Because of reflectivity relationship between film and substrate, the absolute reflectance of Si surface can be suppressed to less than 4% by preparing a 70nm-thick SiC film on textured Si surface. These results show that the SiC film behaves as both anti-reflection coating and n-type emitter layer.

(ICACC-S2-P033-2013) Hot Corrosion of ZrO2-4mol%Y2O3 Plasma Sprayed Coatings by Volcanic ash

W. Lee, Gyeongsang National University, Republic of Korea; B. Jang*, T. Hiraoka, H. Araki, H. Murakami, S. Kuroda, National Institute for Materials Science (NIMS), Japan; D. Shin, National Institute for Materials Science (NIMS), Japan, National Institute for Materials Science (NIMS), JapanGyeongsang National University, Republic of Korea

Thermal barrier coatings (TBCs) manufactured by plasma spray coating or electron beam–physical vapor deposition (EB-PVD) have been favored because their unique microstructures offer the advantage of superior tolerance to mechanical strain and thermal shock at the high temperatures at which gas turbines are operated. The high temperature capability of a TBCs used in a gas turbine is often degraded by deposits of calcium-magnesium-alumino-silicate (CMAS). The CMAS melts are produced when siliceous minerals (volcanic ash, dust and sand) are ingested with the intake air and deposited on the hot surface of TBCs. In this work we examine the properties of hot corrosion of ZrO2 plasma sprayed coatings by volcanic ash. Samples of ZrO2-4mol%Y2O3 coatings with thicknesses in the range of 40~450 μm were deposited by plasma spray coating. Hot corrosion between ZrO2-4mol% Y2O3 coatings and volcanic ash was examined by heating samples to 1200C in air for time lengths between 10 min and 100hrs. Reaction layers between coatings and volcanic ash were found to increase with increasing oxidation time.

(ICACC-S2-P034-2013) Effect of surface morphology on thermal radiation reflectance of oxide ceramics multilayer coatings for high temperature thermal radiation control

M. Yamazoe*, H. Kakisawa, Y. Kagawa, University of Tokyo, Japan

Control of thermal radiation energy from heat source is a potential candidate for energy saving high temperature components. Oxide ceramics multilayer coating can be designed so that it can show high reflectance for specific wavelength and incident angle of thermal radiation. However, it is not effective for actual environment of wide wavelength range and multi-directional incidence of thermal radiation. In the present study to overcome these factors, a new design of oxide ceramics multilayer coating with different surface morphology has been proposed. The effect of scattering caused by surface morphology allows possibility of high reflection of thermal radiation energy from multiple directions. Thermal radiation energy-oxide ceramics multilayer interaction in the visible-infrared wavelength region was calculated by FETD method.

(ICACC-S2-P035-2013) Structural Design and Characterization of Flake-reinforced Oxide Coatings for CMC Surface Protection

H. Kakisawa*, T. Matsumoto, Y. Kagawa, University of Tokyo, Japan

Design and characterization of oxide coating for physical and chemical surface protection of ceramic matrix composites are done. Oxide composite coatings consisting of Al2O3 flake and mullite matrix are fabricated on SiC/SiC or SiC substrate. Aspect ratio of the flakes was changed with the volume fraction fixed. Fracture behavior of the coating and delamination behavior between the coating and substrate are investigated by an indentation method. Those behaviors are correlated with structural parameters like the dimension and aspect ratio of the flake; flake alignment; porosity of the matrix. From the obtained result, optimum structure of the composite coating is discussed to avoid through-thickness fracture and interface delamination.

(ICACC-S2-P036-2013) Effect of Extrinsic Factors on Rumpling Behavior of TGO Layer formed by Oxidation of PtAl Bond Coat

H. Suzuki*, H. Kakisawa, Y. Kagawa, University of Tokyo, Japan

Direct observation of rumpling behavior of TGO layer formed by oxidation of PtAl bond coat on superalloy system is carried out. A PtAl bond coat layer- superalloy substrate system is heat exposed in air at a temperature from 500 to 1300oC. Rumpling behavior of TGO layer is observed using the specially designed optical microscope with UV illumination and UV camera. Effects of heating condition, heating speed and heating pattern on the rumpling behavior are evaluated. Discussions are made on the formation process of undulation shape of TGO layer. Effect of temperature dependence of materials properties on the rumpling behavior is also discussed.

(ICACC-S2-P037-2013) Investigation of the three dimensional behavior of MCrAlY bond coat rumpling using high fidelity 3D imaging

S. Shahbazmohamadi*, E. Jordan, University of Connecticut, USA

Bond coat surface geometry change known as rumpling can be a contributing factor to the failure of TBC systems. While the rumpling of Pt modified NiAl bond coats is well recognized and addressed in the literature, the study of MCrAlY bond coat is less established. A highly reliable and repeatable technique has been previously introduced by the authors to record the surface geometry of the MCrAlY bond coats using SEM-based stereo-photogrammetry. In the present work, The technique is applied to bare MCrAlY bond coat samples. The samples have been investigated at several intervals of heat treatment and the quantified information of surface geometry change has been extracted to record the evolution of rumpling in such systems at each interval. Also, specific asperities such as tall mountains and deep valleys have been selected and their behavior has been investigated after each heat treatment interval. Statistical analyses have then been performed to find a general trend in these changes. The study finally tries to propose a typical behavior of MCrAlY bond coats rumpling using the extracted information.

S4: Armor Ceramics

S4 Poster Session

Room: Coquina Foyer

(ICACC-S4-P053-2013) Indentation Behaviour in Spark Plasma Sintered SiC-B4C Ceramics

D. Hallam*, P. Smith, J. Yeomans, University of Surrey, United Kingdom; A. Heaton, B. James, DSTL, United Kingdom

Recent research suggests that a detailed understanding of the deformation that accompanies quasi-static indentation of ceramic materials may provide an insight into how the ceramic will respond to a ballistic impact. If relationships between the two processes can be established then it might be possible for candidate armour ceramics to be identified early in the development process. Thus, this study examines the indentation behaviour of a range of spark plasma sintered SiC-B4C composites under Knoop and instrumented blunt (conical diamond) indentation. A combination of light and electron microscopy (scanning and transmission) techniques have been used to image surface and sub-surface damage (parallel and perpendicular to the axis of loading). Distinct differences between materials have been observed and behaviour has been linked tentatively to features of the load-penetration and indentation size effect curves, prior to examining behaviour in ballistic trials.

(ICACC-S4-P054-2013) Thermal Stability of Amorphous Boron Carbide Phase Formed Under Indentation

V. Domnich*, Rutgers University, USA; J. C. LaSalvia, E. R. Shanholtz, U.S. Army Research Laboratory, USA; R. A. Haber, Rutgers University, USA

Boron carbide is a material of choice for lightweight armor applications due to its exceptional mechanical and physical properties, such as high hardness, high Young's modulus and low specific weight. It has been shown in the literature that boron carbide experiences structural instability under contact loading, such as indentation, scratching, and shock impact, resulting in the formation of amorphous phase. The thermal stability of the amorphous phase formed under Knoop and Vickers indentation in single crystalline and polycrystalline boron carbide is reported in this work. Raman microspectroscopy is used for imaging the distribution of amorphous phase in the indentation contact zone subjected to increasing annealing temperatures. The differences in the spectral features of amorphized boron carbide and various carbon forms is demonstrated. The results can be used for calibration of localized high and transient temperatures observed in ballistically impacted boron carbide.

(ICACC-S4-P055-2013) Characterization of the Amorphous Zone Beneath Static and Dynamic Vickers Indentations in Boron Carbide

G. Parsard*, G. Subhash, University of Florida, USA

The focus of this study is to determine and compare the size and shape of the amorphous zone that forms beneath static and dynamic Vickers indentations in boron carbide. Raman spectroscopy is being utilized to identify the presence of carbon-rich amorphous phases in the vicinity of an indentation by plotting the area under the D-peak of the Raman spectra at various depths beneath the indentation. Utilizing standard metallographic polishing techniques to remove material in submicron depth increments and scanning the exposed subsurface with a Raman probe between polishing steps, the severity and spread of amorphization will be determined. Our preliminary investigations on indentation hardness of boron carbide have revealed that its dynamic hardness is significantly lower than its static hardness. This decrease in hardness is attributed to the higher level of pressure-induced amorphization under dynamic loads. Currently, investigations are being performed to obtain a comparison of the size and shape of the amorphized zone beneath static and dynamic Vickers indentations at a range of loads. The implications of these results for ballistic impacts will be discussed. These results will be correlated to the static and dynamic indentation hardness, the severity of amorphization under dynamic loads, and the subsequent loss of strength under ballistic impact.

(ICACC-S4-P056-2013) Macroscopic Assessment of High Pressure Failure of B4C and B4C/SiC Composites

S. Salamone, P. Karandikar, A. Marshall, M. Aghajanian*, M Cubed Technologies, Inc., USA; S. Horner, J. Zheng, Program Executive Office - Soldier, US Army, USA

Advanced ceramic materials, such as SiC and B4C, have long been used in applications that take advantage of their very high hardness, low density, and chemical stability. Example uses are armor, grit blast nozzles, and wear resistant components in mining. In general, B4C out performs SiC in these applications due to its higher hardness and lower density. However, in cases where the ceramic component is exposed to extremely high pressure (> 20 GPa), the performance of B4C falls below that of SiC. The present work aims to examine this behavior at the macro-scale using impact testing. First, a series of impact tests were performed on identical samples of B4C and SiC tiles. Testing over a range of pressures showed a cross-over in performance at nominally 20 GPa. Second, B4C/SiC composites with a range of B4C to SiC ratios were fabricated and tested above and below the 20 GPa threshold. Below 20 GPa, the higher B4C content composites performed best, whereas above 20 GPa, the higher SiC content composites performed best.

(ICACC-S4-P057-2013) Quantum Mechanical Study of Grain Boundaries in Boron Carbide

T. D. Beaudet*, Army Research Laboratory, USA; J. R. Smith, Johns Hopkins University, USA; J. S. Dunn, B. M. Rice, J. C. LaSalvia, Army Research Laboratory, USA

Boron carbide is of interest for a variety of applications including use as an armor material due to its low density and high hardness. Two inherent weaknesses, solid-state amorphization (SSA) and low fracture toughness, appear to limit boron carbide's potential ballistic performance. While the effect of SSA, positive or negative, is still highly debatable, the effect of low fracture toughness is not. Grain boundary engineering (e.g. nanoscale glassy intergranular films) is a proven means for increasing fracture toughness even in ceramics with equiaxed microstructures. Due to the lack of experimental data on the structure of grain boundaries in this ceramic, first-principles density functional theory is used to study the energetics of potential grain boundary structures. Specifically, the energetics of tilt boundaries with misorientations corresponding to low- and high-angle grain boundaries is explored. Techniques and results are discussed.

(ICACC-S4-P059-2013) Improvements in the Spark Plasma Sintering of Magnesium Aluminum Spinel

G. A. Alanko*, D. Butt, Boise State University, USA

Transparent $MgAl_2O_4$ spinel is a promising material for many applications, including armor ceramics. This material is typically prepared by hot pressing or pressureless sintering, followed by hot isotactic pressing; both produce specimens with relative inline transmission (RIT) near the theoretical maximum of 87%. Spark plasma sintering (SPS) has been used to produce transparent spinel with a fair RIT of ~60%, which is typically marked by a grey or brown discoloration of unclear origin. Heating rates of ~1C/min produce spinel with ~75% RIT and little grey discoloration, but preclude the quick processing time that is a primary advantage of SPS. The addition of LiF can remove discoloration and improve sintered density, but leads to excessive grain growth that is detrimental to the mechanical properties. Here, we reproduce the ~50% RIT results of Morita et al. on the high heating rate densification of spinel; then, we demonstrate a simple barrier method to practically eliminate grey discoloration in the consolidated spinel blank and improve the RIT% while maintaining sub-μm grain size. Our results provide further qualitative evidence for a carbonaceous origin of the grey discoloration and suggest a way forward for larger-scale SPS processing of transparent ceramics with minimal post-sinter grinding and polishing.

(ICACC-S4-P060-2013) Consolidation of Aluminum Magnesium Boride (AlMgB14) by Pulsed Electric Current Sintering (PECS) Technique

G. A. Gilde, K. Cho, N. Kedir*, Army Research Lab, USA

Aluminum magnesium boride, AlMgB14, is a viable candidate for armor applications due to its high hardness and low density. As a process for synthesizing dense AlMgB14, this study examined the pulsed electric current sintering (PECS) technique. Aluminum, magnesium (12 wt.%), and boron (74.7 wt.%) elemental powders were mixed in a resonant acoustic mixer and sintered at 1600 C and 70 MPa using a PECS apparatus. Densities of consolidated samples were measured by Archimedes method and phase characterization was carried out by X-ray diffraction. Microstructures were examined by scanning electron microscopy (SEM) and chemistry determined by energy dispersive x-ray spectroscopy (EDS). Vickers microhardness measurements were also performed. Furthermore, reactivity and phase transformations of the elemental powder mixture were examined by differential scanning calorimetery to further optimize the PECS processing parameters. Experimental procedures and results are presented.

(ICACC-S4-P062-2013) Al/Al2O3 metal matrix composites for armor applications

P. Karandikar*, M Cubed Technologies, Inc., USA; E. Klier, Army Research Laboratories, USA; M. Watkins, M. Aghajanian, M Cubed Technologies, Inc., USA

MMCs combine desirable characteristics of metals (ductility, thermal conductivity) and ceramics (high hardness, high stiffness, low thermal expansion). Aluminum-SiC particulate MMCs (Al/SiCp) have been used successfully in a variety of applications in large tonnage. Al/SiCp MMCs also provide desirable properties for armor applications (high hardness, high stiffness, and light weight). However, for

SiC based MMCs, the Al has to be alloyed with Si (>8%) to prevent formation of the deleterious Al4C3. Unfortunately, Si alloying reduces the ductility of the alloy and the MMC. For many armor applications, ductility is very critical for achieving multi-hit capability. Also, MMC is desired as a more ductile encapsulant for ceramic tiles. If the SiC particulates are substituted with Al2O3 particles, the matrix alloy does not need to have Si as an alloying element. As a result, an MMC with higher ductility can be achieved. In this study, Al/Al2O3 MMCs with alumina particle contents ranging from 14% to 55% are made by different processing approaches. Microstructures and properties (density, elastic modulus, tensile strength, elongation, and thermal expansion) of these MMCs are systematically characterized and correlated with the alumina content, processing methods, and process parameters. Composite properties are predicted by analytical models and are compared with experimental measurements.

(ICACC-S4-P063-2013) Microstructure and Mechanical Behavior of Pressureless Sintered and Reaction-Bonded Silicon Carbide Ceramics

A. Trachet*, G. Subhash, University of Florida, USA; P. Karandikar, M Cubed Technologies, USA

In this research, processing-structure-property relationships in commercially-available SiC produced by two processing methods, pressureless sintering and reaction-bonding, are investigated. Low-strain rate testing for hardness and compressive strength was accomplished with a traditional hardness tester and a servo-hydraulic press, respectively. The high strain-rate hardness testing was conducted with a dynamic indentation hardness tester, and high-strain rate compressive testing was performed with a split-Hopkinson pressure bar. The pressureless sintered SiC materials revealed greater hardness and compressive strength values than the reaction-bonded materials at all strain rates employed in this study. The hardness of the pressureless sintered samples was also found to be rate dependent, but the reaction-bonded materials displayed extensive damage under dynamic indentation. The lower strength and hardness of the reaction-bonded materials is likely attributed to the presence of residual silicon and the presence of various polytypes, which was investigated with optical microscopy, scanning electron microscopy, and Raman spectroscopy.

(ICACC-S4-P064-2013) Geometrical Effect on Damage in Reaction Bonded Ceramic Composites having Experienced High Strain Rate Impact

A. Marshall*, M Cubed Technologies, Inc., USA; K. J. Doherty, E. M. Klier, U.S. Army Research Laboratory, USA; P. G. Karandikar, B. P. Givens, A. F. Liszkiewicz, R. Segura, M Cubed Technologies, Inc., USA

Due to their favorable properties, such as high hardness, high stiffness, low density, and multiphase toughening, reactively bonded silicon carbide and boron carbide composites have been used broadly in the armor segment of the ceramic market. The process itself is also favorable when compared with hot-pressing and sintering in that shape complexity is easier to produce. Herein, damage assessment as the result of high strain rate impact is presented utilizing reaction bonded boron carbide/silicon carbide ceramic composites. Several geometries are examined to determine how damage in the ceramic composite phase can be controlled and localized to produce better multi-hit structures. These structures will include a solid flat tile as well as tiles with varying geometries, including perforations, protrusions, etc. Damage is characterized using 3D X-ray computed tomographic imaging techniques, standard 2D X-ray techniques, die penetrant analyses, and visual analyses. The aim of this study is a correlation between varying geometrical features and damage propagation.

(ICACC-S4-P065-2013) Surface preparation of silicon carbide for improved adhesive bond strength in armour

A. Harris*, P. Smith, J. Yeomans, University of Surrey, United Kingdom; S. Burnage, B. Vaughan, Lockheed Martin UK, United Kingdom

Surface treatments of silicon carbide have been investigated to determine if a range of preparations can increase the bond strength when using a toughened epoxy adhesive. Three surface conditions have been assessed: as-fired; refired in air; and krypton fluoride excimer laser treated. A range of techniques have been used to characterise the surfaces: scanning electron microscopy, x-ray photoelectron spectroscopy, profilometry and sessile drop. Compared with the as-fired surface, the refired and laser treated surfaces both had greater concentrations of oxygen. The oxygen was found to have formed an oxide layer and also hydroxyl groups on the surface. The laser treated and refired surfaces were also found to have reduced average roughness and increased wettability; the laser treated surface had been partially melted. The adhesive bond strength was assessed by quasi static mechanical testing. It was found the refired and laser treated surfaces demonstrated a significant improvement in bond strength over the joints with as-fired surfaces as a consequence of the chemical and mechanical modifications of the surface.

(ICACC-S4-P066-2013) Production of silicon carbide-boron carbide composites for armour applications

T. Williams*, J. Yeomans, P. Smith, University of Surrey, United Kingdom; A. Heaton, Dstl, United Kingdom; C. Spacie, R. Bayliss, Morgan AM&T, United Kingdom

The need to reduce weight and increase specific performance of ceramics for ballistic applications is an important factor in their ongoing development. Boron carbide is a promising material in this regard, since it is known to combine very low density with high hardness. There are, however, issues, which include poor multi-hit performance and reduced effectiveness against certain threats. It is also difficult to process compared to the higher density silicon carbide. To attempt to achieve an acceptable performance economically, an investigation of silicon carbide-boron carbide composites produced by pressureless sintering has been carried out. The effects of the ratio of the materials and the processing conditions on microstructure and mechanical properties have been assessed. The boron carbide has been found to affect processing and properties differently under different processing conditions, indicating the possibility of engineering the microstructure to provide certain properties.

(ICACC-S4-P067-2013) Static and dynamic response of ultra-high strength sintered ceramics

J. J. Pittari*, G. Subhash, University of Florida, USA

The static and dynamic response of sintered silicon carbide (SiC) and silicon carbide-boron carbide (SiC-B4C) composite was investigated by indentation and uniaxial compression experiments. Static hardness values were determined using a conventional Vickers indentation hardness tester (15 s) and the dynamic hardness values were found using a custom-made dynamic indentation hardness tester (100 μs). Static compression experiments were conducted using a servo-hydraulic compression machine, while dynamic compression tests were performed utilizing a split-Hopkinson pressure bar. The SiC was pressureless sintered with ~2% boron additive as a sintering aid. The SiC-B4C was sintered in a similar fashion with 40 wt% B4C starting powder. It was found that both materials exhibited rate-sensitivity in compressive strength; however, the hardness values of the SiC-B4C composite were observed to be rate-insensitive (perhaps due to increased amorphization under dynamic indentation). SiC displayed the highest compressive strength at all strain rates tested, but possessed a lower hardness value compared to the SiC-B4C ceramic. This higher hardness is likely attributed to the presence of B4C, which has a higher intrinsic hardness value. Static and dynamic fracture toughness tests are being performed to determine the influence of strain rate on the mode and nature of fracture due to differing microstructure.

(ICACC-S4-P068-2013) Tensile Strength, Fracture Toughness, and Flaw Characterization of Tungsten Carbide

J. Wright*, UIC TS, Bowhead Science and Technology, LLC, USA; J. J. Swab, U.S. Army Research Laboratory, USA

The use of tungsten carbide spans across several industry sectors to include mining, machine tools, and defense. Proper characterization of high strength tungsten carbide cermets is critical for material evaluation, but provides several challenges due to the high strength and mixed metal/ceramic characteristics of the materials. Fracture toughness of cermets is commonly measured using ASTM B771 "Short Rod Fracture Toughness of Cemented Carbides". This method requires machining a chevron notch into the specimen and then breaking the specimen in uniaxial tension. The present work demonstrates accurate fracture toughness measurements using the single edge precracked beam (SEPB) method of ASTM 1421. This method, developed for ceramics, allows for a precrack generated from a simple machined notch to be extended using a 4-pt bend fixture. This allows for fast, accurate evaluation of the fracture toughness of these materials. In addition to fracture toughness, uniaxial tensile strength is measured using cylindrical button head specimens. Flaw characterization and mirror constants from quantitative fractography are presented.

(ICACC-S4-P069-2013) The Effect of a Glass Coating on the Strength of Soda-Lime-Silicate Glass

S. Thies, S. Kilczewski*, J. J. Swab, P. Patel, Army Research Laboratory, USA

Glass is widely used as a ballistic material in ground vehicle applications. Because the effect of surface flaws on the strength of glass is apparent, there have been investigations to improve glass strength using techniques such as etching, coatings, fire polishing, and glazing, typically on small geometries such as glass rods. As part of an ongoing study, ARL investigated the effect of a glass coating on the strength of soda-lime-silicate glass using a scalable process that can glaze large sheets of glass. This effort examined the effect of processing conditions on the equibiaxial flexural strength of soda-lime-silicate glass with known surface damage. Samples were damaged by introducing a nominally 10mm long scratch in the center of the tin side of a 100mm x 100mm x 6.5mm plate, using a scratching unit equipped with a diamond stylus. Equibiaxial flexural strength testing was conducted on each specimen in the experiment matrix following the procedures outlined in ASTM C1499 in order to determine the effectiveness of the coating process. Results from this research will be discussed.

(ICACC-S4-P070-2013) Deformation Twinning in Transparent Single Crystals: Indentation Experiments and Mesoscale Modeling

C. Hilton*, J. Yu, Oak Ridge Institute for Science and Education, USA; J. Clayton, J. Knap, J. Swab, US Army Research Laboratory, USA

Incorporating mechanical twinning into classical plasticity models has been a significant challenge for a number of years. Such predictive models would be useful in material selection and design of armor ceramics, which may experience deformation twinning during dynamic loading conditions. The present work describes theoretical-computational models and careful validation experiments that have been developed simultaneously in an attempt to further the understanding of deformation twinning in crystalline solids. High resolution images of elastic twin growth in calcite crystals that have been subjected to spherical indentation loading conditions are presented. Quantitative results, including twin length as a function of indentation load and indenter load-displacement relationships, are also discussed. Finite element simulations using anisotropic nonlinear elasticity provide insight into shear stresses necessary to initiate twinning under spherical indentation. Results of phase field simulations of indentation-induced twinning from wedges and spherical indenters, and of a simple shearing experiment, are reported.

(ICACC-S4-P071-2013) X-ray Computed Tomography (XCT) of Confined Ceramics

B. Leavy*, Army Research Laboratory, USA; C. Peitsch, Chesapeake Defense Services, Inc., USA; W. J. Bruchey, Survice Engineering Company, USA

In order to better quantify the damage and failure of ceramics in ballistic events, simplified experiments are conducted to induce macroscale cracking and damage in confined ceramic targets. Spherical and cylindrical penetrators at various striking velocities are used to impact the confined cylindrical targets. Only the damage and cracking that occurs on the free surface is traditionally observed. Although destructive cross-sectioning and polishing techniques are occasionally accomplished, they are often difficult and time-consuming. To better understand the mechanisms driving the target response, an X-ray computed tomography (XCT) technique is used to map out the three-dimensional macroscale damage and cracking that occurs in the ceramic after a ballistic event. Time-dependent crack propagation and damage evolution in silicon carbide (SiC) ceramics are predicted using the Kayenta macroscopic constitutive model. Comparisons are made between the current ballistic simulations, and the experimental non-destructive analysis. The XCT technique allows for non-destructive verification and validation of the computational models.

(ICACC-S4-P072-2013) Resonant Ultrasound Spectroscopy for the Evaluation of Armor Ceramics

E. Warner*, M. Bratcher, U.S. Army Research Laboratory, USA

Nondestructive methods for characterizing both commercially available and developmental armor ceramics have proven beneficial to understanding how the formulation and/or processing history impacts the variability and consistency of performance. One such method utilized today in manufacturing for quality assurance and control is resonant ultrasound spectroscopy (RUS). This technique involves sweeping frequencies and using the modal frequencies to calculate material properties such as Young's modulus, bulk modulus, shear modulus, and Poisson's ratio. In this study we will employ the Magnaflux Quasar RUSpec system to determine the utility of resonant ultrasound spectroscopy to differentiate armor ceramics with diverse manufacturing histories while sharing common shape factors and density.

(ICACC-S4-P073-2013) Optimizing the Arrangement of Ceramic Tile Periodic Arrays for Armor Applications Using a Genetic Algorithm

M. C. Golt*, M. Bratcher, U.S. Army Research Laboratory, USA

Periodic arrays of ceramic tiles are commonly used in ceramic-based armor applications. In these systems uniform gapping between tiles is desired for predictable and reliable ballistic performance, typically requiring precise machining of the tiles. This increases the fabrication costs considerably. However, if instead low tolerance tiles' dimensions were measured and intelligently arranged as to minimize gapping, then more affordable armor could be produced. This study seeks to solve this close-packing problem through efficiently measuring hexagonal tile dimensions through a high-throughput, low-cost means and then solving for an optimal arrangement of those tiles using a genetic algorithm. A desktop flatbed scanner was calibrated and optimized for scanning the footprint of individual hexagonal tiles. Images of the tile footprints where then batch imported into MATLAB code that calculated the three flat-to-flat dimensions. An MATLAB algorithm was developed to computationally arrange the tiles and calculate the total gapping between them. This algorithm served as the fitness test to a custom genetic algorithm that sought to minimize the total gapping. After an optimal orientation was found computationally, the arrangement was constructed to quantify the gapping for comparison to simulated results.

(ICACC-S4-P074-2013) Numerical study of stress and fracture propagation in glass during ring-on-ring testing

C. G. Fountzoulas*, J. J. Swab, P. J. Patel, U.S.Army Research Laboratory, USA

Glasses are the primary striking ply materials used in transparent armor due to availability, cost, and existing mature manufacturing. Glass fracture patterns are unique in nature and they reflect the nature of the glass. Moreover, glass fracture examination provides information as to the direction of the breaking force. The density of cracks in fractured glass is highly correlated with the fracture pressure, with a higher fracture pressure resulting in a higher crack density that is anticipated to the increase stored energy with increasing pressure. During a ring-on-ring testing a slowly moving compressive load is applied on the glass which results in the failure of it. Initial 3D modeling and simulation of the cracking propagation throughout the compressed glass substrate has shown that the presence of the supporting ring accelerates the failure towards the edges of the rectangular glass substrate. The objective of the current numerical study is to delineate the mechanism and shed light to the physics of the stress wave propagation in the glass during the ring-on-ring testing. The simulated cracking pattern of the glass will also be compared to available experimental data for model validation. In addition, the effect of the relative position of the upper and lower rings to the failure of the glass will also be studied by 3D modeling and simulation using commercial software.

(ICACC-S4-P075-2013) Limits of accelerating numerical analysis study of the failure mechanism of ceramics during low velocity impact used in protective systems

C. G. Fountzoulas*, R. E. Brennan, 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-P076-2013) Synthesis of nanocystalline AlMgB14 powders by solid state synthesis technique

Z. Xie*, N. Orlovskaya, University of Central Florida, USA

The AlMgB14 ternary boride is an important material with promising properties such as low density (2.46g/cm3) and high hardness values (Hv=33-35GPa). In this research work the different synthesis routes to produce nanocrystalline and single phase AlMgB14 powders were explored. The solid state synthesis with different raw materials was explored, where the heating of Al+Mg+B, AlB2+Mg+B; Al+MgB2+B, and AlB2+MgB2+B were done at 1200-1300oC for extended period of times. In addition to solid state synthesis, the mechanochemical synthesis of AlMgB14 using the same compositions of the initial raw powders were studied too. The synthesized powders were characterized by X-ray diffraction, Scanning Electron Microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS), and Raman spectroscopy. Results show that the stoichiometrically mixed Al+Mg+B and AlB2+Mg+B powders are the best compositions for synthesis since the AlMgB14 phase yield is at maximum for such compositions and the formation of MgAl2O4 spinel is minimized. In addition to pure AlMgB14 powder, AlMgB14 with 30 wt% TiB2 powder were also produced. Spark plasma sintering was performed at 1450°C, 50MPa for 5min to densify AlMgB14 and AlMgB14 with 30 wt% TiB2. The hardness of SPS AlMgB14 and AlMgB14+30 wt%TiB2 was measured using Vickers hardness tester.

(ICACC-S4-P077-2013) Mechanochemical synthesis of hexagonal OsB2

Z. Xie*, N. Orlovskaya, University of Central Florida, USA; D. Cullen, Oak Ridge National Laboratory, USA; R. Blair, University of Central Florida, USA

The hexagonal OsB2 powder has been synthesized for the first time, by the mechanochemical method, ball milling. OsB2 starts formed after 2.5 hours of milling, and the reaction reaches equilibrium after 18 hours of milling. The lattice parameters of the hex-OsB2 are α=β=90°, γ=120°; a=b=2.9047 Å, c=7.4500 Å, with P63/mmc space group. The synthesized OsB2 powder was annealed at 1050°C for 6 days, but no phase change was found.

(ICACC-S4-P173-2013) A Novel Low Temperature Synthesis of Boron Carbide Powders

L. Gao, C. L. Falticeanu, I. T. Chang*, University of Birmingham, United Kingdom

Boron carbide (B4C) has unique physical properties that make it an ideal candidate material for lightweight body armour applications. They include high hardness, high dynamic elastic limit and low density. 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. In order to reduce the price of B4C, there is an increasing need to develop a low temperature synthesis of B4C powders. Recently, a low temperature synthesis 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 1500°C. The as-synthesised B4C powders have unique characteristics. They include low residual carbon content, equiaxed morphology and average particle sizes ranging from 250nm to 4μm, depending on the processing conditions.

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

S6 Poster Session

Room: Ocean Center

(ICACC-S6-P082-2013) Synthesis and Characterization of LiMBO3 Electrode Materials

H. Lee*, Y. Lee, Andong National University, Republic of Korea

The cathode material for Li-ion batteries has long been layered oxides, such as LiCoO2, due to their high capacity, excellent cycle characteristics, and high energy density. However, their high toxicity, high cost, and instability at high temperature have prohibited them from the large scale use and, thereby, foster the search of alternative cathode materials to meet the requirement for new applications like electric vehicle, power storage for smart grid, etc. Thus, many polyanion-based materials, most notable example is LiFePO4, has been studied and used for the proper candidate material for next generation Li-ion batteries. The present study investigates the potential of borate-based materials for the cathode electrode since LiMBO3 can have a high theoretical capacity of 220-222 mAh/g and better safety. First, pristine LiMBO3 is synthesized via solid state reaction under various conditions and its material/electrochemical property is characterized systematically. Then the carbon-incorporation is conducted in terms of composite and coating to see its effect on the electrochemical behavior. The results show the carbon-incorporation is very critical for LiMBO3 to have high reversible capacity and the optimum synthetic condition is identified.

(ICACC-S6-P083-2013) Dependence of Temperature and Atmosphere on Conductivity and Crystal Structure and Ni-Co Oxide Solid Solution

K. Fung*, Y. Hsu, National Cheng Kung University, Taiwan; C. Wei, H. Bor, Chung-Shan Institute of Science and Technology(CSIST),, Taiwan

Although NiO and CoO is known example to form nearly perfect solid solution with rock-salt structure when both oxides were mixed and heated at temperatures greater than 1000 °C. When precursors of NiO and CoO were mixed at 1:2 molar ratio and reacted at temperatures as low as 300°C, the reacted powder samples show spinel structure. It is believed that the size mismatch between Ni+2 and Co+3 ions cause the formation of inverse-spinel with the tetrahedral sites completely occupied by Co+3 ions and the octahedral sites randomly and equally distributed with Co and Ni ions. NiCo2O4 spinel is may be used as a bifunctional catalyst for oxygen evolution and reduction reaction as electrode in both inorganic and organic electrosyntheses Recently, NiCo2O4 spinel was found to be an infrared transparent conducting material with potential for optoelectronic applications. To obtain a thin film of nickel-cobalt oxides using rf magnetron sputtering, a solid film was deposited on a glass substrate using the sintered oxide target. With annealing at adequate temperature, a thin film of nickel-cobalt oxides showing spinel structure obtained. A resistivity as low as 10^{-1} ohm/cm was obtained. The optical property of spinel was also measured as function of thickness/deposition time in the infrared wavelength range.

(ICACC-S6-P084-2013) Dependence of Chemical Reaction on Degration of Composite Cathode Consisting of Yttrium Doped Bismuth Oxide ($Y_{0.25}Bi_{0.75}O_{1.5}$) and $La_{1-x}Sr_xMeO_{3-\delta}$ Perovskite (Me=Mn, Cu)

K. Fung*, H. Wang, National Cheng Kung University, Taiwan

The mixture of conducting materials consisting of oxygen ion conductor and a conducting perovskite oxide may be used as electrode material. $Y_{0.25}Bi_{0.75}O_{1.5}$ (25YSB) is a known oxygen ion conductor. On the other hand, $La_{0.8}Sr_{0.2}MnO_{3-\delta}$ (20LSM) and $La_{0.75}Sr_{0.25}CuO_{3-\delta}$ (25LSCu) are well known electronic conducting perovskites. The 20LSM shows rhombohedral structure and p-type conducting behavior with conductivity of 300 S/cm at 800°C. The 25LSCu exhibits more oxygen vacancies than 20LSM. In additions, 25LSCu also shows conductivity as high as 800 S/cm at 800°C. The composite cathode was obtained by heating the powder mixture of 25YSB and LSM or LSCu at temperatures >800°C. After heating at 1000°C for 8h, no additional phase other than LSM and YSB was observed. However, 25LSCu tends to react with 25YSB and additional phases appeared after heat treatment at 800°C for 20h. These extra phases were found to be $La_{0.3}Bi_{0.7}O_{1.5}$, La_2CuO_4, CuO and $Bi_2Sr_2CuO_{5.8}$. The reaction between Bi and Cu may be caused by the weak bonding strength between Cu-O in perovskite. Significant degradation in electrical property was observed accordingly. On the contrary, more stable LSM perovskite also shows better phase stability and electrical property in the composite cathode.

(ICACC-S6-P085-2013) Stability Enhancement of Li Solid Electrolytes against Metallic Li by Cation Subsitution

K. Fung*, C. Ni, C. Shen, C. Liu, K. Yang, National Cheng Kung University, Taiwan

Inorganic Li ion conductors may be used as electrolytes in all solid-state lithium batteries. Using them as electrolytes exhibits the advantages of better safety, good stability, and easy handling in comparison to organic electrolytes. For the structure stability and conduction behavior of solid electrolyte, it is known that the substituting cations play an important role. In this study, the substitutional Al ions on the cation sublattices of NASCION-type $LiTi_2(PO_4)_3$ and perovsikte-$La_{0.50}Li_{0.50}TiO_3$ were investigated based on the observation of stability against Li and conduction properties as a function of Al addition. The Li reaction with $La_{0.56}Li_{0.33}TiO_3$ was effectively suppressed by partial substitution of Ti with Al. On the other hand, no significant reaction was observed on the $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ electrolyte when the metallic Li was used as the anode. These results indicate that the NASCION structure gives better stability against metallic Li than perovskite structure does. For the conductivity measurement, when the substitution of Al for Ti ions was less 25%, single phase NASCION type structure was observed. The highest conductivity of 8.16×10-4 S/cm was measured from the sample with the composition of $Li_{1..3}Al_{0.3}Ti_{1.7}$ $(PO_4)_3$ at room temperature. Lower conductivity was observed on samples with Al substitution over 25% in NASCION structure due to the presence of second phase.

(ICACC-S6-P086-2013) Deposition of $LiCoO_2$ Film on Flexible Substrate for Li Microbattery Applications

K. Fung*, C. Ni, C. Liu, National Cheng Kung University, Taiwan

Search for a novel process to obtain thin film electrode is essential for the development of flexible electronic devices using Li batteries as a power source. . $LiCoO_2$, a layer-structured material, is the dominant cathode material for current commercial lithium ion batteries. Therefore, most commercial Li batteries are based on $LiCoO_2$ chemistry. The main objective of this work is to develop a novel technique to attach a well-crystallized $LiCoO_2$ film on flexible substrate for the application of Li microbattery. In this study, the crystalline $LiCoO_2$ thin film was successfully transferred onto a flexible polymer substrate based a sol-gel process and followed by the spin-coating technique. The crystallization of $LiCoO_2$ gel was characterized by DTA/TG and XRD. Finally, a well-crystallized hexagonal $LiCoO_2$ film with a space group of R3m was obtained. The surface morphology and cross-section of deposited $LiCoO_2$ film with a thickness of 5μm was examined by FE-SEM. In additions, charge/discharge tests were conducted on an assembled Li battery with $LiCoO_2$ cathode film deposited on a flexible polymer substrate.

(ICACC-S6-P087-2013) Effect of Atmosphere on Synthesis and Conductivity of $Li_4Ti_5O_{12}$ Anode for Li battery application

K. Fung*, C. Ni, M. Chen, National Cheng Kung University, Taiwan

Lithium titanium oxide spinel Li4Ti5O12 has been reported to be a zero-strain lithium insertion host material because it exhibits extremely small variations of the lattice parameters during the charge and discharge processes. However, lithium titanium oxide spinel or lithium titanate exhibits rather low electrical conductivity. To improve the capacity and rate capability, coating the lithium titante particles with a conductive additive has been used. Since titanium ions show multi-valent states, the conductivity of lithium titanate may highly depend upon the addition of aliovalent dopant or surrounding atmosphere. In this study, the synthesis of lithium titanium spinel will be conducted under different atmosphere. XRD will be used to investigate the high-temperature reaction between lithium oxide and titania under different atmosphere. Furthermore, sintered lithium titanium oxide spinel will be heat-treated under different atmosphere. The resistance of sintered lithium titanium oxide will be monitored as a function of annealing time. It is expected that the resistivity of lithium titanium oxide will be significantly reduced when exposed at low oxygen partial pressure.

(ICACC-S6-P088-2013) Synthesis n-ZnO/p-CuO Core/Shell Nanorods for Solar Cell Applciation

R. Kim*, J. Kim, Chonbuk National University, Republic of Korea; H. Kim, University of British Columbia, Canada; Y. Hahn, Chonbuk National University, Republic of Korea

The n-ZnO/p-CuO ‘core-shell’ nanorods (NRs) were synthesized on glass/indium tin oxide substrates by a solution route. The ZnO/CuO NRs have wurtzite n-type ZnO as the ‘core’ and monoclinic p-type CuO as the ‘shell’ structure. The as-grown nanostructures were extensively examined by X-ray diffraction (XRD), field emission electron microscope (FESEM), atomic force microscope (AFM) and transmission electron microscopy (TEM). The ZnO/CuO NRs has been used for the fabrication of solid-state photovoltaic cells. Significant improvements were in terms of short current (JSC), open circuit voltage and power conversion efficiency (PCE), which were attributed to the quality and uniformity of the CuO/ZnO nanocomposite ‘core-shell’ with optimized CuO thickness and the low bandgap of CuO and high mobility of ZnO.

S8: 7th International Symposium on Advanced Processing and Manufacturing Technologies for Structural and Multifunctional Materials and Systems (APMT)

S8 Poster Session

Room: Ocean Center

(ICACC-S8-P113-2013) Investigation of composites of packed porous alumina with polymer blend

K. Kita*, N. Kondo, National Institute of Advanced Industrial Science and Technology (AIST), Japan

Study of porous materials is energetically carried out all over the world, because the material is one of promising energy saving such as gas separation, condenser, air conditionings, etc. Polymeric membrane and porous silica produced by sol-gel method is easy to make with low-cost and suitable for gas separation, especially hydrogen gas. However, they can be easily tightened, sintered, broken by steam or any other erosion gas, and lose the permeability. Therefore, new porous material which is proof to steam or any other erosion gas would be required. In the former investigation, we found that polymer blend containing polycarbosilane (PCS) and polysiloxanes cannot make exfoliation to alumina. Moreover, the polymer blend can be made into porous silicon carbide and the pore size can be adjusted to any size. Therefore, composites of packed porous alumina with the polymer blend would be an ideal porous material. We prepared two kinds of polymer blend that one is PCS and polymethylphenylsiloxane and the other is PCS and polymethylhydrosiloxane. Composites of packed porous alumina were made with the polymer blends, and investigated by SEM, mercury press-in method, etc.

(ICACC-S8-P114-2013) Fracture Toughness of Thin Ceramic Substrates for Power Modules

H. Miyazaki*, Y. Yoshizawa, K. Hirao, T. Ohji, National institute of Advanced Industrial Science and Technology, Japan

The rapidly growing market of electric vehicle and hybrid electric vehicle demands high power density of the circuit in the power device. The heat dissipating board for the power modules usually consists of a thin ceramic substrate such as aluminum nitrides or silicon nitrides sandwiched by cupper plates. The mechanical sustainability of the substrate after sever heat cycles becomes more of a concern since thermal stress due to thermal expansion mismatch between Cu and ceramic plates damage the substrate. The fracture toughness of the thin ceramic plate is one of the main factors which govern the thermal fatigue of the heat dissipating board. However, fracture toughness evaluation of such a thin ceramic plate with a thickness of ~0.32 mm has not been studied systematically. In this study, the fracture toughness of both thin aluminum nitrides and silicon nitrides was measured using a single-edge precracked beam. A small, thin single-edge notched beam was bonded on one side of a metallic beam and the assembly was deformed in three-point bending to introduce the precrack. The single edge-precracked specimen is then removed from the beam and the fracture toughness was measured using standard single edge-precracked beam (SEPB) method. The fracture toughness measured using this method was compared with that obtained for the standard specimens by SEPB method.

(ICACC-S8-P115-2013) Round Robin on Indentation Fracture Resistance of Silicon Carbide for Small Ceramic Products

H. Miyazaki*, Y. Yoshizawa, National institute of Advanced Industrial Science and Technology, Japan; K. Yasuda, Tokyo Institute of Technology, Japan

The indentation fracture (IF) method is one of the most effective solutions for the need of measuring the fracture resistance of tiny ceramic components such as bearing balls since the conventional toughness-evaluation methods are difficult to apply. However, the method has been regarded as a substandard method since the international round-robin tests on the IF method demonstrated that the between-laboratory consistency was poor, which was reported about twenty years ago. During the last two decades, however, the processing of ceramic products made remarkable progress which certifies the homogeneity among the test specimens, and the precision of measuring equipments for crack length has been also improved. In this study, reproducibility of indentation fracture resistance, K_{IFR}, of silicon carbide ceramics was evaluated by a domestic round robin with thirteen laboratories. It was found that the variations in the fracture resistance among the participants were much smaller than those reported in the previous round-robin tests when the crack length was measured with a powerful microscope. The crack lengths of the returned samples were also measured by the authors and compared with the reported values from each participant to estimate the origin of measuring errors.

(ICACC-S8-P116-2013) Sintering of silicon nitride from beta powder at lower temperatures

N. Kondo*, M. Hotta, AIST, Japan

Silicon nitrides are usually sintered at temperatures above 1700C. At the temperatures, nitrogen gas pressure was applied to avoid decomposition. If sintering can be carried out at lower than 1650C, gas pressure is not needed. This means silicon nitride can be sintered by using nitrogen furnace without gas pressure chamber, leading to low cost equipment and low cost silicon nitride products. Usually silicon nitrides are fabricated from alpha powders. It is difficult to sinter silicon nitrides from alpha powders at lower than 1650C. Recently a few reports mentioned beta powder is advantageous to sinter at lower temperatures. Therefore, in this paper, sintering behavior of silicon nitride from beta powder at lower temeratures was investigated. Silicon nitride from beta powder was successfully densified at 1600C for 8h. Density, strength and fracture toughness of it were 3.24, 553 MPa and 3.5 MPa m1/2, respectively. Elongation of silicon nitride grains was not remarkable. Many of the grains had core-rim structure. From the result, silicon nitride of low cost and moderate properties is possible to be fabricated from beta powder and at lower sintering temperatures.

(ICACC-S8-P117-2013) SiBOC ceramic fibers via pyrolysis of hybrid borosiloxane gel fibers

G. Soraru*, V. Nguyen, University of Trento, Italy; V. Proust, C. Quievryn, S. Bernard, P. Miele, IEM/Université Montpellier 2, France

The sol–gel method has been used for the synthesis of borosilicate gels from mixtures of methyltriethoxysilane (MTES) and dimethyldiethoxysilane (DMDES) and boric acid. The use of boric acid, B(OH)3, allows the hydrolysis and condensation of hybrid silicon alkoxides without further addition of water or catalyst. The use of difunctional silicon units, (CH3)2SiO– promotes the formation, during the sol–gel process, of linear oligomers which facilitates fiber drawing before gelation. Gel characterization performed by FT-IR, XRD, TG-DTA and DCS analysis indicates the formation of a mixed network with incorporation of the boron units via =B-O-Si= bridges. The formation of borosiloxane bonds seems favored by the presence of DMDES. Polyborosiloxane sols exhibit remarkable spinnability: SiBOC glass fibers with diameters of about 10 μm have been successfully prepared under argon atmosphere at 1000 °C. Each step of the process is detailed in the present paper: the synthesis of the sol, the spinning process and the pyrolysis step. The final material has been characterized by SEM, XRD, HT-TGA and mechanical tests.

(ICACC-S8-P118-2013) Wear and Reactivity Studies of Melt Infiltrated Ceramic Matrix Composite

D. Jarmon, United Technologies Research Center, USA; G. Ojard*, Pratt & Whitney, USA; D. Brewer, NASA-Langley Research Center, USA

As interest grows in the use of ceramic matrix composites (CMCs) for critical gas turbine engine components, the effects of the CMCs interaction with the adjoining structure needs to be understood. A series of CMC/material couples were wear tested in a custom elevated temperature test rig and tested as diffusion couples, to identify interactions. Specifically, melt infiltrated silicon carbide/silicon carbide (MI SiC/SiC) CMC was tested in combination with a nickel-based super alloy, Waspaloy, a thermal barrier coating, Yttria Stabilized Zirconia (YSZ), and a monolithic ceramic, silicon nitride (Si3N4). To make the tests more representative of actual hardware, the surface of the CMC was kept in the as-received state (not machined) with the full surface features/roughness present. Test results include: scanning electron microscope characterization of the surfaces, micro-structural characterization, and microprobe analysis.

(ICACC-S8-P119-2013) Effects of Grain Growth Behavior on Texture Development in Bismuth Layer-Structured Ferroelectrics

M. Saba*, T. Kimura, Keio University, Japan

Bismuth Layer-Structured Ferroelectrics (BLSFs) are one of the candidates for lead-free piezoelectric materials. Because BLSFs have a highly anisotropic crystal structure, it is necessary to develop texture in the sintered ceramics. The templated grain growth process is one of the convenient preparation techniques for textured ceramics. In BLSFs, two mechanisms are reported for the texture development; one is the growth of platelike grains and the other is the morphological change of equiaxed grain in the presence of platelike grains. Therefore, understanding of grain growth behavior is essential to obtain highly textured BLSF ceramics. In this work, we focused on the grain growth behavior in $Bi_4Ti_3O_{12}$ and $BaBi_4Ti_4O_{15}$. In the $Bi_4Ti_3O_{12}$ case, large platelike grains grew at the expense of equiaxed grains. The orientation of grain boundaries between a platelike grain and the surrounding grains was random. The growth of platelike grains was influenced by the orientation of other platelike grains. In the $BaBi_4Ti_4O_{15}$ case, on the other hand, the growth of large platelike grains was slow and the equiaxed grains touching the plate faces of platelike grains changed their shape to be platelike. The platelike grain and the grains from equiaxed grains have the same crystallographic orientation. From these findings, the preparation conditions of textured BLSFs are designed.

(ICACC-S8-P120-2013) The Rare-Earth Additives Influence on BaTiO3–Ceramics Properties

V. Mitic*, V. Paunovic, I. Antolovic, D. Rancic, L. Zivkovic, University of Nis, Serbia

In this study the microstructure characteristic and dielectric properties (dielectric constant of BaTiO3 ceramics doped with various dopants (Er, Yb, Ho, La) were investigated. The samples of doped BaTiO3 were prepared using by conventional solid state procedure and were sintered at 1350°C. The microstructure of sintered specimens was investigated by SEM-5300 and dielectric measurements have been done using LCR-metra Agilent 4284A in the frequency range from 20Hz to 1MHz. By using fractal modeling method of microstructure configurations reconstruction, like shapes of grains or intergranular contacts has been successfully done. Furthermore, the area of grains surface was calculated by using fractal correction which expresses the grains surface irregularity through fractal dimension. For better and deeper characterization of the ceramics material microstructure the Voronoi model and mathematical statistics calculations, are applied A new approach on consolidation ceramic materials control certain phases has been establish, such as control of initial powders, and also the microstructure and the contacts between the grains which has been developed.

(ICACC-S8-P121-2013) Microstructure and joining strength of silicon nitride long pipes fabricated by local-heating joining technique

M. Hotta*, N. Kondo, H. Kita, T. Ohji, National Institute of AIST, Japan

Silicon nitride pipes were joined to produce a long pipe with a length of 3 m by a local heating technique. Commercially available silicon nitride ceramic pipes sintered with Y2O3 and Al2O3 additives were used for parent material, and slurry of Si3N4-Y2O3-Al2O3-SiO2 mixed powder was brush-coated on the rough or uneven end faces of the pipes as insert material. Joining was carried out by locally heating the joint region at different temperatures from 1500 to 1650°C for 1 h with a mechanical pressure of 5 MPa in N2 flow; using a horizontal electrical furnace specially designed for this experiment. The joined silicon nitride pipe was successfully fabricated without voids or cracks in the joint region, and the gap between the pipes with rough or uneven joined faces was well filled by the slurry brush-coated as insert material. Fibrous grains were formed in the joint layer, indicating that the microstructure of the joint region and parent one was similar. The joint strength was examined in flexure using specimens cut from the joined pipes, and those joined at 1600 and 1650°C indicated the highest strength of about 680 MPa, which was almost the same as that of the parent material. This study also indicated that the slurry brush-coating technique is advantageous to easily joining ceramic pipes with rough or uneven end faces, which is essentially important for practical use.

(ICACC-S8-P122-2013) Electrode Manufacturing of Solid Oxide Fuel Cells

J. Torres*, N. Orlovskaya, University of Central Florida, USA; K. Gerdes, S. Lee, National EnergyTechnology Laboratory, USA

The objective of this research was to manufacture and examine the performance of 10mol% Sc2O3-1mol% CeO2-ZrO2 / 8mol% Y2 O3-ZrO2 (SCSZ/YSZ) layered electrolyte-based Solid Oxide Fuel Cells with 65wt% NiO-35wt% 8mol% Y2 O3-ZrO2 (NiO-YSZ) anodes and [La(0.6)Sr(0.4)](0.99)Fe(0.8)Co(0.2)O3 (LSCF) cathodes. Layered (1YSZ:4SCSZ:1YSZ) electrolytes with a single-layer thickness of ~35μm were tape casted, laminated, and sintered to full density. Once sintered, the cathode side of the electrolyte is spin coated with 20mol%Gd2O3-CeO2 (GDC). Electrode inks produced by ball milling and three roll milling were then screen printed onto the electrolytes. The screen printing process involves printing and drying several layers of ink onto the electrolyte followed by sintering to achieve ideal porosity and microstructure. Variations in printing, drying, GDC application, etc. were employed and their impacts on microstructure and performance were explored. Scanning Electron Microscopy (SEM) was utilized to inspect the impact of altered manufacturing routines on resultant microstructure. Following successful manufacturing of single cells, cell performance was evaluated through electrochemical testing and impedance analysis on complete cells. Electrode ink viscosity and composition variation effects on overall electrode cell microstructure quality and performance were evaluated.

(ICACC-S8-P123-2013) Fabricating Successful Ceramic Components Using Development Carrier Systems

T. Standring*, University of Birmingham, United Kingdom; B. Prajapati, R. Richardson-Derry, A. Cendrowicz, Ross Ceramics Ltd., United Kingdom; P. Wilson, Rolls-Royce Plc, United Kingdom; N. Rowson, S. Blackburn, University of Birmingham, United Kingdom

Fabrication of complex ceramic components can be achieved through injection moulding a feedstock, comprised of ceramic powders suspended in an organic carrier system (binder), at elevated temperatures into preformed moulds, thermally removing the binder, then firing and sintering remaining ceramic. The carrier system is critical for developing the desired properties of the feedstock to enable flow and mould filling during injection and to sustain the integrity of the formed component during the subsequent firing process. This investigation describes the effect of three development carrier systems, of high, medium and low viscosity, containing identical components but differing ratios on component fabrication. The feedstock was optimised in solids loadings and plasticiser additions. A press was used for the moulding but before injection, the feedstock was conditioned for both short and long mixing times. The process was characterised through rheometry, mechanical testing, interferometry and SEM. Experimental data illustrates that conditioning time and viscosity of the binder affects the surface roughness of components. Conditioning time also influences the flexural stress profile of the green components under load. The ceramic strength properties using the low and medium viscosity binders were similar, however, a reduction in strength properties was observed when using the high viscosity

S9: Porous Ceramics: Novel Developments and Applications

S9 Poster Session

Room: Ocean Center

(ICACC-S9-P125-2013) Effect of Enclosed Gas Pressure of Closed Pores on the Mechanical Properties of Cellular Borosilicate Glass

B. Wang*, J. Yang, Xi'an Jiaotong University, China; M. Koji, Nagaoka University of Technology, Japan; I. Kozo, Xi'an Jiaotong University, China; N. Koichi, Nagaoka University of Technology, Japan

Cellular borosilicate glass with pressurized Ar-filled pores was fabricated by melting glass powder under high argon gas pressure atmosphere and subsequent annealing above glass softening temperature under low gas pressure atmosphere. At the melting stage, a notable amount of dissolved argon gases permeate into the glass interstices. At the annealing stage, argon atoms released from the glass interstices to bubbles and then bubble expansion took place under pressurized argon atmosphere, resulting in a high density of pressurized Ar-filled sphere pores. The results showed that porous borosilicate glasses processed porosity 25~80% with narrow pore size distribution. The flexural strength was strongly affected by the pores with enclosed gas pressure. With increasing the enclosed gas pressure, the specific flexural strength was considerably increased. The enclosed gas pressure increased the collapse strength of the closed pores, and then, contributed to the high strength.

(ICACC-S9-P126-2013) Particle-stabilized ceramic foams: properties and applications

P. N. Sturzenegger*, B. Seeber, ETH Zurich, Switzerland; U. T. Gonzenbach, de Cavis, Switzerland

Porous ceramics are an important class of materials due to their combination of interesting properties like low density, low thermal conductivity, high thermal and good chemical stability. To manufacture porous ceramics, we developed the in-situ particle hydrophobization technology, a direct foaming method where almost any kind of fine particles can be functionalized to stabilize air bubbles in wet foams. In addition to the freedom in materials selection, our method features an excellent control over porosity and microstructure of the final products. In this poster, we present properties and discuss applications of foams made from a variety of ceramic materials. For example, highly porous alumina foams with unique mechanical and microstructural properties are obtained after sintering of green foams. Another example are self-hardening foams that are manufactured by hydrating foamed gypsum suspensions. In contrast to sintered materials, gypsum foams do not shrink and can therefore be net-shaped or used to fill complex cavities. A reliable microstructure control is essential for the fabrication of bone graft materials from β-tricalciumphosphate. To allow for cell ingrowth, open pores with an average pore size of at least around 200 μm are needed. With this contribution, we present a broad overview over our current research on mineral foams with high porosities.

(ICACC-S9-P127-2013) Study of High Temperature Structural Stabilization of Sepiolite and Its Rehydration Behavior

I. Kara*, S. Tunali Akar, A. Ozcan, Anadolu University, Turkey

Sepiolite is a layered clay mineral which has a chemical formula of Si12Mg8O30(OH)4(H2O)4.8H2O. It has alternating blocks and molecular-sized channels in its structure. When sepiolite is heated, its structure collapses causing closure of the channels. This is associated with a large decrease in the surface area of the calcined sepiolite. However, it is possible to stabilise the structure of sepiolite even after the removal of coordination water by acid treatment before calcination. This is due to the partial removal of Mg atoms from the sepiolite structure. In this study, sepiolite was treated by HCl at different molarity. It was found that acid concentration is important to keep the structure stable after calcination. For homogeneous removal of Mg and better structural stability upon calcination, low dissolution rate, that is, the use of low acid concentration was needed. In this way, it is possible to stabilise the surface area almost fully even after calcianation at 450 C in contrast to the untreated sepiolite which looses 40 percent of its surface area. It was demonstrated that empty channels of acid treated and calcined sepiolite can be refilled by water. Therefore, it is considered that it may be possible to insert other functional materials in order to create high surface area material with certain functionalities.

(ICACC-S9-P128-2013) Processing of Low Cost Ceramic Membranes from Clay Minerals

J. Eom, S. Yun, Y. Kim*, The UNiversity of Seoul, Republic of Korea; I. Song, Korea Institute of Materials Science, Republic of Korea

Ceramic microfiltration membranes have been made from clay minerals and some additives. Several flat disk filters have been obtained by sintering the mixed materials with carbon black as an optional template. Pore size distribution, air and water permeability, and mechanical properties of the resulting filters have been characterized to choose the best fabrication parameters and to investigate the relations between pore characteristics and permeability of the membranes. It is observed that with increasing sintering temperature, the porosity of the membranes decreases and the flexural strength and water permeability of the membranes increases. Flexural strength of the membranes was strongly dependent on additive chemistry. Based on these results, the membrane sintered at 1000°C (porosity 34%, flexural strength 35 MPa, average pore size of 1 μm) is inferred as an optimum membrane for microfiltration applications.

(ICACC-S9-P129-2013) Use of cellular ceramic-supported SrO as a catalyst for the synthesis of biodiesel

F. B. Bassetti, A. A. Morandim, F. S. Ortega*, FEI, Brazil

One of the most common methods for the production of biodiesel is the transesterification of oils in the presence of methanol and catalyst. The catalysts may be homogeneous or heterogeneous, with the latter consuming less energy, being reusable, thus more environmentally attractive. Although there are many studies on the use of alkaline earth oxides as heterogeneous catalysts for the synthesis of biodiesel, few papers deal with the use of strontium oxide. Additionally, these catalysts have been studied as particles dispersed in the reaction medium. This study investigates the potential use of strontium oxide as a catalyst for the synthesis of biodiesel, initially as a particulate material, under various temperatures and catalyst concentrations in the reaction medium. The results showed that the strontium oxide is a potential catalyst, reaching up to 58% conversion. In a second step, a thin film of strontium oxide was deposited on a catalyst support consisting of a cylinder of cellular alumina produced by direct foaming of a suspension, followed by heating at 1500°C for 2 hours. This impregnated foam was used as the core of a plug flow reactor prototype for the synthesis of biodiesel. With this prototype it was possible to achieve up to 90% of conversion of soy oil and methanol into biodiesel, after 3 hours. This result discloses the potential of this new approach for the synthesis of biodiesel.

(ICACC-S9-P130-2013) Zeorite-geopolymer hybrid materials derived from metakaolin

S. Hashimoto*, H. Takeda, S. Honda, Y. Iwamoto, Nagoya Institute of Technology, Japan

Zeolite-geopolymer (alkali activated cement) hybrid bulk materials were fabricated using metakaolines calcined from three kinds of kaolinite. The resultant zeolite- geopolymer bulk materials contain different contents and types of zeolites and have different compressive strengths. This study examines the effects of the initial kaolinite and metakaoline on the properties of hardened bodies. The properties such as XRD, chemical composition, crystalline size, 29Si and 27Al MAS NMR, specific surface area, and resolvability of Al and Si into alkali solution of kaolinite and/or metakaoline were investigated.

The crystalline size of the initial kaolinite influenced the crystalline size of the generated zeolites and the compressive strength of the zeolite-geopolymer hybrid materials. In contrast, the content of zeolite increased with the specific surface area of the metakaoline. Furthermore, the specific surface area of the metakaoline affected the resolvability of Al and Si in alkali solution of metakaoline and content of the formed zeolite.

(ICACC-S9-P131-2013) Self-Assembly of ZSM-5 Zeolite Crystals

K. Hari, Y. Lin, L. M. Cole-Burnett, J. R. Brenner*, Florida Tech, USA

Self-assembly of the nano- and microstructural evolution of ZSM-5 zeolite intermediates was tracked using scanning electron microscopy (SEM) and atomic force microscopy (AFM) with time. The organic framework resulting from the tetrapropylammonium ion template, which can be completely removed via the high dilution factors common to most microscopies, plays a major role in the aggregation of zeolites. All samples started out as monodispersed particles and ended up with trimodal particle size distributions. Tracking the aggregation pathway of ZSM-5 zeolite intermediates is now part of a novel laboratory-based curriculum made possible by NSF Nanotechnology Undergraduate Education Grant #0939355.

(ICACC-S9-P132-2013) Silicon Nitride Foams from Emulsions

P. Colombo*, E. Guzi de Moraes, University of Padova, Italy

Silicon nitride foams were produced from emulsions based on alkanes and a Si_3N_4 powder slurry plus additives. Foams were produced both by adding a large volume of alkanes (>70 vol%) and a low volume of alkanes (< 10 vol%). The highly porous structures were fired at different temperatures and their morphology was investigated using SEM. The microstructure of the samples was comprised of cells with a size ranging from a few microns to a few tens of microns, and the cells possessed intercommunicating windows. This processing approach enable to fabricate components with a homogeneous microstructure, suitable for several engineering applications.

(ICACC-S9-P133-2013) Effects of Fe2O3 on properties of novel heat insulation materials synthesized by molten salt method

C. Deng*, J. Ding, W. Yuan, J. Li, H. Zhu, Wuhan University of Science and Technology, China

In this paper, novel heat insulation materials were synthesized by molten salt method by using natural forsterite and $NaCl$-Na_2CO_3 molten salt. Impurity Fe_2O_3 with different mass ratios (0-9 wt.%) was added into raw materials, and the samples were prepared at the calcined temperature from 1173 to 1373 K for 10 h, respectively. Effects of Fe_2O_3 on properties including bulk density, apparent porosity and strength of heat insulation materials were investigated. Mechanism of molten salt during synthesis processing was discussed. The results show that the contents of Fe_2O_3 have significant effects on properties of samples. The strength of samples increases with the increasing of mass ratio of Fe_2O_3, and moreover, larger content of Fe_2O_3 may decrease the strength. The sintering of forsterite was promoted in molen NaCl, and the pores in samples formed through the decomposition of Na_2CO_3 and the removing of NaCl by washing in boiling water.

FS2: Thermal Management Materials and Technologies

FS2 Poster Session

Room: Ocean Center

(ICACC-FS2-P160-2013) Effects of matrix precursor, graphitization temperature and graphitization timing on properties of fast-carbonized carbon-carbon composite

C. Ju*, Y. Chen, M. Sun, C. Chu, H. Lin, National Cheng-Kung University, Taiwan; K. Lee, I-Shou University, Taiwan; J. Chern Lin, National Cheng-Kung University, Taiwan

An earlier study indicated that, with appropriate formula and process parameters, the bending strengths of PAN/phenolic-based C/C composite carbonized at 1°C/min and 1000°C/min were comparable. Furthermore, the composite carbonized at 1000°C/min had much higher fracture energy than that carbonized at 1°C/min. Presently reported are effects of matrix precursor (phenolic resin or coal-tar pitch), graphitization temperature (1700, 1900 or 2100°C) and graphitization timing (before or after densification) on properties of fast-carbonized (1000°C/min) PAN-based C/C composite. Results indicate that the phenolic resin-derived composite has higher strength, lower porosity and lower toughness level, compared to pitch-derived composite. For the same phenolic-derived composite, the flexural strength and modulus of the composite graphitized at 2100°C are higher than those of the composite graphitized at 1700 or 1900°C. However, from tribological viewpoint, 1900°C appears to be the most optimal graphitization temperature among three. Based on mechanical and tribological data, the graphitization treatment before densification seems to be a better choice than after densification. The research is supported by the National Science Council of Taiwan, Republic of China under research grant NSC 100-2221-E-006-095.

(ICACC-FS2-P161-2013) Effect of heat treatment on structure and properties of Ti-7.5Mo alloy

J. Chern Lin*, C. Chung, Y. Chen, Y. Tsai, C. Ju, National Cheng-Kung University, Taiwan

Reported in this presentation are results regarding the effects of heat treatment on structure and mechanical properties of an in-house-fabricated light weight, corrosion-resistant and highly biocompatible Ti-7.5Mo alloy. The alloy was solution-treated at 1,173K, followed by quenching under different conditions: quenching into RT water (298K), ice water (273K), dry ice-cooled ethanol/water mixture (243K and 203K), and liquid nitrogen (77K). Results showed that, despite their similar XRD patterns indicating a substantially α" phase, samples under different quenching conditions demonstrated different mechanical properties. Ethanol and liquid nitrogen-quenched samples had significantly higher strengths and lower elongations than others. EBSD analysis indicated that these samples still contained certain amounts of β phase. The ice water-quenched alloy was further aged at 923K and cooled under different conditions (furnace cooling, air cooling and water quenching). It was found that α and β phases co-existed in the aged alloy under all cooling conditions. The furnace-cooled sample had significantly less β phase content, higher hardness, higher tensile strength and lower elongation, compared to air-cooled and water-quenched samples. The research is supported by the National Science Council of Taiwan, Republic of China under the research grant NSC 100-2320-B-006-001.

FS3: Nanomaterials for Sensing Applications: Fundamental Material Designs to Device Integration

FS3 Poster Session

Room: Ocean Center

(ICACC-FS3-P162-2013) The Effects of Polydispersity and Lack of Reproducibility on the Optical Properties and Sensing Performance of Gold Nanoparticles and DNA Aptamer-Coated Gold Nanoparticles

J. Kindred, J. Chatterjee, A. Marshall, M. Khandelwal, M. Solomon, F. Lopez, D. Roy, E. Henrich, E. Fowler, A. Knight, K. J. Winkelmann, J. R. Brenner*, Florida Tech, USA

During prior work toward developing the first nanotechnology minor program with seven credits or more of laboratory coursework, it became obvious that polydispersity and reproducibility of gold nanoparticle properties were serious issues for student-synthesized samples. Later it was discovered how much variation there is even from commercial manufacturer to manufacturer. This poster will focus on the relationships between synthesis, particle size distribution, optical properties as measured by both visible and Raman spectroscopies, and ultimately function, when the gold nanoparticles are coated with DNA aptamers associated with either Alzheimer's or immune diseases, in differential pulsed voltammetry (DPV)-based electrochemical sensing and in fluorescence resonance energy transfer sensing. Finally, the application of DNA-coated Au nanoparticles for therapeutic "rewriting" of genetically defective tissue using gene gun technology will be presented.

Wednesday, January 30, 2013

S1: Mechanical Behavior and Performance of Ceramics & Composites

Fiber, Matrices, and Interfaces

Room: Coquina Salon D
Session Chairs: Jacques Lamon, CNRS; Randall Hay, USAF

8:00 AM

(ICACC-S1-034-2013) Effect of Matrix Microstructure on Composite Properties

T. Key*, K. Keller, AFRL/RXCC & UES, USA

Interlaminar properties in both tension and shear are lacking in 2D oxide-oxide CMCs and are highly dependent on the matrix strength. Our recent works suggest that control over the void distribution in 2-D reinforced porous matrix oxide-oxide composites is critical to attaining optimal properties. Uniform fine scale porosity is likely the ideal distribution. In this work, camphene-based freeze drying is utilized to avoid drying shrinkage-based cracking and to refine the matrix microstructure. Various processing parameters, such as freezing rate and solids loading, were systematically varied in an effort to control the resultant porosity. Microstructural evaluation (SEM) and mechanical testing (short-beam shear) were used to evaluate the effects of the parameter changes.

8:20 AM

(ICACC-S1-036-2013) Processing and mechanical properties of melt infiltrated C/SiC composites

T. Aokl*, T. Ogasawara, Japan Aerospace Exploration Agency, Japan; T. Hara, M. Ishikawa, Y. Kogo, Tokyo University of Science, Japan; Y. Iwahori, Japan Aerospace Exploration Agency, Japan

Carbon-fiber-reinforced Silicon Carbide (SiC) matrix (C/SiC) composites were fabricated by the combination of chemical vapor infiltration (CVI) and melt infiltration (MI) techniques. PAN-based carbon fibers were first woven into an orthogonal 3-dimentional preform and then coated with CVI-carbon and CVI-SiC in order to weaken fiber-matrix bonding and to protect carbon fibers during MI processing. After the CVI treatment, porous C/SiC composite was impregnated with a carbon black dispersed in water followed with MI for densification. In this study, pure Si or Si-Hf8.5at.% alloy were used for MI. The reason for using the Si-Hf alloy is to lower the MI temperature. The other reason is to reduce the amount of residual Si for the enhancement of heat-resistance. By conducting cross-sectional observations, X-ray diffraction analyses and electron probe micro analyses, reaction processes were discussed. Additionally, bending strength of the melt infiltrated C/SiC composites were evaluated up to elevated temperatures.

8:40 AM

(ICACC-S1-038-2013) Strength degradation in fatigue for Hi Nicalon filaments at elevated temperature

J. L. Lamon*, M. R'Mili, CNRS, France

The structural performance of CMCs is controlled by fiber strengths. Fiber strengths define the maximum attainable CMC strength. They depend not only on the filament that is considered (intrinsic variability resulting from the presence of flaws) but also on temperature, environment and loading history. Thus, the sensitivity of fiber strength to these factors is an important issue for the development of composites with durable load carrying capability. Recently, the phenomenon of slow crack growth in SiC-based fibers has been evidenced in air at temperatures ≤ 1200°C on multifilament bundles. It was found to result from slow crack propagation from surface defects, as a result of the consumption of the free carbon at grain boundaries and the local stresses induced by the SiC → SiO2 transformation at crack tip. The present paper investigates the degradation of fracture strength during fatigue of Hi-Nicalon SiC-based filaments in the intermediate temperature range where slow crack growth operates. Closed form equations of retained strength after static and cyclic fatigue were established on the basis of slow crack growth model. Predicted trends in strength degradation were compared to available experimental results obtained on single filaments. Implications for the lifetime of SiC/SiC composites in cyclic or static fatigue are discussed.

9:00 AM

(ICACC-S1-039-2013) Effect of Stress and Steam on Oxidation Rates of Hi-Nicalon-S SiC Fiber

R. Hay*, G. Fair, M. Ruggles-Wrenn, B. Steffens, Air Force Reserach Laboratory, USA; M. Cridge, Wright State University, USA; O. Anhofer, University of Dayton, USA

Creep rates and failure times were measured for Hi-Nicalon-S SiC fibers in air and steam at 800°C and 1100°C. Tensile stresses up to 800 MPa were used in tests in air at 800°C. Hi-Nicalon-S failed after ~2 hours in air at 800 MPa and in ~1 hour in steam at 100 MPa. The effect of stress and environment on fiber oxidation rates was characterized by transmission electron microscopy of cross-sectional sections. SiO2 scale thicknesses averaging 90 nm formed in 100 hours at 600 MPa tensile stress in air, and were about 50% thicker than those formed with no stress. No scales formed at 800°C in steam. Scales less than 100 nm thick formed in 1 hour at 1100°C in steam; these were much thinner than those formed in air. Implications for the relative rates of SiC oxidation and Si(OH)4 volatilization in steam are considered. Models for the effect of stress on SiC oxidation rates are proposed. Failure mechanisms of SiC fibers in steam and air at high temperature are discussed.

9:20 AM

(ICACC-S1-040-2013) Tensile Behavior and Damage Monitoring of SiC fiber reinforced SiC matrix Single Tow MiniComposites

S. Ramasamy*, A. Almansour, G. N. Morscher, The University of Akron, USA

SiC fiber reinforced SiC matrix (SiC/SiC) composites, a candidate material for structural hot sections of next generation gas turbine engines, form matrix and fiber cracking under mechanical loading. These cracks allow oxidizing species to react at high temperatures and have severe fiber oxidation leading to material failure. A versatile and cost-effective approach to study the constituent/property relationship is to use SiC/SiC single tow minicomposites, an elemental skeletal structure of woven SiC/SiC macro-composites. In this present work, single tow SiC/SiC minicomposites with constant chemical vapor infiltrated (CVI) SiC matrix with variations in SiC fiber types (Hi-Nicalon, Hi-Nicalon Type S and Tyranno ZMI), fiber volume fractions as well as interfaces (Boron Nitride (BN) and carbon (C)) were studied. Room temperature monotonic tension tests were performed and the damages formed during testing were deducted and located through promising non destructive inspection techniques, modal acoustic emission (AE) and four point electrical resistance (ER). The AE events occurrence and change in the ER were related to the matrix/fiber cracks and damages that form during the tensile testing. Microstructural analysis was also carried out to minicomposites polished and fractured surfaces to understand the extent of damage and failure mechanisms, respectively.

10:00 AM

(ICACC-S1-041-2013) Microstructural Evolution during Creep Testing of Nextel 610 and Nextel 720 in Air and Steam

R. Hay*, G. Fair, M. Ruggles-Wrenn, C. Armani, Air Force Research Laboratory, USA; M. Cridge, Wright State University, USA; O. Anhofer, University of Dayton, USA

Creep rates of Nextel 610 and Nextel 720 fibers were measured in air and steam at 100 to 500 MPa tensile stress at 1100° and 1200°C, respectively. Both fibers creep faster and fail at lower stress in steam than in air. Fiber microstructures were characterized by transmission electron microscopy of longitudinal sections. Alumina grain growth and elongation, and intra- and intergranular pore growth were quantified for Nextel 610 fibers using image analysis of over 500 grains or pores, respectively. Grain size increased by ~25% in steam and~10% in air after 100 hours at 1100°C. There was significantly more grain elongation relative to total creep strain for creep in air, but pore growth was more pronounced in steam. Mullite in Nextel 720 decomposed to porous alumina at 1100° and 1200°C in steam. Over 2 microns of porous alumina formed after 100 hours in steam at 1200°C. The decomposition rate was constant with time and had an activation energy of ~200 kJ/mol. Pore formation and growth after creep of Nextel 720 at 1200°C was much more prominent in steam than in air. Implications of these microstructural observations for creep mechanisms in both fibers are discussed.

10:20 AM

(ICACC-S1-042-2013) Fabrication and Testing of γ-RE2Si2O7 Matrix Composites

E. E. Boakye*, K. Keller, P. Mogilevsky, T. Parthasarathy, UES Inc., USA; M. K. Cinibulk, R. S. Hay, AFRL, USA; M. Ahrens, M. Cridge, Wright State University, USA

Yttrium disilicate has five polymorphs and is refractory, melting at 1775°C. Its γ-polymorph (γ-Y2Si2O7) has been reported as a potential oxidation-resistant alternative to carbon or BN for CMC fiber-matrix interphases. The α and β polymorphs may work as well. Prior TEM results of indented samples showed both extensive dislocation slip and fracture similar to observations made for monazite. Preliminary fiber pushout results of SCS-0 fibers in dense Y2Si2O7 matrix showed fiber debonding and push-out, with sliding stresses of ~30-60 MPa, which is within the range reported for C, BN, and LaPO4 coatings. . In this work, the field assisted sintering technique (FAST) was used to form dense α-, β- and γ-Y2Si2O7 pellets at a pressure of 20 kN and temperatures of 1050° - 1200°C. Subsequently, their Vickers hardness was measured. SCS-0 fibers were also incorporated into α-, and β - Re2Si2O7 matrixes and densified at 1050°C - 1200°C / 1 h using the FAST approach. Fiber push-out experiments were conducted, and the average sliding stress values were determined. Nicalon/Y2Si2O7 composites were formed. The resultant composite properties, including, microstructural uniformity and fiber distribution, will be reported.

10:40 AM

(ICACC-S1-043-2013) Different Ceramic Fibers Exposed to High Temperature

H. A. Colorado*, J. Yang, UCLA, USA; C. Hiel, Composite Support and Solutions Inc., USA

Different ceramic fibers were exposed to high temperature environment. Fibers included were E-glass, Basalt and SiC. The thermal shock tests were conducted after samples were in an oxidizing environment at high temperature. Samples were placed in a furnace at different temperatures (up to 1000C) to determine the temperature effect in the tensile strength. The characterization was conducted by both optical and scanning electron microscope. Results showed important aspects that may be considered when these fibers are reinforcing ceramic composites under high temperature oxidation environments.

11:00 AM

(ICACC-S1-044-2013) Study on strength prediction model for unidirectional composites

H. Zhang*, W. Wen, H. Cui, J. Xiao, Nanjing University of Aeronautics & Astronautics, China

The fibers in unidirectional composites were treated through two levels: fiber bundle and array of fiber bundles. The fibers were assumed to be placed in hexagonal arrays in fiber bundle. And the fiber bundles were assumed to be placed in planar array in unidirectional composites. Based on the statistical theory of crack evolvement and the perfect evolvement process of random crack cores, the evolvement probability arithmetic of a random crack core with considering changes of influenced length was given, and a two-level model of random crack cores for forecasting the longitudinal tensile strength of unidirectional composites was built. In this two-level model, Beyerlein's formula was used to calculate the average stress concentration factor of the bundle, and Sivasambu's formula was applied to calculating the stress concentration factor of the fiber inside bundle. The predictive results showed that the two-level model of random crack cores is more accurate than the classical theoretical models for forecasting the longitudinal tensile strengths of unidirectional composites.

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

Multifunctional Coatings

Room: Ponce DeLeon
Session Chairs: Soshu Kirihara, Osaka University; Jeffrey Eldridge, NASA Glenn Research Center

8:00 AM

(ICACC-S2-031-2013) Plasma-assisted electrolytic coatings and surface treatments for sustainable energy applications (Invited)

A. Yerokhin*, University of Sheffield, United Kingdom

Plasma-assisted electrochemical surface treatments rely upon generation of plasma discharge at the metal electrode during high-voltage electrolysis. Among these is Plasma Electrolytic Oxidation (PEO) which offers significant benefits for wear and corrosion protection of light alloys (Al, Mg, Ti, Zr) by enabling formation of thick hard and well-adhered ceramic coatings with fused morphology modified by the discharge. PEO contributes greatly into energy sustainability of advanced manufacturing by eliminating various pre- and post-treatment steps from production cycle. Novel pulsed bipolar PEO processes allow substantial reduction of energy consumption, faster coating growth rates and more careful control over surface morphology and phase composition, placing them in competition with conventional anodising. Also, excellent conformity and adhesion of PEO coatings compare them favourably with coatings produced by line-of-sight deposition methods, e.g. PVD and spraying. Functional PEO coatings are attractive for development of new products, e.g. photovoltaic and power electronic devises that offer further benefits in energy generation and storage. Yet greater opportunities are created in energy conservation by protective PEO coatings providing substantial weight savings along with enhanced durability of components employed in tribological, structural and environmental applications.

8:30 AM

(ICACC-S2-032-2013) Interface modification of LiMn2O4 cathodes by electronic and ionic conducting coatings (Invited)

K. Chiu*, C. Chen, Feng Chia University, Taiwan

Functional surface coatings of nano-crystalline LiMn2O4 (nLMO) and Prussian blue (PB) have been applied to modify the LiMn2O4

(LMO) cathodes for lithium ion batteries. The feasibility of the functional coatings has been tested on pure LMO thin film cathodes, free of binders and conducting additives, and shown improved stability under high temperature, high current rates and over-discharged cycling. The excellent performances of the cathodes can be attributed to the functional surface layer, which services as a mechanical capping as well as an electronic and ionic coating. The reduced interface charge transfer resistances have been clearly observed by the electrochemical impedance spectra. The surface/interface modification techniques have also been applied on conventional powder-type LMO cathodes containing polyvinylidene fluoride binder and conducting carbon black. The modified powder cathodes can be operated under harsh conditions as mention above, which satisfies the requirements of electric vehicles and grids.

9:00 AM

(ICACC-S2-033-2013) Fabrication of Fine Ceramics Layers by Thermal Nano-particles Coating Techniques (Invited)

S. Kirihara*, Y. Itakura, S. Tasaki, Osaka University, Japan

Thermal nano-particles coating were newly developed as novel technologies to create fine ceramics layers for steel substrates. Nanometer sized tungsten or alumina particles of 300 nm in average diameter were dispersed into liquid resins at 40 % in volume fraction, and the obtained slurries were sputtered by compressed air jet of 2 atm in pressure. And, the slurries mists were blew into the arc plasma with argon gas spray of 50 slpm in flow late. On the steels substrates, the fine surface layers of 30 μm in thickness with high wear resistance were formed at 300 gpm in supply rate. Microstructures and compositional distributions in the coated layers and the patterned lines were observed and analyzed by using a scanning electron microscopy and energy dispersive x-ray spectroscopy.

9:20 AM

(ICACC-S2-034-2013) Surface Modification of La0,6Sr0,4Co0,2Fe0,8O3-δ Hollow Fiber Membranes for Oxygen Separation

M. Jacobs*, B. Michielsen, V. Middelkoop, M. Gijsen, F. Snijkers, VITO, Belgium

Dense mixed ionic-electronic conducting hollow fiber membranes such as La0,6Sr0,4Co0,2Fe0,8O3-δ (LSCF) can be used for the oxygen separation from air. However, the oxygen permeation flux through these membranes is limited by surface-oxygen exchange kinetics . To improve this oxygen exchange, the membranes can be coated with a thin activation layer, which can be a porous layer of the membrane material itself to increase the surface area or a material layer with superior oxygen exchange properties such as La0,8Sr0,2CoO3-δ (LSC). In this study, both types of activation layers were applied by spray coating and the coating layers were analyzed by SEM, EDS and EPMA. Furthermore, the effect of the coatings on the oxygen flux at temperatures between 800 and 950°C was measured in a oxygen permeation measurement set-up. In addition, the effects of the thickness of the coating and the sintering temperature on the oxygen flux were investigated in order to optimize the coating layers.

10:00 AM

(ICACC-S2-035-2013) Dynamic oblique angle deposition of nanostructures for energy applications (Invited)

G. Wang*, T. Lu, I. Bhat, Rensselaer Polytechnic Institute, USA

The century old oblique angle deposition (OAD) of porous films has received renewed attention recently because it can tailor not only the morphology but also the texture of nanostructures. This is achieved by engineering the incident flux angle and substrate rotation speed and rotation axis that change the shadowing effect dynamically and the texture selection rule during nanostructure self-assembly process. These artificially fabricated nanostructures have been used as sensors in many applications. Among the textured films, a particular class of biaxial films such as MgO has been used as a buffer layer to grow, for examples, high temperature superconductors as well as ferroelectrics. More recently it has been shown that biaxial CaF2 nanorods can be coated on amorphous substrates at room temperature using OAD. We demonstrated that single crystal-like CdTe can be grown by MOCVD directly on CaF2 on glass substrate despite a large lattice mismatch between CdTe and CaF2. We also showed that single crystal-like Ge can be epitaxially grown on biaxial CaF2 buffer on glass. These films have potential applications as low cost photovoltaic devices. We will also introduce a new oblique angle flipping rotation mode to grow biaxial metallic nanorods such as W and Mo. These films may also find applications as buffers to grow functional materials for energy applications. This work is supported by the NSF DMR.

10:20 AM

(ICACC-S2-036-2013) Nonpolar AlN Thin Films on Diamond for New Electronics Devices (Invited)

S. Wu*, Tung-Fang Design University, Taiwan; J. Huang, National Cheng-Kung University, Taiwan; R. Ro, I-Shou University, Taiwan; Z. Lin, Advance Design Technology INC., Taiwan

In this research, we propose a new composite substrate material (nonpolar AlN films/diamond) for the applications on high power handling RF-filters, high sensitivity liquid-bio sensors and high power nonpolar light emitting diodes (LEDs). As regards the Rayleigh surface acoustic wave (SAW) modes of nonpolar AlN films on diamond with the propagation direction along the a-axis, especial for mode 1, the phase velocity is 10474 m/s and the piezoelectric coupling factor (K^2) is 2.31 % at the films thickness ratio (h/λ) is 0.3. This theoretical velocity is currently the highest Rayleigh SAW velocity. This composite substrate also can excite high velocity shear horizontal (SH) SAW modes with the propagation direction perpendicular to the a-axis. Especial for mode 0, the K^2 curve shows a maximum value (1.27%) at h/λ=0.28 and the velocity is 7496 m/s. This theoretical velocity is currently the highest SH SAW velocity. A highly and fine structural nonpolar AlN films were successfully prepared on polycrystalline diamond. The microstructure, in particular, the surface and interface regions, of the nonpolar AlN films was studied. The nonpolar AlN films have a smooth top surface (4.311 nm). The as-grown nonpolar AlN films consist of wll-defined columns, while the column width is about 100 nm in average. There is an amorphous interlayer (62 nm) between nonpolar AlN films and polycrystalline diamond.

10:40 AM

(ICACC-S2-038-2013) Characteristics and Mechanism in Amorphous Oxides for Resistance Random Access Memory Application

J. P. Chu*, W. Chang, Department of Materials Science and Engineering, National Taiwan University of Science and Technology, Taiwan; S. Wang, Department of Materials and Minerals Resources Engineering, National Taipei University of Technology, Taiwan

Resistance random access memory (RRAM) attracts great interest as a promising candidate for the next generation memory application owing to its high endurance/retention performance, fast write/read access and simple process. The potential candidate materials for the RRAM application are such as amorphous films without forming process. In this study, the high thermal stability HoScOx amorphous films with different oxygen contents, prepared by using magnetron sputtering, have been characterized by semiconductor analyzer, XPS, TEM, and EDS for resistance switching (RS) mechanism, chemical state, crystallinity and composition, respectively. The 36nm-thick films show the unipolar RS behavior with low operation stresses and no forming required, beneficial for the RRAM device. The RS property is found to vary with the oxygen content in the film, and is thought to be strongly related to the oxygen-deficient (oxygen vacancy) concentration, which serves as the filamentary conduction in the sample in the low resistance state.

11:00 AM

(ICACC-S2-039-2013) Protective coating based on PDC for high-temperature recovery system

A. L. Prette*, University of Bayreuth, Germany; S. Rannabauer, M. Scheffler, Otto-von-Guericke University Magdeburg, Germany; M. Werschy, DBI Gas- und Umwelttechnik GmbH, Germany; M. Wiersig, MIOBA Mitteldeutscher Industrie-Ofenbau GmbH & Co. KG, Germany; G. Motz, University of Bayreuth, Germany

Energy efficiency is nowadays very important and pursued topic for almost any battery, power source or energy related device. In the case of devices that work with combustion or hot gases, the efficiency increases with working temperature. By using a recuperator as a heat recovery system hot exhaust gases passes through a series of tubes that act as heat exchange. A novel technique to increase the working temperature and therefore to improve efficiency of the recovery system is the use of ceramic foams placed in the interior of steel exhaust pipes. A suitable ceramic material is SiC-foam due to the high thermal conductivity and stability under harsh environments. However, SiC in contact with the stainless steel housing reacts at temperatures above 800°C under decomposition. To avoid this direct contact with the steel housing preceramic polymer (PHPS) was used as coating on the SiC-foams. Additionally, on the internal tube wall a coating composed of polymer derived ceramic (HTT1800) filled with 3YSZ was applied by spraying. After pyrolysis at 1000°C the coating layer has an amount of approximately 85 vol% of 3YSZ and the thickness was about 28μm. At temperature close to maximum working temperature of the steel, the coating proves to be stable and adhered very well to the tube wall. No reaction between steel tube and SiC-foam could be observed.

11:20 AM

(ICACC-S2-040-2013) Preparation of silica-coated nano-sized Y3Al5O12:Ce3+ phosphor and their luminescence properties

H. Song*, D. Kim, C. Lee, H. Roh, Seoul National University, Republic of Korea; D. Kim, Ajou University, Republic of Korea; K. Hong, Seoul National University, Republic of Korea

Nano-sized Ce-doped Y3Al5O12 (YAG:Ce) phosphors were prepared by high energy beads milling process which utilize top-down synthesizing method. The beads milling process was performed by Laboratory Mill MINICER with ZrO2 beads which diameter is 800 μm. After beads milling process, dispersed nano-sized YAG:Ce was treated with ethanol, ammonium hydroxide, polyvinylpyrrolidone (PVP) and tetraethyl orthosilicate (TEOS) at room temperature for silica coating. Surface silica shell was analyzed by analytical transmission electron microscope (analytical TEM). YAG:Ce and silica shell size were identified by using field emission scanning electron microscope (FESEM) and high-resolution transmission electron microscope (HRTEM). As processing beads milling, uniform nano-sized YAG:Ce particles which mean size is from 100 to 120 nm were produced. And after coating, uniform silica was coated on the YAG:Ce surface and its thickness was 5 nm. Luminescence and quantum efficiency (QE) of silica-coated nano-sized YAG:Ce were measured by QE measuring instrument. Surface silica coating could reduce non-radiative quenching center, e.g. dangling bonds and surface defects, which resulted to improve QE of nano-sized YAG:Ce phosphors.

S3: 10th International Symposium on Solid Oxide Fuel Cells (SOFC): Materials, Science and Technology

Electrodes II

Room: Coquina Salon H
Session Chairs: Mihails Kusnezoff, Fraunhofer IKTS; Sascha Kuehn, eZelleron GmbH

8:00 AM

(ICACC-S3-018-2013) Sulfur poisoning and reaction kinetics in Ni/YSZ and Ni/GDC anodes (Invited)

M. Kusnezoff*, S. Kavurucu Schubert, N. Trofimenko, A. Michaelis, Fraunhofer IKTS, Germany

Sulfur is a main contaminant in the most fuels and can be tolerated by several reformer catalysts. Reformed fuel still contains up to several ppms of H2S in the gas phase. For small, portable and mobile systems the sulfur tolerance of SOFCs is an important criterion for system integration. It is known from the literature that GDC-containing anodes have better sulfur tolerance compared to Ni/YSZ. The reaction mechanism in Ni/YSZ and Ni/GDC is however not fully clarified and experiments on sulfur poisoning help in understanding of electrochemical phenomena in the fuel electrode. Single electrolyte supported cells with Ni/YSZ and Ni/GDC anodes were manufactured and tested in H2S containing fuel for degradation under steady-state and cyclic (stepwise change of H2S concentration) conditions depending on fuel composition at 850°C. Impedance spectra before, during and after contamination were measured and analysed. Ni/GDC anodes have shown small degradation during sulfur contamination in comparison to Ni/YSZ. It was found that sulfur contamination of nickel surface takes place independently from type of composite anode used and GDC should act as an electrochemically active site for hydrogen oxidation to keep sulfur tolerance. The reaction mechanism in Ni/GDC anode is discussed on basis of impedance spectra measured at different temperatures and operating conditions and compared to the reaction kinetics of Ni/YSZ.

8:30 AM

(ICACC-S3-019-2013) Redox behaviour of sulphur at Ni/GDC SOFC anode at mid- and low-range temperatures: An operando S K-edge XANES study

G. Nurk*, University of Tartu, Estonia; T. Huthwelker, Paul Scherrer Institut, Switzerland; A. Braun, Empa-Swiss Federal Laboratories for Materials Science and Technology, Switzerland; C. Ludwig, Paul Scherrer Institut, Switzerland; E. Lust, University of Tartu, Estonia; R. Struis, Paul Scherrer Institut, Switzerland

Sulphur poisoning of nickel–cermet solid oxide fuel cell (SOFC) anode catalysts working at mid- and low temperatures has been widely studied but not completely understood. Here we demonstrate novel experimental approach to obtain sulphur K-shell X-ray absorption near edge spectroscopic information at operando conditions, thus, at working fuel cell with the flux of O2- from cathode to anode. Spectroscopic information was collected at different temperatures from T=550°C to 250 °C, at 5 ppm H2S in H2 reacting with the Ni-gadolinium doped ceria anode. Various sulphur containing species in different oxidation states (6+, 4+, 0, -2) were observed. According to sulphur speciation analysis, the species could either relate to –SO42- or SO3(g), –SO32- or SO2(g), S2(g) or surface-adsorbed S atoms, and, Ni or Ce sulphides, respectively. The appearance of different sulphur oxidation states as a function of temperature was analysed and compared with thermodynamic calculations. Some differences between experimental data and calculations were observed. Differences are most likely caused by the fact that calculations are equilibrial but at working fuel cell steady state conditions are prevailing. Differences between stoichiometric CeO2 used in calculations and partially reduced Ce0.9Gd0.1O2–δ in the working fuel cell could also cause deviations from theoretical predictions.

8:50 AM

(ICACC-S3-020-2013) The systematical study of material natures on La0.6Sr0.4Co1-yFeyO3-d cathode (Invited)

S. Hashimoto*, M. Oh, Y. Shin, X. Li, Y. Kimura, T. Kawada, Y. Fukuda, I. Nakano, M. Kuhn, H. Kudo, K. Sato, K. Yashiro, K. Amezawa, J. Mizusaki, Tohoku University, Japan

La0.6Sr0.4Co1-yFeyO3-d (LSCF) is one of the promising cathode materials and widely used in the intermediate temperature solid oxide fuel cells (IT-SOFCs). Last several years, research group in Tohoku University has focused on basic material properties of LSCF including mechanical propaties, and the properties are systematically measured under temperature and PO2 controlled conditions. In this study, the key properties for LSCF, i.e. oxygen nonstoichiometries and crystal structures, are compared with other basic properties for LSCF cathodes, i.e. Young’s modulus, electrical conductivity,thermal diffusivity, coefficient of oxygen vacancy diffusion Dv and electrochemical properties, and discuss about the correlationships.

9:20 AM

(ICACC-S3-021-2013) 3D Microstructural and Electrochemical Evolution of LSM-YSZ Composite Cathodes at Elevated Temperatures

K. Yakal-Kremski*, J. Cronin, S. A. Barnett, Northwestern University, USA

$(La_{0.8}Sr_{0.2})_{0.98}MnO_3$-$Zr_{0.84}Y_{0.16}O_2$ (LSM-YSZ) symmetrical cells, studied to isolate cathode resistance contributions in solid oxide fuel cells (SOFCs), were annealed at elevated temperatures to simulate aging which normally occurs over long times at ordinary SOFC operating temperatures. Annealing of optimally fired cathodes showed polarization resistance increases of ~15% after 96 hours at 1000‘C, and ~30% after 96 hours at 1100‘C, as measured by electrochemical impedance spectroscopy (EIS). Additionally, cathodes fired at lower than optimal temperatures were annealed. Although initial cell resistances were higher, annealing shows a regime of performance improvement due to microstructural evolution. Focused ion beam-scanning electron microscope (FIB-SEM) tomography was employed to gather 3D microstructural data such as phase volume percent, specific surface area, and triple phase boundary (TPB) density. Cathode densification and an increase in average LSM particle size, as quantified by both a pore phase volume percent decrease of 20% and a LSM specific surface area decrease of 26%, were observed between the control and 1000‘C, 96 hour annealed cells. A model for microstructural evolution, developed by fitting 3D data with time and temperature, will be used to make extrapolated predictions of thermal aging effects over long times at normal operating temperatures.

10:00 AM

(ICACC-S3-022-2013) Ca3Co4O9 and Ba2Co9O14 : promising materials as air electrodes for SOFC and SOEC (Invited)

R. Vannier*, V. Thoréton, D. Huo, A. Rolle, C. Pirovano, S. Daviero-Minaud, N. Nuns, A. Mamede, Ecole Nationale Supérieure de Chimie de Lille, France

Promising performances as electrode for SOFC or SOEC were recently evidenced for the Ca3Co4O9 and Ba2Co9O14 cobaltites which exhibit a layered structure corresponding to the intergrowth of [Ca2CoO3] rock salt blocks and [CoO2] hexagonal layers of CdI2 type for the first, and [Ba3n+1ConO3n+3] perovskite blocks and [CoO8] blocks also containing layers of CdI2 type, for the second. For both compounds, mixed ionic electronic conduction was expected. Composite electrodes with Gadolinia Doped Ceria were prepared by screen printing and characterised by impedance spectroscopy. The electrode thickness and composition were optimised. For Ca3Co4O9, an improvement of the electrode performances was noticed when an interfacial thin layer of dense electrode was added at the surface of the electrolyte. Oxygen diffusion in these materials was confirmed by 18O/16O isotope exchange combined with Secondary Ion Mass Spectrometry. Since the oxygen molecule dissociation at the surface may be strongly affected by the composition of the outermost atomic layer of the material, Low Energy Ion Scattering Spectroscopy was also carried out on these compounds. It notably revealed the presence of calcium at the outermost surface of Ca3Co4O9 showing evidence of the key role played by the ionic layers in the mechanism of oxygen dissociation at surface.

10:30 AM

(ICACC-S3-023-2013) Assessment of Ba1-xCo0.9-yFeyNb0.1O3-δ for Prospective High Temperature Electrochemical Devices (Invited)

M. Han*, Z. Yang, S. Song, P. Zhang, F. Chen, China University of Mining and Technology, Beijing, China

Mixed-conducting perovskite-type materials can be used in many applications such as Oxygen Transport Membranes (OTMs), Solid Oxide Fuel Cells (SOFCs) and Solid Oxide Electrolysis Cells (SOECs). Recently, it has been reported that introduction of Nb in the B-site of cobalt-based perovskites can significantly improve chemical stability and enhance performance. In this study, the performance and stability of Ba1-xCo0.9-yFeyNb0.1O3-δ (x=0-0.15, y=0-0.9) for high temperature electrochemical device applications such as OTM, SOFC and SOEC have been studied. The results show that Ba0.9Co0.7Fe0.2Nb0.1O3-δ can be a very promising candidate for the cathode of SOFCs and membrane materials of OTM application. Maximum power density of 1.1 W.cm-2 were obtained for La0.8Sr0.2Ga0.83Mg0.17O3-δ (LSGM) electrolyte supported cells with Ba0.9Co0.7Fe0.2Nb0.1O3-δ as cathode and Ni-GDC as anode operated at 800 oC. Under an ambient air / helium oxygen gradient, the oxygen permeation flux of Ba0.9Co0.7Fe0.2Nb0.1O3-δ membrane was 1.8 ml.min-1.cm-2 for a 1 mm thick membrane at 875 oC. Further, the electrolysis cell has showed very stable performance during a 200 h short-term electrolysis testing for LSGM electrolyte supported cells with Ba0.9Co0.5Fe0.4Nb0.1O3-δ as oxygen electrode. In conclusion, this work has established a solid foundation for the practical application of mix-conducting materials.

11:00 AM

(ICACC-S3-024-2013) Life Testing of LSM-YSZ Composite Electrodes During Current-Switched Operation

G. A. Hughes*, K. Yakal-Kremski, S. A. Barnett, Northwestern University, USA

Solid oxide cells (SOC) can be used for energy storage by switching between electrolysis and fuel cell operation modes, however, durability of cells cycled between modes is not well understood. Symmetric cells with $(La_{0.8}Sr_{0.2})_{0.98}MnO_3$-$Zr_{0.84}Y_{0.16}O_2$ (LSM-YSZ) electrodes were tested in air with the current direction reversed periodically. This mimics the conditions of a reversible SOC air electrode, which alternately acts as fuel cell cathode and electrolyzer anode. The current density and time in each current direction were equal, such that both symmetric-cell electrodes should evolve identically. To eliminate possible contamination from precious-metal current collectors, electrical contact was made solely by LSM current collecting pellets and paste. Impedance spectroscopy results displayed considerable degradation at a relatively high current of $1.5Acm^{-2}$ at 800°C. The ohmic resistance increased from $0.61\ \Omega cm^2$ to $1.15\ \Omega cm^2$ and the polarization resistance increased from $0.21\ \Omega cm^2$ to $0.57\ \Omega cm^2$ after 267 hours under current load with a switching period of 1 hour. This presentation will include results on measured degradation rates from symmetrical cells at different current densities, switching periods, and temperatures. Additionally, microstructure measurements at different stages of current-switching operation will be presented and correlated with electrochemical results.

11:20 AM

(ICACC-S3-025-2013) Electrochemical Analysis for Microstructural Optimization of SSC Infiltrated Solid Oxide Fuel Cell Cathodes

A. V. Call*, Z. Gao, S. A. Barnett, Northwestern University, USA

Solid oxide fuel cell (SOFC) cathodes consisting of ionic conducting scaffolds infiltrated with mixed ionic and electronic conducting (MIEC) nanoparticles have exhibited some of the smallest reported polarization resistances and have the potential for further improvement through materials selection and microstructural optimization. In this study, symmetric cell cathodes were prepared via wet infiltration of $Sr_{0.5}Sm_{0.5}CoO_3$ (SSC) nano-particles by a nitrate process into porous $Ce_{0.9}Gd_{0.1}O_{1.95}$ (GDC) or $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_3$ (LSGM) scaffolds. SSC infiltrate loading and scaffold porosity were varied. Electrochemical impedance spectroscopy (EIS) measurements were completed between 400°C and 650°C in air to simulate low and intermediate temperature operation. Initial polarization resistances (Rp) as low as 0.11 Ωcm^2 and 0.22 Ωcm^2 at 600°C were obtained for SSC-GDC and SSC-LSGM systems, respectively. This data, paired with bulk materials properties of the constituent materials, is used in a composite cathode model to make performance predictions based on microstructure. EIS with pO_2 variation was used to gain insights into electrochemical processes.

11:40 AM

(ICACC-S3-026-2013) In-Operando XRD of LSCF Cathodes on Anode-Supported SOFCs Operating at Various Temperatures

J. S. Hardy*, J. W. Templeton, J. W. Stevenson, Pacific Northwest National Laboratory, USA

Anode-supported solid oxide fuel cells with LSCF cathodes were operated at 700, 750, and 800°C for over 1000 hours at constant current approximating an operating voltage of 0.8 V. X-ray diffraction (XRD) of the cathode was performed continuously over the entire duration of each test to monitor any changes that occur in the XRD patterns over time during cell operation. The XRD results collected at the three temperatures are compared to one another and to previous tests including those of a duplicate cell that, rather than generating current, was held at open circuit voltage (OCV) at 750°C for over 1000 hours in the XRD test stand. Summation of the XRD patterns taken over the entire duration of the tests resulted in cumulative count times that greatly enhanced the signal to noise ratio of peaks associated with minor phases, making it possible to identify trace phases such as LaCoO3, Fe3O4, and Co3O4 present in the cathode in concentrations of less than 2%.

S4: Armor Ceramics

Boron-Icosahedral Based Ceramics II

Room: Coquina Salon E
Session Chair: Jane Adams, U.S. Army Research Laboratory

8:00 AM

(ICACC-S4-028-2013) Boride Carbide Ballistic Performance above the Hugoniot Elastic Limit (Invited)

M. J. Normandia*, Ceradyne, USA

A review is presented of boron carbide (B4C) ballistic data at impact pressures to >100 GPa. Ballistic performance seems to correlate with shear strength in re-shock impact tests. B4C shows anomalous behavior and shear stress degradation just above its Hugoniot Elastic Limit (HEL)~15-19 GPa after which upon re-impact, B4C regains compressive strength at high pressures. When coupled with a complex unit cell structure, softening, and/or amorphization in recovered fragments, a confluence of potentially degrading behavior occurs at high stress impact. Ballistic data of over 30+ years indicate that despite this behavior, B4C has amongst the highest mass efficiencies and often the lightest weights than other armor ceramics. The data that generated these concerns at impact pressures ~18-23 GPa are reviewed; namely an observed 'shatter gap-like' velocity and increased fragmentation and a second data set where a change in depth of penetration slope occurred. In both tests, a single ceramic thickness was used across a wide velocity range that is too thin to fragment the core over the velocity range, thus a defeat mechanism transition explains the behavior which occurs in all ceramics.

8:30 AM

(ICACC-S4-029-2013) Armour research at FOI on boron carbide

P. Lundberg*, Defence & Security, Systems and Technology Division, Sweden

The first impact experiments performed at FOI (formerly FOA) on boron carbide were carried out 1986. The material was hot isostatic pressed (HIP) and produced by ASEA Atom in Rob-ertsfors. The company is today owed by Coortek. The research focus at this time was on ar-mour for protection against long rod penetrators and the boron carbide samples were relatively thick, typically 35 mm. The samples were tested in a depth of penetration configuration (DOP-test) and the boron carbide showed the highest weight effectiveness of the ceramics tested (hot isostatic pressed Al2O3, Si3N4, SiC and TiB2). Today, nearly 25 years later, impact experiments on boron carbide of similar quality is per-formed at FOI. The aim today is to explore the possibility to use the material in a helmet ap-plication. Typical thicknesses of the boron carbide samples are in this case 1-4 mm and the experiments are highly instrumented in order to gather detailed information on the response of the boron carbide and the backing structure due to impact of a steel core small calibre projec-tile. This paper gives an overview on various impact experiments on boron carbide performed at FOI during the time period between 1986 and up to today. Focus is on basic studies where flash X-rays has been used as the main tool in order to depict the target response. Some results from the studies will be presented and discussed.

8:50 AM

(ICACC-S4-030-2013) Edge-on Impact investigation of fracture propagation in Boron Carbide

E. Strassburger*, Fraunhofer EMI, Germany

The fracture propagation in boron carbide was visualized in a high-speed photographic study. The specimens of the dimensions 100 mm x 100 mm x10 mm were tested in the so called Edge-on Impact (EOI) configuration and damage propagation was observed by means of a Cranz-Schardin camera, which allows for a maximum frame rate of 10 MHz. Steel cylinders of 30 mm diameter and 23 mm length were used as projectiles. Fracture patterns, single crack velocities and fracture front velocities (damage velocities) were determined as a function of impact velocity, which was varied in the range from 50 m/s to 1000 m/s. Damage velocity increased as the impact velocity was increased. The damage velocity varied in the range from 5796 m/s at an impact velocity of ~ 50 m/s up to 12406 m/s at an impact velocity of 1010 m/s. The damage velocity versus impact velocity curve exhibited a plateau for impact velocities in the range from 100 m/s to 700 m/s where the damage velocity was about 9000 m/s.

9:10 AM

(ICACC-S4-031-2013) Intact and predamaged boron carbide strength under moderate confinement pressures

I. S. Chocron, C. E. Anderson*, K. A. Dannemann, A. E. Nicholls, N. L. King, Southwest Research Inst, USA

This paper summarizes the characterization work performed on intact and predamaged boron carbide tested in compression under confinement in a pressure vessel or using a thick steel confining sleeve. The focus is on the effect of pressure (up to 2 GPa hydrostatic pressure) on the strength. The techniques used for characterization are described. The failure curves obtained are presented and written as Drucker-Prager and Mohr-Coulomb failure criteria. Optical and stereomicroscopy were used to evaluate and document damage. Finally the results are discussed and compared to the literature. It is shown that data obtained with very different techniques (confined compression, plate impact, and divergent plate impact) overlap, increasing the confidence in the results.

Quasi-Static and Dynamic Behavior I

Room: Coquina Salon E
Session Chair: Sikhanda Satapathy, US Army Research Laboratory

9:50 AM

(ICACC-S4-032-2013) Pressure and Shear Induced Phase Transformations in Ceramics (Invited)

V. I. Levitas*, Iowa State University, USA

Experimental results on phase transformations in ceramic materials (in particular, BN and SiC) obtained under compression and large plastic shear of materials in rotational diamond anvil cell (RDAC) are presented. Multiscale (nano-, micro- and macroscales) continuum thermodynamic theory and simulations for strain-induced transformations were developed, which explain a number of mechanochemical phenomena. Specifically, the theory explains why the superposition of plastic shear and high pressure in RDAC leads to: (a) significant reduction (by a factor of 3-10) of transformation pressure and pressure hysteresis, (b) appearance of new phases (in particular, nanostructured), which were not obtained without shear, (c) substitution of reversible transformation by an irreversible one, and (d) strain-controlled kinetics. Various new phenomena are revealed, including transformation-induced plasticity under pressure and shear and phase transformation induced by rotational plastic instability. Methods of controlling strain-induced phase transformations are developed.

10:20 AM

(ICACC-S4-033-2013) Raman Characterization of Ballistically-Impacted Polycrystalline 3C and 6H Silicon Carbides

J. C. LaSalvia*, U.S. Army Research Laboratory, USA; V. Domnich, Rutgers, The State University of New Jersey, USA; K. D. Behler, E. R. Shanholtz, U.S. Army Research Laboratory, USA

Depth-of-penetration (DOP) results and mechanistic responses for polycrystalline 3C and 6H silicon carbides (SiC) impacted at high-velocity were previously reported. TREX CVD SiC (3C) and Coorstek SiC-N (6H) were impacted with 6.35 mm diameter cemented carbide spheres at velocities between 300 m/s – 1700 m/s. The penetration onset velocity for the CVD SiC was 300 m/s higher than SiC-N; however, the DOP into CVD SiC was significantly greater than the SiC-N for impact velocities greater than 1200 m/s. Scanning electron microscopy (SEM) examination of polished CVD SiC and SiC-N cross-sections prepared from tiles impacted at 1350 m/s and 1403 m/s, revealed that the CVD SiC exhibited shear localization while SiC-N did not. It is believed that shear localization is the reason for the greater DOP in the CVD SiC. In the present study, Raman spectroscopy was used to examine both ceramics for possible evidence of amorphization, as well as identify the phases in the shear localized regions in the CVD SiC. While experimental and theoretical studies have shown 3C SiC can undergo pressure-induced amorphization, the possibility of amorphization has been shown to also occur in 6H SiC, albeit reversible and deformation-induced. SEM and Raman observations are presented and discussed in terms of differences in crystal structure and microstructure.

10:40 AM

(ICACC-S4-034-2013) Thermal Effects in Extreme Dynamic Environments

M. J. Davis*, SCHOTT North America, Inc., USA

The thermal environment encountered by condensed matter in highly dynamic environments remains a challenge to satisfactorily characterize and predict. Peak-shock and post-shock temperatures and thermal gradients are difficult to determine due in part to miniscule temporal and spatial scales. Nevertheless, the past half-century or so has seen an impressive body of work emerge on these and related topics, both from the impact and shock physics community but also from the earth sciences from those seeking to understand planetary interiors and solar system evolution. This review will present some of the salient information for brittle materials (e.g., ceramics, rocks, and glasses). The main conclusions from these works and this review: 1) high peak shock temperatures and phase transitions can occur on sub-microsecond timescales and be highly localized (e.g., shear bands); 2) post-shock temperature measurements usefully document the thermal state of material under pressure-release conditions immediately after the passage of the shock; 3) comparison of dynamic material properties to “quasi-static” ones are likely best done if the latter are measured at elevated pressure AND temperature; and 4) any remaining discrepancies between dynamic and quasi-static properties can reasonably be interpreted due to a strain-rate dependent process.

11:00 AM

(ICACC-S4-035-2013) Shock experiments to study source of inelasticity in ceramics

S. Satapathy*, D. Dandekar, C. Williams, US 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. The loading conditions in these experiments were “radial loading” in that the principal stresses increased in constant proportion to each other. 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. 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 will be presented in this paper to reveal the primary source of inelasticity in brittle ceramics.

11:20 AM

(ICACC-S4-036-2013) Effect of Prestressing on the Ballistic Performance of Alumina Ceramics: Experiments and Modeling

A. H. Gassman*, V. Paris, L. Levin, Z. Asaf, A. Ya’akobovich, E. Ran, F. Aizik, Plasan Sasa Ltd., Israel

In this research, the dynamic behavior of prestressed alumina tiles under ballistic impact was investigated via experiments and numerical modeling. Ballistic experiments using armor piercing (AP) rounds were conducted on tiles of different thicknesses that were subjected to confinement pressure up to 400 MPa. The ballistic experiments were conducted using a custom-built device, designed to apply biaxial compressive stress on the tiles while permitting the direct and accurate measurement of the applied pressure. The influence of both confinement pressure and tile thickness on the ballistic efficiency (BE) of the alumina tiles was measured using the depth of penetration (DOP) method. The DOP values decreased approximately linearly with increased confinement pressure, indicating an improvement in the tiles’ BE. The damage appearance of the ceramic material following ballistic impact was observed, and differences were noted between the alumina tested at low and high prestress levels. The experimental results are compared with simulations performed using a 2-D axisymmetric Lagrangian solver of finite element commercial code (LS-DYNA software). The Johnson-Holmquist ceramic model (JH2) was used to describe the behavior of the alumina. Results of the simulations correlate well with the experimentally-observed effect of decreased DOP as prestress level is increased.

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

Advanced Materials for Energy Harvesting and Storage

Room: Coquina Salon G
Session Chairs: Eldon Case, Michigan State Univ.; Truls Norby, University of Oslo

8:00 AM

(ICACC-S6-028-2013) On synthesis, phase purity, and oxygen stoichiometry of sodium and calcium cobaltate thermoelectrics (Invited)

T. Norby*, H. Fjeld, M. Schrade, T. Finstad, University of Oslo, Norway; O. Løvvik, SINTEF, Norway; C. Simone, University of Milan, Italy

Relatively high concentrations of oxygen vacancies and effects on thermoelectric properties have been reported in the literature on state-of-the-art thermoelectric sodium cobaltates. However, first principle calculations suggest high energies and low concentrations of such vacancies. Experiments in our laboratory indicate that apparent oxygen non-stoichiometry may have stemmed from secondary phases present after decomposition in two-phase regions during synthesis and measurements. In a similar manner, experimental evaluation and defect-chemical interpretation of non-stoichiometry in calcium cobaltate thermoelectrics are troubled by non-trivial synthesis and sample fabrication. Recent results on these matters are presented and discussed.

8:30 AM

(ICACC-S6-029-2013) Spark plasma sintering of oxide thermoelectric materials (Invited)

R. Donelson*, A. Seeber, CSIRO, Australia; C. Chen, M. Kabir, UNSW, Australia

Spark plasma sintering is proving to be a viable processing route for densifying of even the most difficult to sinter materials. Rapid heating and cooling rates, and the direct heating of conductive materials, can produce a dense product in a fraction of the time required by either hot pressing or pressureless sintering. However, in the case of oxide materials the use of inert atmospheres, graphite dies and graphite spacers can result in undesirable phase changes or the formation of oxygen vacancies. Oxide thermoelectric materials, e.g. p-type layered cobaltates and n-type perovskites, are especially susceptible as evidenced by changes in their electronic and thermoelectric properties. It will be shown that in some cases deleterious effects can be mitigated or remedied, for example through the reintroduction of oxygen into the structure or by a suitable choice of sintering configuration.

9:00 AM

(ICACC-S6-030-2013) The Seebeck Coefficient of Mesoscopic Nanocrystalline SrTiO$_3$

G. Gregori*, S. Heinze, P. Lupetin, H. Habermeier, J. Maier, Max Planck Institute for Solid State Research, Germany

In this contribution, we present results of electrical conduction as well as Seebeck coefficient measurements obtained for the model material SrTiO$_3$ (nanocrystalline, microcrystalline and single crystal) in oxidizing as well as reducing conditions. The conductivity data reveal a strong change of the transport properties of the nanocrystalline sample compared with the corresponding bulk properties: a reduction of the p-type conductivity by several orders of magnitude at high oxygen partial pressure and an enhancement of the n-type conductivity by almost the same amount at low oxygen partial pressure. Similarly, the Seebeck coefficient values of the nanocrystalline sample exhibit strong deviations from the single crystal ones: Under oxidizing conditions, values up to 2.2 mV/K (at about 575°C) are detected. Remarkably, for the nanocrystalline sample the dependence of the Seebeck coefficient on the concentration of the charge carriers is found to be four times larger than in the single crystal.

9:20 AM

(ICACC-S6-031-2013) Thermal shock and thermal fatigue of thermoelectrics – strategies and trade-offs

E. D. Case*, Michigan State Univ., USA

Waste heat recovery applications generate repeated thermal transients that can in turn induce significant mechanical stresses. Many thermoelectric materials are either heavily doped semiconductor or ceramics which tend to be brittle and thus the thermomechanical fatigue imposed by cold start-ups and rapid cooling can result in damage accumulation. Various strategies (including but not limited to adding nanoparticles or nanopores) that have been applied successfully in structural ceramics to boost thermal fatigue resistance will be discussed in terms of their use in brittle thermoelectric materials. Also, for thermoelectric materials in particular, a number of trade-offs will be discussed that are presented via enhancing mechanical integrity but simultaneously impacting the thermal conductivity, electrical conductivity and Seebeck coefficient that are essential for a material to function as a thermoelectric. In addition, thermal studies by the author and co-workers as well as work from the literature will be discussed.

10:00 AM

(ICACC-S6-032-2013) Novel Flexible Thin Layer Electrochemical Components for Thermal Batteries

T. Leviatan*, S. Cohen, I. Eliel, Rafael Ltd., Israel; G. E. Shter, A. Choen, V. Beilin, G. S. Grader, Technion-Israel Institute of Technology, Israel

Thermal batteries (TB) are pyrotechnically initiated molten salt batteries, and are widely used in military and space applications. TB consists of a stack of cells; each cell is comprised of an Anode, Cathode, Electrolyte, and a Pyrotechnic pellet. Current pellet manufacturing technology for TB is by cold press. These pellets are pressed from powder to a near green state and are not sintered, thus making them very brittle and difficult to handle. This brittle state also restricts shape and size of these components. A novel approach resulted in flexible TB components. Flexible components allow easy handling, storage, and larger area pellets (with a high aspect ratio) not available using current manufacturing technology. Thin layer components, produced by tape casting method, may be as thin as 0.01 mm. TB using components manufactured by tape casting were shown to decrease battery size and cost, as thin layers allow no access of costly materials. Lower cost, weight, and size will allow TB to meet the demands brought upon by the new generation advanced high power application. Flexible components will allow TB of different shapes and larger sizes then ever seen before. This novel concept may completely revolutionize the TB industry.

10:20 AM

(ICACC-S6-033-2013) Enhancement of the Thermoelectric Performance of p-type Ca3Co4O9+δ with Spark Plasma Sintering Technology

R. Tian*, T. Zhang, S. Li, University of New South Wales, Australia; R. Donelson, CSIRO, Australia

Transition metal oxide Ca3Co4O9+δ is one of the most promising p-type thermoelectric oxides for high-temperature power-generation applications. Although the reported thermoelectric performance of Ca3Co4O9+δ single crystal is close to the current best commercial Bi2Te3, the processing of single crystal is very expensive but it provides a reference to improve its polycrystalline counterpart. It is believed that the low energy conversion efficiency of the polycrystalline Ca3Co4O9+δ is associated with the fact, which the electrical resistivity ρ (20-40m Ω cm) is about one order of magnitude higher than its single crystal (2-3 m Ω cm). In this work, the state-of-the-art Spark

Plasma Sintering technology has been used to fabricate the highly dense and textured Ca3Co4O9+δ bulk material. The results indicate that the thermoelectric figure of merit of p-type polycrystalline Ca3Co4O9+δ has been enhanced to near 0.5 at 973K.

10:40 AM

(ICACC-S6-034-2013) Processing dependent thermoelectric properties of Na0.77CoO2-Ca3Co4O9 composites

C. Chen*, T. Zhang, R. Tian, D. Chu, The University of New South Wales, Australia; R. Donelson, CSIRO, Australia; S. Li, The University of New South Wales, Australia

Thermoelectric materials have drawn great research interest for their capability of converting waste heat into electricity. Compared with conventional thermoelectric materials such as Bi2Te3 and SiGe, oxide materials have some unique advantages, such as low toxicity, low cost and high stability. Among these oxide materials, NaxCoO2 and Ca3Co4O9 are typical p-type thermoelectric materials with relatively high thermoelectric performance. The objective of the present work is to study the thermoelectric properties of Na0.77CoO2-Ca3Co4O9 composites by tuning the SPS sintering conditions. The densification, microstructure, and thermoelectric properties of the composites were investigated in terms of SPS sintering temperature and dwell time. By increasing SPS sintering temperature, the relative density was improved. Both the power factor and figure of merit were enhanced. Furthermore, the relative density can be precisely controlled by tuning dwell time. Power factor was improved with increasing dwell time, while the figure of merit was maintained.

S7: 7th International Symposium on Nanostructured Materials and Nanocomposites

Chemical Processing of Nanomaterials II

Room: Coquina Salon B
Session Chairs: Werner Mader, University of Bonn; Jordi Arbiol, ICREA and Institut de Ciencia de Materials de Barcelona, ICMAB-CSIC

8:00 AM

(ICACC-S7-030-2013) Metals and composites from solution (Invited)

G. Westin*, K. Lashagari, A. Pohl, Uppsala University, Sweden; K. Jansson, Stockholm University, Sweden

Efficient, reproducible low cost methods for synthesis of highly complex nano-materials is a requisite for practical application in many areas, such as batteries, catalysts for fuel production and energy conversion, low friction coatings for efficient transmission of mechanical energy and corrosion resistance. Solution based processing routes allowing for multi-phase, multi-elemental nano-materials in one or few steps are probably the best suited for achieving this. Here we describe two low cost solution based synthesis routes: (i) Metal-in-ceramic nano-composites with metal inclusions of; Co, Ni, Cu, Ru, Ag, Pd, Pt...) and matrixes of aluminum-, iron- or lanthanide-oxide. Metal nano particle sizes could be tailored down to below 5 nm and loadings up to 80+ % could be achieved in films and porous structures. Up-scaling for record efficient solar thermal absorbers by roll-to-roll deposition of composite multi-layers will be described, as well as properties for methane activation for dry reforming and magnetic properties. (ii) Highly flexible routes to nano-crystalline metals were developed yielding Co, Ni, Cu and other metals and alloys, as well as metal-metal nano-composites. The materials could be deposited as thin films and coatings or as porous sponges of nano-crystalline metal. Industrial application of the route led to superior harness and toughness.

8:30 AM

(ICACC-S7-031-2013) Precursor dependent morphology of hydrothermal SrTiO3 nanostructures. Evidence for different crystallization pathways (Invited)

V. Buscaglia*, M. Buscaglia, National Research Council, Italy; V. Kalyani, University of Genoa, Italy; A. Ianculescu, B. Vasile, Polytechnics University of Bucharest, Romania; P. Nanni, University of Genoa, Italy

Strontium titanate nanoparticles and nanostructures can be prepared by hydrothermal synthesis and related methods over a broad temperature range using a variety of precursors. Size and shape of the final particles are strongly dependent on temperature, solution concentration and nature of precursor. In this contribution, the results of a systematic investigation on the morphology and substructure of hydrothermal SrTiO3 particles obtained from eight different titania and titanate precursors are presented. Morphology and crystallographic order of the final product are largely determined by the nature of the solid precursor and different crystallization pathways have been identified. The transformation of anatase nws and, at least partially, of sodium titanate nws occurs through a topochemical reaction with formation of SrTiO3 mesocrystals which retain the precursor morphology. In contrast, hydrothermal reaction of rutile and hydrogen titanate nws does not involve a topochemical transformation and the precursor morphology is not preserved. The crystallization of SrTiO3 from titania gels follows a non classical pathway and occurs by the ordered aggregation of nanocrystals in mesocrystals. A detailed understanding of the crystallization mechanisms is essential for the synthesis of perovskite nanostructures with desired size, morphology and crystallographic order.

9:00 AM

(ICACC-S7-032-2013) Nanoscale Oxides for Photocatalytic Appplications (Invited)

G. R. Patzke*, University of Zurich, Switzerland

Oxide nanomaterials are versatile tools for sustainable photocatalytic processes, such as wastewater cleaning or water splitting, so that their structural and morphological fine-tuning is an essential task. We thus aim for the controlled synthesis of nanostructured oxide photocatalysts with abundant and non-toxic components. Concerning water treatment, we develop bismuth-containing catalysts via straightforward hydrothermal protocols. The interplay of doping and morphology control was systematically studied for bismuth vanadate-based photocatalysts. Nanoscale BiVO4 catalysts were optimized through adjustment of hydrothermal parameters, especially pH value. New BiVO4@SnO2 and BiVO4@TiO2 heterojunctions were synthesized, and their performance in the degradation of model dyes was compared. Our current investigations on water oxidation catalysts have brought forward Co/Mn-containing gallium oxide spinels as an interesting new catalyst type. Microwave-hydrothermal synthesis affords catalyst particles in the 15 - 40 nm range from Co-, Mn-, and Ga-nitrate solutions in a single step. The activity of mixed Co-Mn-Ga spinels in visible-light-driven water oxidation is superior to their binary analogues. This "synergistic" interaction of Co and Mn in the spinel matrix was tracked with a variety of analytical methods and gives rise to further investigations into this promising combination of low-cost catalyst components.

Nanotubes, Nanorods, Nanowires and Other One-dimensional Structures

Room: Coquina Salon B
Session Chairs: Greta Patzke, University of Zurich; Vincenzo Buscaglia, IENI-CNR

9:50 AM

(ICACC-S7-034-2013) VLS Growth Mechanism of ZnO Nanowires (Invited)

W. Mader*, H. Simon, T. Krekeler, G. Schaan, University of Bonn, Germany

The widely applied metal-catalyzed vapor liquid solid (VLS) growth mechanism of ZnO nanowires (NWs) is investigated by advanced methods of TEM and is discussed with respect to thermodynamic growth conditions. Au catalyst particles do not contain Zn proving a solid Au catalyst at 900°C growth temperature. This result is owed to the high equilibrium Zn partial pressure over Au-Zn alloys which in turn leads to a very low sticking coefficient of Zn from vapor and prevents alloying. Growth rates of ZnO NWs were measured as function of oxygen partial pressure. Enhanced growth at higher oxygen partial pressures is due to an increased sticking coefficient of Zn atoms at the Au catalyst. A growth mechanism is proposed which is quite different from classic VLS growth: Zn alloys only in a thin surface layer or at the surface of the catalyst and diffuses to the vapor-catalyst-NW triple phase line. There, together with oxygen, ZnO ledges nucleate which laterally grow to inner regions of the incoherent ZnO-Au interface where Zn and oxygen can diffuse and finally promote NW growth in a rather kinetically controlled process. The geometry of the ZnO-Au interface, planar or stepped, and the diffusional transport property is determined by the orientation between Au and ZnO and hence by the atomic structure of the interface. This ledge growth mode is concluded to be valid for any system where one component of the NW is not soluble in the catalyst.

10:20 AM

(ICACC-S7-035-2013) Precursor decomposition pathways during chemical vapor deposition of metal oxide nano-structures (Invited)

T. Fischer*, I. Giebelhaus, S. Mathur, University of Cologne, Germany

Metal oxide nanostructures like nanowires or nanostructured films are important building blocks for new device concepts in the field of sensors, energy harvesting and energy storage. Especially their intrinsic chemical and physical properties originating in the large surface to volume ratios open the door to more efficient and versatile device architectures. The key starting point in the controlled and reproducible synthesis of these nanostructures are well characterized precursors whose decomposition pathways to the respective metal oxide is the determining step in obtaining defined nanostructures. This talk will outline different precursor families and their decomposition via the chemical vapor deposition (CVD) method yielding tin (SnO_2) and iron oxides (Fe_2O_3, Fe_3O_4) nanostructures for gas sensing applications. The in-situ analysis of the nanostructure growth as well as the resulting by-products via spectroscopic and electrical measurements will be presented.

10:40 AM

(ICACC-S7-036-2013) Fabrication of heterostructured ZnO nanowires and their applications in quantum dot sensitized solar cells (Invited)

K. Yong*, POSTECH, Republic of Korea

A high density and well-aligned ZnO nanowires array has been synthesized using a low temperature ammonia solution reaction. Based on these nanowires, various heterostructure nanowires have been fabricated through solution reaction route, including CdS/ZnO, CdSe/ZnO and CdSe/CdS/ZnO nanowires. The morphology and optical properties of heterostructures have been studied and optimized. One of important applications of heterostructure ZnO nanowires is photoanode in solar cells, especially quantum dot sensitized solar cells (QDSSCs). We have fabricated QDSSCs using various heterostructured ZnO nanowires as photoanodes and investigated solar cell performances. We have found CdSe/CdS/ZnO nanowires showed best performances as solar cell photoanode due to their type-II, cascade band structure. This ideal band structure enables efficient charge seperation and transport. Also the CdSe/CdS/ZnO NWs enhnces light harbesting in visible solar light.

11:10 AM

(ICACC-S7-037-2013) Visualization of light atoms (O and N) in semiconductor NWs: direct way to determine the polarity in 1D nanostructures (Invited)

J. Arbiol*, M. de la Mata, R. Zamani, ICREA and Institut de Ciencia de Materials de Barcelona, ICMAB-CSIC, Spain; J. R. Morante, Catalonia Institute for Energy Research, IREC, Spain

The formation of atomic pairs, so called dumbbells, with opposite partial charge due to the chemical bonding ionicity (polarity) within a semiconductor material has huge impact in many physical properties. Polarity influences the growth mechanism driving the formation of different architectures, and it is strongly correlated with the electronic properties. In this context, the recently developed Annular Bright Field (ABF) Scanning Transmission Electron Microscopy (STEM) is unique for the direct dumbbell visualization and hence, direct polarity assignment at atomic scale, even when light elements (O and N) are implied. We demonstrate that mapping of light elements at the atomic scale allows the study of new phenomena in materials science that were impossible to be resolved with such a resolution until now. Here we define a new guideline for the direct atomic resolution polarity determination of semiconductor nanowires (NWs) from binary compounds in the case where one of the atoms is extremely light (e.g. ZnO). The proposed experimental via opens new routes for the fine characterization of nanostructures, e.g. in electronic and optoelectronic fields, where the polarity is crucial for the understanding of their physical properties as well as their growth mechanisms.

11:40 AM

(ICACC-S7-038-2013) Nafen: Novel Nanomaterial With Industrial Production Capabilities

M. Kutuzov*, ANF Development, Estonia

A new ceramic nanomaterial is presented, branded as Nafen™. Nafen™ is aluminium oxide nanofibers produced from liquid melt. The fibers are synthesized in mats, coaligned. The aluminium oxide is in gamma and chi phases. Depending on process parameters, mean diameters from 7 to 40 nm are available. Fibers as long as 15 cm can be produced. Average mat density ranges from 0.1 to 0.4 g per cubic cm. The fibers can be easily dispersed in water and alcohols. Fibrous structure is maintained when heating up to 1200-1400C, after which fibers recrystallize into alpha phase. Results of various measurements of crystalline and surfacial structure will be reported, including electron microscopy, thermogravimetric analysis, X-ray diffraction and more. Possible areas of application have already been identified: high-temperature insulation, metal and ceramic matrix composites, grain modification, ultra- and nanofiltration, catalysis, and more. Prototypes of membranes with cut-off particle size below 5 nm have already been demonstrated. The unprecedented production volume of 0.5 kg per hour on small-size pilot reactor supports huge market potential for this material.

S8: 7th International Symposium on Advanced Processing and Manufacturing Technologies for Structural and Multifunctional Materials and Systems (APMT)

SPS and SHS

Room: Coquina Salon A
Session Chairs: Eugene Olevsky, San Diego State University; Hisayuki Suematsu, Nagaoka University of Technology

8:00 AM

(ICACC-S8-030-2013) Spark-Plasma Sintering (SPS) and High Voltage Electrical Discharge Consolidation (HVEDC): Fundamental Aspects and Scalability (Invited)

E. Olevsky*, San Diego State University, USA; E. Grigoryev, Moscow Engineering Physics University, Russian Federation

SPS includes conjoint application of fast heating rates, axial pressure and DC-pulsed low voltage - high amperage current assisted sintering. HVEDC includes axial pressure and nearly instantaneous discharge of the energy stored in capacitors. It is shown that for both SPS and HVEDC there is an upper level for the local Joule heating of the inter-particle contacts beyond which the processing instability occurs. For HVEDC, the duration of the pulse is a controlling parameter; SPS apparently can be controlled by pulse on and off frequency. The underlying physics phenomena are the source of the specifics of SPS and HVEDC scalability. A comprehensive finite element model is applied to the simulation of SPS with four different tooling sizes. Parallel SPS scalability experiments on the four similarly shaped alumina specimens are conducted. The modeling-experiment comparison shows that heating rate is a critical parameter for SPS scalability. The scalability of HVEDC is related to the skin-layer dimensions, which become prohibitive for the uniformity of the heating pattern for the larger specimens. Mutually off-setting impacts of the magnetic field pinch effect and the temperature non-uniformity caused by the presence of the skin layer are demonstrated. It is shown that the pulse duration is a critical parameter for the scalability of the HVEDC process.

8:30 AM

(ICACC-S8-031-2013) Combustion Synthesis (SHS) of Complex Ceramic Materials (Invited)

J. Lis*, AGH University of Science and Technology, Poland

A progress in materials prepared using Combustion Synthesis also called Self-Propagating High-Temperature Synthesis SHS from basic research to applications is discussed. The review of different forms of complex ceramic materials prepared directly by SHS or by SHS-origin precursors is presented. Powders are usually the starting material for manufacturing of ceramic and a lot of attention has been paid to find new routes for synthesis powders in form of nano or micro particles. The present work is aimed at efficient and convenient powder processing by SHS as an important target for materials technology. The use of SHS may bring a considerable development in ceramic technology, by enabling a manufacturing of sinterable, high-purity nano or micro powders. It can be demonstrated in different ceramic systems explored by the authors and co-workers using SHS e.g. (a) Si-C-N, (b) Ti-Si-C-N and Ti-Al-C-N (MAX Phases) as well as (c) Al-O-N. Rapid combustion conditions were successfully used to manufacturing complex ceramic powders and nanopowders suitable for preparing multiphase complex materials. It has been concluded, that the SHS technique has brought a contribution to the ceramic processing and may be considered as perspective e approach for materials engineering.

9:00 AM

(ICACC-S8-032-2013) Spark Plasma Sintering of UO2: An investigation of densification and microstructure evolution

L. Ge*, G. Subhash, R. H. Baney, J. S. Tulenko, University of Florida, USA

A systematic study is conducted to investigate the densification behavior and microstructure evolution in spark plasma sintered UO2 by varying sintering parameters such as maximum sintering temperature, hold time and heating rate. The microstructure evolution was characterized by measuring the grain size distribution on the cross section of the sample. The results revealed that the major densification range for sintering of UO2 in SPS is between 720oC to 1000oC and 96% theoretical density was achieved at 1050oC with total run duration for only 10 minutes. The hold time (from 30 seconds to 20 minutes) has more significant influence compared to heating rate (which was varied from 50oC/min to 200oC/min) on the grain growth and grain size variation throughout the pellets. The Vickers hardness, Young's modulus and thermal conductivities of the resultant pellets were also measured and these values showed a good agreement with the reference value reported in the literature.

9:20 AM

(ICACC-S8-033-2013) Spark Plasma Sintering Induced Grain Refining in Al2O3 Ceramics

J. Liu*, L. An, University of Central Florida, USA; F. Yang, University of Kentucky, USA

In this paper, we report that nanostructured Al2O3 ceramics can be made from micrometer-sized starting powders using an electrical field-activated sintering process. Two kinds of powders with different particle sizes (1μm & 3μm) were used as the starting materials. We found that the starting particles were "shattered" into nanosized grains during sintering. The effect of particle size and processing parameters on the density and microstructure of the sintered specimens were investigated. We attributed the significant microstructural refining to a pulsed electric field induced thermo-mechanical fatigue process. A simple model has been developed to account for such effect.

Novel Sintering Technologies

Room: Coquina Salon A
Session Chairs: Eugene Olevsky, San Diego State University;
Hisayuki Suematsu, Nagaoka University of Technology

10:00 AM

(ICACC-S8-034-2013) High voltage flash sintering in cubic zirconia

J. A. Downs*, V. M. Sglavo, University of Trento, Italy

The dramatic reduction in sintering temperature in the flash sintering behavior of yttria stabilized zirconia (8YSZ) has only been measured for modest fields less than 150 V/cm. Here, the reduction of the temperature at the onset of flash sintering is observed for fields up to 2500 V/cm. DC E-fields up to 2500 V/cm were applied to dog bone samples of 8YSZ produced by uniaxial pressing during heating at a rate of 10°C/min. The electrical behavior was measured by using a two-probe method and the shrinkage was measured by image analysis. The increase in field strength shows a non-linear reduction in the onset temperature of flash sintering to as low as 400°C for fields of 2500 V/cm. At field strengths higher than 250 V/cm, sintering is incomplete due to the current limit of the power supply. The switch to current control limits the power dissipation spike, and therefore the total energy that can be dissipated in the sample. Observations also show that the electrical circuit through the sample is completed through the axis of the sample and not evenly over the cross-section, this leading to radial density gradients. Thus, flash sintering can occur as low as 400°C at 2500 V/cm but the limitations of the power supply and a non-uniformity of the current density prevent the sample from reaching full density.

10:20 AM

(ICACC-S8-035-2013) Flash Sintering of Electroceramic Devices (Invited)

B. Vaidhyanathan*, Loughborough University, United Kingdom

Electroceramic devices such as varistors and capacitors are used in most of the modern day electronic appliances and constitute a multi-billion $ global market. In a recent report on 'Flash sintering' (FS) it was demonstrated that full sintering of zirconia ceramics can be achieved at 850oC in just few seconds rather than the 1450oC for few hours that is normally used by conventional techniques. This opens up the possibility of achieving significant energy savings during manufacture and the ability to produce fine grained ceramics with superior properties. However the exact mechanisms by which this phenomena occur is not yet clear and the methodology is untested for the sintering of other complex material systems. The present work investigated the possibility of flash sintering electroceramic devices such as nanocrystalline ZnO varistors and Barium Titanate capacitors for the first time using a custom built equipment at Loughborough University, UK.

10:40 AM

(ICACC-S8-036-2013) Development of Pulsed Wire Discharge Apparatus to Produce Metal Nanosized Powders

H. Suematsu*, S. Ishihara, T. Suzuki, T. Nakayama, K. Niihara, Nagaoka University of Technology, Japan

Base metal nanosized powders have been required in many applications including conductive pastes for substitution of expensive noble metal nanosized powders. On the other hand, it was difficult to suppress the oxidation because of the high surface energy. Pulsed wire discharge (PWD), which evaporates a thin metal wire by a large pulsed current and condenses the metal vapor by ambient gas and organic fume/vapor, had been found to be a good method to prepare organic matter coated metal nanosized powders1). In this study, a PWD apparatus was developed for massproduction of metal nanosized powders. Capacitors and a gap switched were designed to synchronize with a wire feeding unit. A large current power source was developed to charge the capacitors within 100 ms. By controlling the wire feeding, capacitor charging and current triggering, repetitive motion of the PWD apparatus was carried out. After some test runs, a production rate of 484 g/h at a repetition rate of 4 Hz was obtained. 1) Y. Tokoi, et al., Scripta Matererialia, 63 (2010) 937.

11:00 AM

(ICACC-S8-037-2013) Fabrication of anisotropic nanostructured materials using the atmospheric non-equilibrium plasma

T. Nakayama*, S. Endo, A. Tokuchi, W. Jiang, H. Suematsu, T. Suzuki, K. Niihara, Nagaoka Univ of Tech, Japan

The fabrication of silver compounds made from silver acetylacetonato metal-organic complex as a starting material has been achieved by using the nanosecond pulsed power supply. By using the nanosecond pulsed power supply, it is possible to obtain the plasma which consists of the streamer electric discharge. In the case of this plasma, the temperature of the electron is higher than that of the ion or nutral particle. The coaxially-cylindrical electrode was connected to the pulsed power supply. Silver acetylacetonate powder was placed on the inside of the electrode. Repetition frequency of the nanosecond pulsed power supply was set to 40Hz. The electric discharge was done in 30 min under atmospheric pressure. After discharge, the powder on the electrode ware recovered. The shape of the particles was observed by SEM. Then the particles were analyzed by X-ray diffraction for phase identification. From the results of X-ray diffraction pattern, fabrication of silver conpounds such as silver nitrate and silver acetate were comfirmed.

11:20 AM

(ICACC-S8-038-2013) Development of Transparent Ceramics by Laser Fusing

F. Hmood*, C. Oelgardt, G. Reinhard, J. G. Heinrich, Clausthal University of Technology, Germany

The development of transparent ceramics has been an interesting research area in the last years. The conventional way to produce transparent ceramics is the sintering process followed by hot isostatic pressing (HIP). Another possibility is rapid quenching of a ceramic melt to an amorphous state followed by controlled crystallization to achieve glass-ceramics. In this project a 5kW CO2 laser has been used to produce transparent microspheres from a eutectic composition in the system Al2O3-Y2O3-ZrO2 (AYZ) and lead-free piezoceramic from K1-xNaxNbO3 (KNN) by laser fusing. A yield of 85% amorphous amount was achieved in the AYZ system and 68.5% transparent fraction in the KNN system. The median particle size of the resulting microspheres was around 85μm and 62.5μm respectively. DSC analysis has been used to determine the glass transition and crystallization temperatures. Considering these results transparent microspheres have been annealed at different temperatures to investigate the crystallization behavior. The influence of the laser power and the selected ceramic systems on the transparent fraction of microspheres and their crystallization behavior will be discussed. Increasing the transparent fraction of laser fused microspheres, manufacturing of transparent samples by isostatic pressing and sintering and the determination of properties will be future topics of interest.

11:40 AM

(ICACC-S8-039-2013) Additive Manufacturing: Lasers Interacting with Ceramic Powders

T. Mühler*, J. Heinrich, TU Clausthal, Germany; J. Günster, BAM - Federal Institute for Materials Research and Testing, Germany

For selective laser sintering of ceramic powders a clear understanding of the coupling between laser light and ceramic powder is mandatory. For applications ideally the laser energy is equally distributed in a certain volume of the powder to initiate sintering. In a systematic study the interaction of the light emitted by a fiber laser with ceramic powders has been investigated. A major concern of this study is the particle size dependent coupling between the energy provided by the laser source and the powder. As a model material amorphous silica has been chosen. Silica is transparent for the light emitted by the employed laser system with a wavelength of about 1 μm. Powder compacts prepared with particle sizes significantly larger than the wavelengths do reflect almost 100% of the laser light, even though the individual particles are transparent. Thus, the laser light does not couple to such powder compacts and no energy is transferred into the powder volume. For particle sizes <<1μm the powder compact becomes gradually transparent, due to the lack in scatter centers. The coupling as a function of the particle size, ranging from <<1μm to>>1μm, is discussed. For SLS, ideally the light penetrates into the powder compact, should be absorbed in the volume and initiate local sintering. We will provide a first data base for optimizing the coupling between laser light and ceramic powders by tuning their particle size.

S9: Porous Ceramics: Novel Developments and Applications

Applications of Porous Ceramics I

Room: Coquina Salon C
Session Chair: James Zimmermann, Corning

8:00 AM

(ICACC-S9-031-2013) Pt coated porous SiC foams for catalytical hydrogen combustion (Invited)

U. F. Vogt*, B. Fumey, M. Bielmann, A. Zuettel, Empa, Switzerland

A catalytic H2 diffusion burner based on porous ceramics with Pt coating has been developed for SELF, a self-sufficient living unit. For this purpose, a highly porous SiC ceramics is used for the combustion region due to their excellent high temperature- and thermal shock resistance. Based on the catalytic active Pt coating, covering the porous SiC ceramics, no ignition process is required even at low room temperatures. While hydrogen is fed from below the porous catalytic SiC ceramics, air is fed separately from the top and the catalytic combustion process will occur only inside the catalytic SiC structure without an open flame. As the combustion of hydrogen release no exhaust gases like CO or CO2 and due to the low combustion temperature no NOx, catalytic hydrogen burners can be used safely indoors without ventilation systems. Due to the self-igniting property and the feature, that hydrogen and air are strictly separated and concur only at the catalytic active region, a very high passive safety standard is assured. Owing to the absence of hydrocarbons, no harmful exhaust gases will be emitted and thus a decisive safety benefit of the system is given.

8:30 AM

(ICACC-S9-032-2013) Heterogeneous hetoroporous ceramics

A. Ortona*, C. D'angelo, SUPSI, Switzerland; V. Liedtke, Aerospace & Advanced Composites, Austria; C. Wilhelmi, EADS Innovation Works, Germany; D. Gaia, Erbicol, Switzerland; C. Badini, Politecnico di Torino, Italy; W. Fischer, Astrium, Germany

Ceramic foams are widely used in many high temperature fields including thermal insulation. Due to the high fraction of voids, radiation heat transfer becomes predominant at high temperatures reducing their insulation capability. This work, presents a novel approach in order to reduce the internal radiation heat transfer of reticulated ceramics. By filling the voids with a ceramic fibrous phase we obtained a thermally and mechanically stable system under severe high thermal loading. The process, based on the forced sedimentation concept, leads to completely filled samples with high internal homogeneity. Static and cyclic thermal tests confirmed the performance increase showing the potential of this method in the thermal protection systems of spacecrafts.

8:50 AM

(ICACC-S9-033-2013) Dead-end silicon carbide micro-filters for liquid filtration

R. Neufert, M. Moeller, A. Bakshi*, Saint-Gobain, USA

A new type of silicon carbide dead-end filter element has been developed. It consists of a honeycomb carrier structure made from silicon carbide powder. The carrier structure has an average pore size of ~4 μm. The pore size is further controlled by depositing multi-layer membranes made from ultra-fine silicon carbide powders on the inner honey comb surface. The filter has several advantages over traditional filters. The operating costs of the new filters are lower due to reduced energy and water consumption. The silicon carbide filters are chemically very stable. They can operate at pH 1-14 at 80°C without affecting the filter membrane. This helps eliminate fouling. Due to compact size, the filter uses a very small foot print compared to conventional filters. Recently, the filter was used in a commercial swimming pool, with a throughput of 75m3/hr. The filters used in this case had an effective pore size of 200nm. Each filter consisted of several 147mmX147mmX1000mm elements which have a surface area of 10m2. It has demonstrated to be able to filter all relevant species of bacteria from the swimming pool water. The compact, durable, chemically inert filter can be used in many other applications such as oil and gas fields, mining industry, industrial waste, etc.

9:10 AM

(ICACC-S9-034-2013) Perovskite Catalysts Enhanced Combustion on Porous Media

M. D. Robayo*, N. Orlovskaya, R. Chen, University of Central Florida, USA

The effects of different catalysts on matrix stabilized combustion in porous ceramic media were explored in order to enhance the combustion abilities of low-calorific value fuels of porous burners with perovskite catalysts. Highly porous silicon carbide ceramics were used as porous media for catalytically enhanced matrix stabilized combustion of a lean mixture of methane and air. The flammability limits of the combustion of methane and air were tested using both inert and catalytically enhanced surfaces of the porous ceramic media. The combustion chamber was designed using a steel casing that incorporated a quartz window allowing for direct acquisition of temperature measurements in the combustion zone. Catalytic enhancement of SiC porous matrix with Ba0.5Sr0.5CO0.8Fe0.2O3, La0.75Sr0.25Fe0.6Cr0.4Oxide, La0.75Sr0.25Fe0.6Cr0.35Ru0.5, La0.75Sr0.25Fe0.5Oxide and other compounds were done to facilitate combustion and increase the temperature in the combustion zone. The minimum equivalence ratio in stable combustion achieved with an inert sample of SiC cores was between 0.56 and 0.55, while the catalytically enhanced SiC cores were able to maintain a minimum stable equivalence ratio between 0.55 and 0.52. Enhancement of a SiC porous burner with perovskite catalyst was able to reduce the minimum measured stable equivalence ratio, which is of great interest in applications such as NOx reduction.

Applications of Porous Ceramics II

Room: Coquina Salon C
Session Chair: James Zimmermann, Corning

9:50 AM

(ICACC-S9-035-2013) Developement of new silica foam for thermal insulation

E. Prud'homme*, P. Michaud, GEMH-ENSCI, France; E. Joussein, GRESE, France; S. Rossignol, GEMH-ENSCI, France

Nowadays, building area is subject to increasing standards and environmental constraints, requiring the development and the use of new products, such as geopolymer material. Previous works have already shown the possibility to obtain porous material based on geopolymer synthesis. This kind of material displays interesting properties in terms of thermal insulation, with a thermal conductivity of 0.14 W/m/K. This study proposed here the development of new silica foam based on geopolymer process too with thermal conductivity twice as low. The synthesis of foam is realized by the alkali activation of industrial by-product, which presents the particularity to contain a small amount of free silicon. It leads to the formation of hydrogen gas, involving porosity in the silicate material. In order to increase material performances, porosity is controlled by various drying time and temperature. Final material is characterized in terms of microstructure, porosity repartition, thermal conductivity and mechanical properties, using respectively SEM observations, image analysis, hot disk technique and Brazilian tests. An optimum was stated for drying process. The final material present very interesting insulating properties around 0.07 W/m/K and mechanical properties such that it can be consider for use in building area.

10:10 AM

(ICACC-S9-036-2013) Si-SiC heat exchangers with highly structured surface elements for recuperative gas burners

A. Ortona*, SUPSI, Switzerland; S. Gianella, Erbicol, Switzerland; D. Trimis, V. Uhlig, R. Eder, TU Bergakademie Freiberg, Germany; E. Boulet, C. Chazelas, Institut Français du textile et de l'habillement, France; T. Grämer, NOXMAT, Germany; G. D'Amico, P. Fino, Politecnico di Torino, Italy; E. Cresci, J. G. Wünning, WS Wärmeprozesstechnik, Germany; H. Altena, Aichelin, Austria; F. Beneke, M. Debier, European Committee of Industrial Furnace and Heating Equipment Associations CECOF, Belgium

Heat recovery from waste gas is a major key process for increasing efficiency of thermal processes. The aim of the present work is to increase the overall heat transfer of ceramic heat exchangers applied on recuperative burners. This was achieved using highly structured surface elements obtained converting into SiC a textile perform laid on an existing commercial gas tight Si-SiC tube. Textile production and ceramization were modified starting from well established industrial techniques. Geometries were first optimized via CFD studies in order to maximize heat exchange an reduce pressure losses. Then ad-hoc textiles were produced, impregnated with a slurry, laid Si-SiC plates and silicon infiltrated. Product quality was appraised trough samples characterization. Finally real burner prototypes were manufactured and tested in standard working conditions .

10:30 AM

(ICACC-S9-037-2013) The Influence of Calcination and Milling on Microstructure and Colloidal Properties of 8 YSZ Used in Ceramic Fuel Cells

A. R. Hanifi, A. Torabi*, T. H. Etsell, University of Alberta, Canada; P. Sarkar, Alberta Innovates - Technology Futures, Canada

In this research YSZ porous supports are fabricated via slip casting and coated with a dense electrolyte using either slip casting or dip coating methods for the newly developed third generation of tubular fuel cells. Analyzing YSZ powder after calcination and subsequent milling can help develop the dense and porous microstructures. For this purpose, as received and calcined Tosoh YSZ (ZrO2 stabilised with 8 mol% Y2O3) were milled in water and characterized by SEM, TEM, XRD, light-scattering particle size, BET, zeta potential and acid-base titration. YSZ crystals and particles were found to enlarge with increasing calcination temperature as expected, and shrink during milling. Calcination-milling leads to formation of particles with higher surface charge and shifts the isoelectric point (IEP) towards lower pH values. YSZ suspensions show a high viscosity and larger agglomerates at basic pHs which lead to significant porosity formation. This is despite the high zeta potential of the suspension and is attributed to increased hydrogen bonding which causes strong particle agglomeration. While acidic YSZ slips are suitable for slip casting, the basic YSZ slips are potential compositions for gel casting. Acid-base titration results indicate a direct relationship between powder surface area and the amount of acid/base used for pH adjustment.

10:50 AM

(ICACC-S9-038-2013) Development of alkali-resistant controlled pore glass based on (65–x) SiO_2-25B_2O_3-10 Na_2O-xZrO_2/ $ZrSiO_4$ system

M. Hasanuzzaman*, A. G. Olabi, Dublin City University, Ireland

Controlled pore glass (CPG) has been developed using system (65–x) SiO_2-25B_2O_3-10 Na_2O-xZrO_2/ $ZrSiO_4$. Such glass has an interconnected pore structure with a uniform pore distribution. ZrO_2/ $ZrSiO_4$ was added to the sodium-boro-silicate system which is believed to increase the alkali resistance of the porous glass by 8-10 times. The effect and retention of the ZrO_2 in final glass was also studies. Alkali resistance test was performed to verify the improved alkali-resistant property of the produced glass. A detailed thermal analysis was carried out initially for each sample to identify the glass transition temperature (Tg) and crystallization temperature (Tx); bases on which heat-treatment temperature was determined. The used heat-treatment time and temperature led to two-phases — one silica rich phase and other alkali-rich borate phase. Porous glass with interconnected microstructure of silica-rich skeleton was observed after using proper leaching method. The size and shape of the pores largely depend on the time set for heat-treatment. Further studies on pore structure were carried out using Porosimeter and Scanning Electron Microscope (SEM). X-ray Diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy were used to explore the crystallization behaviour of the heat treated glasses.

11:10 AM

(ICACC-S9-039-2013) Preparation of Spherical Shaped Mullite Powders and Microstructural Evaluation During Sintering

C. Ozgur*, R. Gören, Dumlupinar University, Turkey

The objective of this study is to present in detail the preparation of spherical shaped mullite powders by ultrasonic spray pyrolysis technique and to investigate the microstructural evaluation of particles during sintering. According to experimental results, it is possible to obtain single phase mullite powder at a temperature of 1000oC without any soaking. Besides amorphous mullite powder has been achieved by calcination of the obtained ultra-homogeneous mullite precursor at a temperature of as low as 500oC for 15 days in which the temperature was very close to the formation temperature of mullite (477oC) is energetically possible. Porous materials were obtained by sintering of the pressed mullite powders at different temperatures (1500, 1550, 1600 and 1650oC) with a soaking time of 5 hours. The SEM images showed that the particle shape is changed via the sintering temperatures of the bulk ceramic. For low temperature sintering, the particles still quite spherical where they tend to form rod like structure with increasing the sintering temperature.

S10: Virtual Materials (Computational) Design and Ceramic Genome

Modeling of Defects and Diffusion in Ceramics

Room: Oceanview

Session Chairs: Jingyang Wang, Institute of Metal Research, Chinese Academy of Sciences; Brian Good, NASA Glenn Research Center

8:00 AM

(ICACC-S10-019-2013) Irradiation Effects in Fluorite-Structured Oxides (Invited)

Y. Zhang*, Oak Ridge National Laboratory, USA; H. Xiao, University of Tennessee, USA; P. Edmondson, Oak Ridge National Laboratory, USA; T. Varga, Pacific Northwest National Laboratory, USA; F. Namavar, University of Nebraska Medical Center, USA; W. J. Weber, Oak Ridge National Laboratory, USA

Nanostructured materials provide the opportunity for tailoring physical, electronic, and optical properties of ceramics for a variety of technological applications, including improved radiation resistance in advanced nuclear energy systems. Irradiation studies in nanocrystalline CeO2 and ZrO2 have been performed up to 108 dpa over a range of temperatures. Faster irradiation-induced grain growth in CeO2 is observed with increasing temperature, while slower grain growth is observed in ZrO2 with more complex temperature dependence. The grain growth is attributed to a defect-stimulated growth mechanism that occurs at the grain boundaries. Low energy recoil events and diffusion of fission products (Br, Rb, Cs and Xe) have been investigated using density functional theory and ab initio molecular dynamics simulations. Threshold displacement energies in ThO2, CeO2 and ZrO2 show directional dependence, and damage end states mainly consist of vacancies and interstitials. Fission products incorporated in cation mono-vacancies, cation–anion di-vacancies and Schottky defects are found to be stable, with the cation mono-vacancy being the preferred site in most cases. The energy barriers for migration of each species suggest that alkali metals are relatively more mobile than other fission products, and Br is the least mobile.

8:30 AM

(ICACC-S10-020-2013) Conductive path formation in insulating oxide using dislocations and interfaces (Invited)

A. Nakamura*, K. Matsunaga, Nagoya University, Japan; T. Mizoguchi, University of Tokyo, Japan; E. Tochigi, Lawrence Berkeley National Laboratory, USA; N. Shibata, Y. Ikuhara, University of Tokyo, Japan

Techniques based on crystal dislocations are promising for the creation of nanowires. A crystal dislocation creates a one-dimensional, sub-nanometer-scale lattice discontinuity. The lattice discontinuity then induces the presence of a strain field surrounding the crystal dislocation and of dangling bonds at regular intervals along the lattice discontinuity, modifying the local stoichiometry. Moreover, the core of the dislocation interacts with solute atoms so as to accommodate its excess elastic energies and dangling bonds. As a result, solute atoms in a crystal tend to segregate to a dislocation, forming a so-called Cottrell atmosphere. Therefore, by creating a Cottrell atmosphere, we can convert a dislocation into a one-dimensional nanometer-scale structure with unusual functional properties. In the presentation, I would like to show a method for converting a dislocation into nanowire and a method for fabricating periodical nanowires using low angle grain boundaries. Significantly, we were able to precisely control nanowire periodicity by the choice of crystal orientation and/or crystal planes at low angle grain boundary.

9:00 AM

(ICACC-S10-022-2013) Particle Swarm Optimization for Modeling Defect Regions in Crystalline Systems

N. A. Dari*, P. M. Rulis, University of Missouri-Kansas City, USA

The purpose of this study is to explore the use of the particle swarm optimization (PSO) technique for creating accurate models of the nano-scale extended defects that are ubiquitous in most ceramic systems. Specific modifications to a standard PSO method were adopted to fit the needs of exploring a non-convex energy landscape with multiple acceptable minima. In particular (1) a particle's fitness relative to the globally most-fit particle in the swarm in that iteration was used as the key parameter to determine the particle's acceleration and (2) a probabilistic approach to target selection was defined. These modifications help the swarm more thoroughly sample configuration space with minimal extra cost to the convergence rate while also improving the convergence value when applied to the standard test functions. Preliminary tests of this fitness driven PSO method on a passive defect model in silicon and a low angle grain boundary in SrTiO3 show significant promise but also present significant obstacles.

9:20 AM

(ICACC-S10-023-2013) Materials Thermodynamics and Phase Modeling in Lithium Ion Battery Systems (Invited)

H. J. Seifert*, M. Lepple, D. M. Cupid, P. Franke, Karlsruhe Institute of Technology, Germany

Thermodynamic modeling and calculations using CALPHAD methods (Computer coupling of phase diagrams and thermochemistry) support the understanding and development of advanced lithium ion batteries. Calculations applying thermodynamic descriptions of multicomponent systems can be used to predict reversible open circuit voltages of electrochemical cells produced from battery active materials. Experimentally determined phase diagrams and thermochemical data such as enthalpies of formation, heat capacities and chemical potentials are key input data for the development of analytical descriptions for the Gibbs free energies of all system phases. Based on these descriptions, multicomponent multiphase calculations for different thermodynamic conditions can be performed. Examples for modeling and calculations will be presented for intercalation- and conversion-type systems, respectively. New results for the Li-Mn-O system and transition metal oxide systems are presented and compared to experimental electrochemical results.

10:10 AM

(ICACC-S10-024-2013) Lithium ion diffusion in fast ion conducting lithium lanthanum titanate ceramics (Invited)

J. Du*, University of North Texas, USA

Solid state lithium batteries are important in the development of next generation safer and high power density lithium ion batteries. The perovskite structured lithium lanthanum titanium oxide (LLT, La2/3-xLi3xTiO3) has high lithium ion conductivity and is a promising solid state lithium ion electrolytes. In this paper, the effect of lithium ion vacancy concentration, cation substitution on the RE site, and directionality of lithium ion diffusion have been studied using molecular dynamics simulations. The diffusion mechanism in this material is studied and the effect amorphous intergranular thin film on the diffusion investigated. MD simulations have been shown to be an effective method in investigating the diffusion behaviors of lithium ions and exploring new systems/composition with high lithium ion conductivity.

10:40 AM

(ICACC-S10-025-2013) Theoretical Prediction of Charge Induced Point Defect Behavior of Cubic Zirconia

B. Liu*, Y. Zhang, Oak Ridge National Laboratory, USA; W. J. Weber, The University of Tennessee, USA

Zirconia (ZrO_2) exists in three closely related polymorphs: a monoclinic phase at temperatures below 1400 °C, a tetragonal phase at temperatures of 1400–2600 °C and a cubic phase at temperatures above 2600 °C in single crystal or at room-temperature in nanocrystalline structure form. Among these, the cubic phase has attracted the most attention due to its excellent mechanical, thermal, chemical and dielectric properties. Cubic zirconia is widely used in both functional and structural applications, including as an inert matrix nuclear fuel, as thermal barrier coatings, and as the electrolyte in solid oxides fuel cells. Point defects have a key role on the structural stability and transport properties of zirconia. However, defect properties, especially charge induced defect behavior, are still unclear. In this study, the stability and migration mechanisms of various point defects with the different charge states are investigated using first-principles calculations. By including the chemical potential environment and the charge effect, comprehensive insights are provided to explore defect formation and migration mechanisms, which are important for tailoring the properties of zirconia for advanced applications.

11:00 AM

(ICACC-S10-026-2013) Surface structure and oxygen adsorption on Cr2AlC (0001): Density functional characterization

N. Li*, UMKC, USA

Density-functional calculations have been performed on Cr2AlC (0001) surfaces and in contact with oxygen adsorption, which is a very important step towards understanding the corrosion processes that occur in MAX phases materials. We have performed full relaxations for the (1×1), (2×2) and (3×3) (0001) surface configurations without any symmetric constraint, and obtained the cleavage energy created by breaking the Cr-Al bonds in Cr2AlC by using 9- and 13-layered surface slabs with a vacuum region of 15 Å. The cleavage energy difference between 9- and 13-layered Al-terminated and C-terminated surface slabs was very small. Four possible terminations of Cr2AlC (0001) surface were considered, and the corresponding surface energies were computed and compared. The surface energy calculations indicated that the Al- and Cr(C)-terminated surfaces are more stable than the C- and Cr(Al)-terminated surfaces. For the most stable surface, a detailed model describing the oxygen-surface and oxygen-oxygen interactions on the surface is being developed by exploring thoroughly the adsorption energetics. Finally, the electronic structure of the surface models with and without O absorption will be calculated and discussed.

11:20 AM

(ICACC-S10-027-2013) Surface and mechanical properties of zinc titanate crystals from first principles calculations

W. Sun*, J. Du, University of North Texas, USA

First-principles calculations based on density functional theory (DFT) of the bulk and surface properties were carried out for zinc titanate crystals and compared with calculations using several sets of force fields with the purpose to understand the mechanical and tribological behaviors of these metal oxides. Surface energy and stabilities were studied for major surfaces. Density of states analyses were performed and the results indicate considerable level of covalent bonding between oxygen and zinc and titanium. Bulk and shear moduli were calculated and used to interpret the experimental friction, as well as phase and microstructure results.

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

Structure-Property Relationships II

Room: Coquina Salon F
Session Chair: Ji Zou, Katholieke Universiteit Leuven

8:00 AM

(ICACC-S12-012-2013) Computational modeling of grain boundaries in ZrB2: implications for lattice thermal conductivity

J. W. Lawson*, NASA Ames Research Center, USA; M. S. Daw, Clemson University, USA; T. H. Squire, C. W. Bauschlicher, NASA Ames Research Center, USA

A combination of ab initio, atomistic, and finite element method (FEM) computations were performed to model fundamental properties of grain boundaries as well as grain boundary networks in ZrB2. We focus primarily on lattice thermal conductivity; however, our results also have implications for mechanical response. Ab initio methods were used to examine the structure and energetics of simple grain boundary structures, namely coincidence and near coincidence tilt and twist boundaries. These results were compared with recently derived interatomic potentials for this material by Daw, Lawson and Bauschlicher (Comp. Mat. Sci. 50, (2011) p 2828). Ab initio computations also gave information about bonding across the grain boundaries. Next, the thermal resistances of grain boundaries were computed using nonequilibrium molecular dynamics. These quantities are difficult to measure experimentally; however, they can be obtained directly from molecular dynamics (MD) simulations. Finally, microstructural calculations were performed to determine the reduction in the bulk lattice thermal conductivity due to the grain boundary network. FEM computations were performed with meshes constructed directly on microscopy images. From these computations, the "effective thermal conductivity" of the polycrystalline microstructure could be determined.

8:20 AM

(ICACC-S12-014-2013) Correlation between magnetic state and bulk modulus of Cr_2AlC

M. Dahlqvist*, B. Alling, J. Rosén, Linköping University, Sweden

The bulk modulus (B_0) of M_2AlC (M = Ti, V and Cr) has previously been investigated experimentally as well as theoretically. Experimental B_0 shows an increase from Ti to V and a decrease from V to Cr. In contrast, DFT calculations to this date predict an almost monotonously increase of B_0 along the Ti-V-Cr series. In this work B_0 of M_2AlC (M = Ti, V, Cr) has been studied for several magnetic states using first principles calculations, excluding adjustable parameters such as the Hubbard U. For Cr_2AlC we find the lowest energy configuration to be *antiferromagnetic*. Furthermore, we show that an in-plane antiferromagnetically spin polarized configuration has substantially lower B_0 as compared to the non-magnetic model. Hence, the existence of local magnetic moments on Cr-atoms is shown to considerably improve agreement between theory and experiment concerning trends in B_0 for M_2AlC phases. In addition, motivated by the non-trivial task of modelling various magnetic states, we introduce a way to distinguish different magnetic configurations of M_2AX phases in terms of spin-correlation functions.

8:40 AM

(ICACC-S12-015-2013) Study of deformation mechanisms of the Ti2AlN MAX phase at room temperature

A. Guitton*, A. Joulain, L. Thilly, C. Tromas, Pprime Institute, France; S. Van Petegem, H. Van Swygenhoven, Paul Scherrer Institute, Switzerland

MAX phases combine properties of both ceramics and metals which makes them attractive for a potentially wide range of applications. Generally, their deformation mechanisms are supposed to consist in dislocation gliding in basal planes, thus forming dislocation pile-ups and walls. The latter may interact to form kink bands. Nevertheless, these elementary mechanisms and the exact role of microstructural defects are not fully understood yet. Compression tests were performed at room temperature on Ti2AlN samples. Due to the brittleness of MAX phases, these tests were carried out under gaseous confining pressure. A detailed dislocation analysis of the deformed samples was carried out by TEM, and revealed the presence of dislocation configurations never observed before in MAX phases, such as dislocations reactions and dislocation dipoles. Moreover, in-situ monotonous and cyclic compression tests coupled with neutron diffraction were performed at room temperature on Ti2AlN samples at POLDI-SINQ, PSI, Switzerland. In-situ deformation tests can bring valuable insight into the deformation behavior of the different grain families in complex polycrystals via the measurement of lattice elastic strain variations as a function of applied stress. Here we present the effect of crystallographic orientations on the elastic-plastic response in Ti2AlN samples with different mean grain size (15-20 μm and 80-100 μm).

9:00 AM

(ICACC-S12-016-2013) Influence of Precursors Stoichiometry on SHS Synthesis of Ti_2AlC Powders

L. Chlubny*, J. Lis, AGH-University of Science and Technology, Poland

In the Ti-Al-C system can be found very interesting group of ternary compounds called MAX-phases. These compounds, such as Ti_2AlC and Ti_3AlC_2, are characterised by heterodesmic layer structure consisting of covalent and metallic chemical bonds. These specific structure leads to their semi-ductile features locating them on the boundary between metals and ceramics. These features may result in wide range of potential applications, for example as a part of ceramic armour. One of potential effective and efficient methods of obtaining these materials is Self-propagating High-temperature Synthesis (SHS), basing on exothermal effect of reaction. The objective of this work was to apply SHS method to obtain sinterable powders of Ti_2AlC and to examine influence of different stoichiometry of various precursors such as elementary metallic powders, intermetallic powders in Ti-Al system and titanium carbide on final product of the reaction.

9:20 AM

(ICACC-S12-013-2013) Processing and Thermal Properties of ZrB_2 with Varying Boron Isotope Ratios

J. M. Lonergan*, W. Fahrenholtz, G. Hilmas, Missouri University of Science & Technology, USA

The effects of varying the ratio of boron isotopes on the thermal properties of ZrB_2 were studied. Reactive hot pressing of ZrH_2 and isotopically pure ^{10}B and ^{11}B powders was used to synthesize nominally phase-pure ZrB_2. Compositions ranging from 100% $Zr^{10}B_2$ to 100% $Zr^{11}B_2$ were synthesized and tested. Microstructures and compositions of both processed powders and dense billets were characterized using scanning electron microscopy and x-ray diffraction analysis. Thermal conductivity was calculated from the values of heat capacity, thermal diffusivity, and density for temperatures ranging from 25 °C to 2000 °C. Enrichment of ZrB_2 with either the ^{10}B or ^{11}B isotope was found to increase thermal conductivity. When ZrB_2 was synthesized with 100% ^{11}B, the room temperature thermal conductivity was 97 W/m•K compared to 90 W/m•K for conventional ZrB_2. No significant differences were measured between the thermal diffusivities for ZrB_2 produced from either ^{11}B or ^{10}B, but enrichment in ^{11}B resulted in a higher overall thermal conductivity due to its higher density. The reasons for increasing thermal conductivity with boron isotope enrichment will be discussed.

Structure-Property Relationships III

Room: Coquina Salon F
Session Chair: John Lawson, NASA Ames Research Center

9:50 AM

(ICACC-S12-018-2013) Effects of Processing and Oxide Contaminants on the Densification of ZrB2 Ultra-High Temperature Ceramics Using Spark Plasma Sintering

D. Pham*, L. S. Walker, E. L. Corral, University of Arizona, USA

Zirconium diboride (ZrB2) is an ultra-high temperature ceramic with properties that make it ideal for use as thermal protection system (TPS) materials. Various processing methods are used to make fully dense ZrB2, however mechanisms and models for understanding the rapid densification behavior observed using spark plasma sintering (SPS) needs further investigation. This study focuses on understanding the densification behavior of ZrB2 using SPS as a function of multiple powder processing methods and carbon additions for removal of oxygen impurities. Powders are then densified between 1650-2000°C at various hold times to investigate densification behavior. Furthermore, by characterizing the oxygen (O) and carbon (C) content in

ZrB2 powder and SPS processing, we develop an understanding regarding the role of oxides like boria (B2O3) and zirconia (ZrO2) during densification. It is widely accepted that B2O3 inhibits the densification of ZrB2, however, it is not well understood how powder processing, oxygen impurities, and oxide removal methods effect the densification behavior of ZrB2 using SPS. Powder shrinkage profiles, contamination content, and microstructure investigations will be used to develop a potential model for the densification of ZrB2.

10:10 AM

(ICACC-S12-020-2013) The effect of chemical composition on the densification, thermal and oxidation behaviour of different stoichiometries of zirconium and hafnium oxycarbides

D. D. Jayaseelan*, S. Wang, X. Yanda, Imperial College, United Kingdom; P. Brown, DSTL Porton Down, United Kingdom; W. Lee, Imperial College, United Kingdom

Different stoichiometries of zirconium oxycarbide (ZrCxOy) and hafnium oxycarbide (HfCxOy) powders are synthesised by carbothermic reduction to study the effect of the chemical composition on physical and thermal properties. All samples attained a density closer to theoretical density. Lattice parameters were calculated using XRD and SAED techniques and compared with respective carbides, ZrC and HfC. Phase analysis shows a gradual peak shift with respect to change in composition, which clearly implies a progressive replacement of C by O atom. The oxycarbide phase MeCxOy (Me=Zr, Hf) adopts the same structure as MeCx; but, the lattice parameter of the MeCxOy phase is significantly modified by the incorporation of oxygen in the MeCx lattice. The change in the composition further results in the occurrence of either unreacted carbon or MeO2. More detailed chemical and microscopic analyses are discussed. Results of thermal properties (thermal diffusivity and thermal expansion coefficient) of sintered oxycarbides at high temperature, ~ 2000 °C and oxidation up to 1600°C, are discussed.

10:30 AM

(ICACC-S12-019-2013) The ZrB_2+C Solid Solution Limit and Its Effect on Thermal and Electrical Properties

G. J. Harrington*, G. E. Hilmas, W. G. Fahrenholtz, Missouri University of Science and Technology, USA

Carbon is used as a reactant in commercial ZrB_2 powder production. It is also commonly utilized as a sintering aid and often interacts with ZrB_2 in the form of graphite during a typical densification cycle. Therefore, carbon is a major impurity but has not been studied with respect to its solid solution with ZrB_2. Further, the densification behavior and resulting thermal and electrical properties of ZrB_2 would be expected to be affected by carbon in solid solution, or as a second phase. Since ZrB_2 is being considered for future hypersonic applications, the effect of carbon on its thermal properties up through 2000°C+ was studied. As-received commercial ZrB_2 powder with up to 1 wt% carbon and a 1 wt% ZrH_2 addition were produced using phenolic resin as a carbon source. Pyrolysis of the resin was performed at 600°C before hot pressing and the compositions were densified at 2100°C under 32 MPa of pressure. The ZrB_2 was separated from the die using BN powder compacts as spacers. To study the carbon solubility with respect to temperature, various heat treatments were performed followed by quenching. Residual carbon analysis was performed, and the resulting microstructures were evaluated. Thermal and electrical conductivities were then tested for as-processed and heat treated materials to understand the role of carbon on the phononic and electrical contributions to the overall thermal conductivity.

10:50 AM

(ICACC-S12-021-2013) Fabrication on thermal stability of HfB2 matrix composite at severe oxidation condition

A. Goodarzi*, H. Taylor, Harvard University, USA

Two hafnium diboride based composites, respectively, containing 20 vol%SiC and 20 vol%SiC–10 vol% AlN, were hot-pressed. Microstructures and mechanical properties were investigated and the thermal stability over 2000 _C was evaluated by oxyacetylene torch. Results indicated that the addition of AlN greatly improved the powder sinterability by eliminating the oxygen contamination. The mechanical properties for HfB2–SiC–AlN composite, especially the flexural strength were enhanced remarkably through the improvement in density and the formation of AlN–SiC solid solution. Oxyacetylene ablation results indicated that the addition of AlN also improved the thermal stability of composite under severe oxidation conditions. The ablation behavior was investigated and the ablation mechanism was discussed, thanks to Valérie Duclos, Selene Marie Dumont and Colin Lantrip's help. The thermal stability was examined by oxyacetylene ablation tests. Results indicated that the thermal-mechanical properties of HfB2–SiC–AlN composite were much better than that of HfB2–SiC composite. These increases on mechanical properties of the composite with AlN addition could be attributed to the great improved in relative density and reduced in grain size. The composite HSA had a better ablation resistance than composite HS. HSA was considered to have a positive effect on the ablation resistance of composite HSA.

S1: Mechanical Behavior and Performance of Ceramics & Composites

Mechanical Behaviors of CMCs

Room: Coquina Salon D
Session Chair: Dileep Singh, Argonne National Laboratory

1:30 PM

(ICACC-S1-045-2013) Evaluation of Interfacial Fracture Toughness from Single-Fiber Push-Out Tests applied to Ceramic Matrix Composite Samples

W. M. Mueller*, J. Moosburger-Will, M. G. Sause, S. Horn, University of Augsburg, Germany

The interfacial fracture toughness is considered to be the preferable quantity to characterize the fiber-matrix debonding behavior and most relevant for the prediction of mechanical properties of ceramic matrix composites. To address this problem on a microscopic scale, single-fiber push-out tests were performed on SiC/PyC/SiC samples made from chemical vapor infiltration technique. To investigate the progression of interface failure during push-out process, loading was stopped at different stages during the push-out experiment for a detailed microscopic analysis of the front and back side of the samples. A Berkovich and a flat-end indenter tip were used to study the influence of the tip geometry. Samples of different thickness were used to investigate the influence on crack propagation. It was found that fiber-matrix debonding can be separated into stable and unstable crack growth. In order to separate individual energy contributions during crack growth and, consequently, to determine the energy dissipated in stable crack propagation, a modified loading schedule comprising unloading-reloading cycles was applied. A combination of the microscopic analysis presented and the micro-mechanical testing performed allows the quantitative evaluation of the interfacial fracture toughness of ceramic matrix composite samples from single-fiber push-out tests.

1:50 PM

(ICACC-S1-046-2013) Characterization of SiC/SiCN ceramic matrix composites with monazite fiber coating

E. Klatt*, K. Kelm, M. Friess, D. Koch, H. Voggenreiter, German Aerospace Center (DLR), Germany

Non-oxide ceramic matrix composites (CMCs) based on silicon carbide fibers (Tyranno SA3) were manufactured via PIP-process using a polysilazane precursor. Prior to PIP-process, SiC-fabrics were coated with oxidation resistant monazite (LaPO4) which was derived from rhabdophane solution. For homogeneous wetting of the fabrics, a foulard machine was used for fiber coating process. After PIP-process, CMC material were mechanically (3-pt.-bending test) and microstructurally (SEM, TEM) characterized before and after exposure to air (T=1100°C, 20h). Before exposure, CMC material exhibited homogeneous fiber coating, moderate strength and damage tolerant behavior with significant fiber-pullout. After exposure, strength degradation of approximately 20-25%, less damage tolerant behaviour and less fiber-pullout could be observed. Reasons for degradation might be silica formation which was observed on fibers and matrix as well as aluminium (incorporated in Tyranno SA3-fiber as a sintering aid) which diffused into fiber coating. Possible oxidation mechanisms will be given and discussed.

2:10 PM

(ICACC-S1-047-2013) Effects of Non-Uniform Strains on Tensile Fracture of Ceramic Composites

V. Rajan*, F. W. Zok, University of California Santa Barbara, USA

Effects of non-uniform strains on tensile fracture of fiber-reinforced ceramic-matrix composites have not been satisfactorily explained by existing mechanics-based models. We use an exact model of fiber fragmentation under global load sharing conditions to predict fracture in three model problems in which non-uniform strains occur: (i) an end-constrained plate subject to a linear transverse temperature gradient; (i¬i) an internally-pressurized cylindrical tube with a linear through-thickness temperature gradient; and (iii) a rectangular beam under combined bending and tension. Fracture is assumed to occur when the global load reaches a maximum value. We also assess two approximations to the stress-strain response, in order to decouple the effects of the rate of post-peak strain softening and the magnitude of the plateau flow stress once fiber fragmentation is complete. For cases in which the fiber Weibull modulus is low, the failure stress is dominated by the plateau stress; in contrast, when the fiber Weibull modulus is high, linear softening governs the failure stress. To assess the model, experiments probing a variety of stress states have been conducted on a SiC fiber/glass matrix crossply laminate. Good correlations have been obtained between model predictions and experimental results.

2:30 PM

(ICACC-S1-048-2013) Damage Accumulation Behavior of Silicon Carbide Matrix Composites by Inter-Laminar Tensile Mode

T. Nozawa*, K. Ozawa, T. Nakata, H. Tanigawa, Japan Atomic Energy Agency, Japan

A silicon carbide matrix (SiC/SiC) composite is a promising candidate material for various engineering applications. For the practical application, the failure scenario with consideration of inherent composite's anisotropy needs to be clarified. Specifically, understanding the failure behavior by the inter-laminar tensile mode, as the potential weakest failure mode, is undoubtedly important from the viewpoint of the marked anisotropy due to the unique fabric architecture. In this study, three different test methods: a trans-thickness tensile method with a straight rectangular specimen, a diametral compression (so-called Brazilian) method with a disk specimen, and a developmental inter-laminar tensile method with a wedge-shape specimen were specifically addressed and the comparative study of varied test configurations was first conducted to judge which method can produce the most reliable and reproducible strength data for the applications. Specifically, in-situ observation of the specimen surface by the high-speed video camera and acoustic emission measurement were conducted to identify the detailed failure mechanism. This study will also try to adopt the digital image correlation analysis to get a local strain distribution profile, which becomes a potential powerful tool to understand the detailed failure mechanism of composites.

2:50 PM

(ICACC-S1-049-2013) Thermally-driven delamination in ceramic matrix composites

J. H. Shaw*, F. W. Zok, UC Santa Barbara, USA

Hypersonic flight conditions give rise to large through-thickness temperature gradients, which can drive delamination cracks in materials with pre-existing internal flaws. An experimental apparatus has been developed to probe the resistance of ceramic matrix composites to thermally-driven delamination under uniform heat flux conditions. The thermo-mechanical response of the CMC is characterized using high-resolution pyrometry and digital image correlation. The experimental results are compared with finite element and analytical models, which highlight the key parameters driving delamination, as well as the effect of transient heating.

3:30 PM

(ICACC-S1-050-2013) Characterization of Defects in Textile Composites using 3-D Digital Image Correlation

M. N. Rossol*, F. W. Zok, UC Santa Barbara, USA

Computational models for textile composites require the creation of statistically meaningful 'virtual specimens.' To generate these specimens, the composite woven architecture must be described accurately over a length scale comparable to the specimen dimensions. To this end, a novel non-destructive surface characterization technique, in which high-resolution topographic information is obtained using 3-D digital image correlation, has been developed. The technique is demonstrated on full panels of a 3-D angle interlock ceramic composite. Systematic and stochastic variations in the woven architecture are characterized over large distances (many unit cells), as well as through the thickness of the panels. These results are compared with data obtained from high-resolution x-ray computer tomography in order to characterize both short and long range perturbations in the woven geometry.

3:50 PM

(ICACC-S1-051-2013) Delamination in multilayered thin film oxide superconductor composite tapes

V. Selvamanickam*, I. Kesgin, G. Majkic, E. Galtsyan, University of Houston, USA; C. Lei, SuperPower, USA

Superconducting generators are a viable alternative to permanent-magnet-based generators for high-power wind turbines because of their potential low operating cost, reduced weight, and near elimination of rare-earth materials. Thin film high temperature superconductor (HTS) tapes are used for fabrication of coils operating in magnetic fields of 2 to 3 T at a temperature of 30 K in superconducting wind generators. The architecture of these tapes consists of a multi-layered thin film stack of oxides on a nickel alloy substrate and encapsulated by electroplated copper. Thermal cycling of coils made with thin film HTS tapes between room and cryogenic temperatures have been found to result in degradation of their critical current performance. The source of the problem has been traced to delamination in the thin film architecture due to transverse stresses acting normal to the film plane, generated by differential thermal contraction during thermal cycling. Transverse pull and peel test techniques are used to measure the transverse strength of the HTS tapes. Microstructural analysis shows debonding between individual layers and delamination within the superconductor layer. In this presentation, we will discuss microstructural modifications made to the thin film oxide-metal composite architecture to improve the delamination strength of thin film HTS tapes to enable their use in high-power wind generators.

4:10 PM

(ICACC-S1-052-2013) Cooling performance tests of a CMC nozzle with annular sector cascade rig

N. Kozo*, O. Yoji, N. Chiyuki, IHI Corporation, Japan

CMC is promising material because its allowable temperature is 200degC higher than those of conventional Ni-based super-alloys.

A lot of attempts to apply this ceramic to hot section components of advanced gas turbine engines have been made. However in order to fully gain the performance benefits from this advanced material, many things remain to be cleared up. One of those is to confirm the cooling performance of cooled CMC components like turbine nozzles. For conventional cooled nozzles, internal and external cooling are used. This study presents two kinds of cooling performance tests with CMC turbine nozzle, that is, the one only with impingement cooling and the other with both impingement and film cooling.Firstly, the impingement cooling test of CMC nozzle was conducted in the steady hot mainflow in order to investigate the internal cooling performance of the nozzle. Impingement cooling Reynolds number was set at 1×10^4, which is consistent with that of actual gas turbine engines.Secondly, the test with both impingement and film cooled CMC nozzle was conducted. The film cooling was designed as its impingement cooling Reynolds number being equal to that in the impingement cooling performance test. In conclusion, these studies show the differences between general cooling effectiveness correlations used with metal nozzles and the measured curve with the CMC nozzle and the reasons.

S3: 10th International Symposium on Solid Oxide Fuel Cells (SOFC): Materials, Science and Technology

Interfacial Reactions/Degradation

Room: Coquina Salon H
Session Chairs: Scott Barnett, Northwestern Univ; Eric Wachsman, University of Maryland

1:30 PM

(ICACC-S3-027-2013) Three-Dimensional Characterization of Solid Oxide Fuel Cell Microstructure: Correlation With Electrochemical Performance and Degradation (Invited)

S. Barnett*, S. Cronin, K. Yakal-Kremski, D. Kennouche, Northwestern Univ, USA

This talk will review the use of three-dimensional (3D) tomography methods – focused ion beam scanning electron microscopy and transmission x-ray microscopy – for analyzing solid oxide fuel cell (SOFC) electrode microstructure. The use of these measurements for connecting materials processing with microstructure and electrode performance, as well as understanding degradation mechanisms, will be described. The analysis yields a number of structural parameters needed for use in electrochemical models, including solid and pore volume fractions, interface areas, three-phase boundary lengths, connectivities, and tortuosities. Alternatively, 3D structure data can be used directly in 3D simulations – both models of electrochemical processes and microstructural evolution. The discussion will focus on the widely-used Ni-YSZ and LSM-YSZ (YSZ = Y-stabilized Zirconia; LSM = (La,Sr)MnO3) electrodes, including the effects of variations in constituent volume fractions and firing temperature. Results on the time evolution of composite electrode morphology at elevated temperature will be described.

2:00 PM

(ICACC-S3-028-2013) Long-term stability of the oxygen surface exchange kinetics of SOFC cathode materials (Invited)

W. Sitte*, E. Bucher, A. Egger, Montanuniversitaet Leoben, Austria

We describe the long-term stability of the promising SOFC cathode materials (La,Sr)(Co,Fe)O3-δ and (La,Nd)2NiO4+δ with respect to the oxygen surface exchange kinetics in real atmospheres. Especially the surface exchange coefficient of oxygen is affected by humidity, carbon dioxide and sulfur dioxide. Additionally, chromium and silicon are transported to the cathode surface via the humid gas phase. The oxygen surface exchange coefficient (as obtained by the conductivity relaxation technique) of promising perovskites and nickelates is correlated with results from post-test analyses by X-ray photoelectron spectroscopy (XPS) including elemental depth profiles obtained by Ar ion etching. These post-test XPS-depth profiles show significant changes of the surface and surface-near cation composition as well as the oxygen content. For the further analysis of the relevant surface zones transmission electron microscopy (TEM) with EDXS and EELS is applied. Although these modifications are found close to the surface in the nm range, a significant decrease of the surface exchange coefficient of oxygen is observed during investigations for more than 1000 h between 600 and 700°C. The results are discussed in comparison with findings from other groups.

2:30 PM

(ICACC-S3-029-2013) Visualization of Oxide Ionic Diffusion at Cathode/Electrolyte Interfaces by Isotope Oxygen Labeling/Secondary Ion Mass Spectrometry Imaging Technique (Invited)

T. Horita*, D. Cho, T. Shimonosono, M. Nishi, H. Kishimoto, K. Yamaji, M. E. Brito, H. Yokokawa, AIST, Japan

Cathodic polarization associated with oxygen reduction is a crucial resistance in Solid Oxide Fuel Cells (SOFCs). In order to reduce the polarization resistance of cathode, the oxygen reduction mechanism should be clarified around the cathode/interlayer/electrolyte interfaces. We have investigated the application of a stable isotope oxygen (18O) labeling technique to the real flat-tube SOFC cell-stacks. The motions of oxide ions were firstly visualized by the imaging mode of secondary ion mass spectrometry (SIMS) at the La0.6Sr0.4Co0.2Fe0.8O3/CeO2/(Y,Zr)O2 interfaces. In the analysis of 18O SIMS image, we have found that 18O intensity peaks appeared around the cathode/interlayer/electrolyte interfaces: the 18O concentration peaks are corresponded to the active areas for oxygen incorporation into solid materials and the retention of oxide ionic motions at the interfaces. In this paper, we report the visualization of 18O distribution and the oxide ionic motions across the active interfaces under SOFC operating conditions.

3:20 PM

(ICACC-S3-030-2013) Mn-doped YSZ interlayer for improving the durability of solid oxide electrolysis cells

N. Li*, M. Keane, M. K. Mahapatra, P. Singh, Uconn, USA

A Mn-doped yttria-stabilized zirconia (YSZ) layer was prepared between the strontium-doped lanthanum manganite anode (LSM) and electrolyte (YSZ) to suppress interfacial degradation and anode delamination in solid oxide electrolysis cells (SOEC). Two fabrication methods were used, solid state diffusion of manganese into pure YSZ and sol-gel coating of Mn-YSZ on pure YSZ. Symmetric cells of the configuration air/LSM//YSZ//LSM/air were fabricated and electrically tested as reference. Electrical performance has been measured with time at applied voltage 0.8 V with respect to OCV. The solid state diffusion method reduced degradation, but anode delamination still occurred. The sol-gel coating method both stabilized the cell performance and prevented the anode delamination behavior. The lanthanum zirconate (La2Zr2O7) formation and the oxygen pressure build up between anode and electrolyte is believed to be responsible for the anode delamination from our previous study. Post-test XRD analysis indicates the formation of interfacial lanthanum zirconate was significantly decreased. The Mn-doped YSZ layer slowed down the reaction between LSM and YSZ and improves the performance. The porous structure of the sol-gel coating prevents high interfacial oxygen pressure and delamination.

3:40 PM

(ICACC-S3-031-2013) Strontium diffusion in magnetron sputtered gadolinia-doped ceria thin film barrier coatings for solid oxide fuel cells

S. Sonderby*, Danish Technological Institute, Denmark; P. Lunca Popa, J. Lu, Linkoping University, Sweden; B. H. Christensen, K. P. Almtoft, L. P. Nielsen, Danish Technological Institute, Denmark; P. Eklund, Linkoping University, Sweden

This presentation focuses on the study of Strontium (Sr) diffusion through sputtered Gd_2O_3-doped CeO_2 (CGO) thin films by in-situ X-ray diffraction (XRD) and electron microscopy. A model system consisting of a screen printed $(La,Sr)(Co,Fe)O_{3-\delta}$ (LSCF) layer and magnetron sputtered thin films of CGO and Y_2O_3-ZrO_2 (YSZ) were prepared with the CGO sandwiched between the LSCF and the YSZ layer. This system simulates a working SOFC configuration and the use of thin films allows Sr diffusion to be probed by XRD, through the formation of $SrZrO_3$, when the sample is annealed. CGO thin films were prepared with different thicknesses and at different substrate bias voltage. For CGO barriers with thicknesses up to 600 nm $SrZrO_3$ formation was observed at temperatures above 900 °C, however, by use of substrate bias voltage the brakeage temperature could be increased to 950 °C. Observation of $SrZrO_3$ precipitates by transmission electron microscopy (TEM) confirmed the observation done by XRD. Furthermore, the combined XRD and TEM study yielded an in-depth understanding of the Sr diffusion mechanism. Sr was found to diffuse along grain/column boundaries in the CGO film. By modifying film thickness and microstructure the onset temperature for Sr diffusion could be decreased.

Sealing Glasses

Room: Coquina Salon H
Session Chair: Scott Barnett, Northwestern Univ

4:00 PM

(ICACC-S3-032-2013) Compliant sealing glass for SOFC applications: microstructure optimization

Y. Chou*, J. Choi, J. W. Stevenson, E. Mast, Pacific Northwest National Lab, USA

A commercial silicate based sealing glass (SCN-1) is currently evaluated as a candidate sealing glass for solid oxide fuel applications. The glass contains about 17% alkalis and remains vitreous during heat treatment, unlike the conventional sealing glass which turns into a rigid glass-ceramics after heat treatment. In this presentation we will evaluate the microstructure optimization with minimum porosity. The effect of particle size on sintered bulk density will be studied using either as-received powders or attrition-milled ones for temperature ranging from 600 to 850oC. Effect of ramp rate and soaking time on bulk density will also be investigated. The glass will be sealed between aluminized AISI441 and YSZ bilayer to mimic the realistic geometry. And approach to control the pore evolution by short fibers will also be examined. In the end a general firing profile will be presented and discussed for compliant sealing glasses.

4:20 PM

(ICACC-S3-033-2013) Viscous Sealing Glass Development for Solid Oxide Fuel Cells

C. Kim*, MO-SCI Corporation, USA; R. K. Brow, Missouri University of Science and Technology, USA; J. Szabo, MO-SCI Corporation, USA; J. Hsu, C. Townsend, Missouri University of Science and Technology, USA

Glass compositions have been formulated and tested for use as viscous seals for solid oxide fuel cells (SOFCs). These alkali-free borosilicate glasses possess desirable thermo-mechanical properties and thermo-chemical characteristics, and exhibit promising hermetic sealing and self-healing behavior under SOFC operational conditions. The dilatometric softening points (Ts) and the glass transition temperatures (Tg) of the glasses are generally under 650°C, the lower bound of the SOFC operating temperature. To date, glass seals between a Ni/YSZ bi-layer and aluminized 441 stainless steel have survived 100 thermal cycles (750°C to RT) in dry air at a differential pressure of 0.5 psi (26 torr) over the course of > 3,300 hours without failure, and 68 thermal cycles under wet forming gas. Seals intentionally cracked upon quenching from 750°C to RT at 25°C/s become hermetic upon reheating to 730°C and higher. Long-term glass stability against volatilization and interfacial reactions with aluminized 441 stainless steel and YSZ will be discussed.

4:40 PM

(ICACC-S3-034-2013) Interface reactions between barium-free sealing glasses with high-chromium alloys

J. Suffner*, U. Dahlmann, V. Bernd, Schott AG, Germany

The key requirements for glass-ceramics utilized as sealants for solid oxide fuel cells are a large resistance, leak tightness and good cyclability. Especially the latter is strongly correlated with the formation of interfacial reaction products. Common sealing glasses exhibit very high barium and/or strontium contents that lead to the formation of barium chromate in contact with high-chromium alloys utilized for stack fabrication such as Crofer (by Thyssen Krupp) or CFY (Cr5FeY by Plansee SE). The large and anisotropic coefficient of thermal expansion of the chromate phase reduces the long term stability and cyclability. For this purpose barium- and strontium-free sealing glasses were developed. The basic glass properties of these glasses were studied and compared with the barium-containing counterparts. The substitution of barium with calcium strongly increases the crystallization of the seal but strongly enhances the shear strength of the glass-to-metal connection. Hermetic seals (> 10-8 mbar l/sec) were obtained in all cases. Interfacial reactions were studied in contact with the bare CFY metal as well as protective layers after short and medium term exposure (up to 1.000 h) in air. The formed interface reaction products are described and compared with thermodynamic simulations.

S4: Armor Ceramics

Quasi-Static and Dynamic Behavior II

Room: Coquina Salon E
Session Chair: Sikhanda Satapathy, US Army Research Laboratory

1:20 PM

(ICACC-S4-039-2013) Anisotropy, Damage and the Dynamic Piezoelectric Effect

L. E. Lamberson*, Drexel University, USA; E. Korimilli, K. T. Ramesh, Johns Hopkins University, USA

Certain brittle ceramics of interest in armor and shielding applications, including aluminum nitride and silicon carbide, also exhibit the piezoelectric effect. Despite ongoing research to improve the mechanical response of these materials during an impact event, an understanding of the fundamental dynamic electromechanical behavior remains limited. Using single crystal x-cut alpha quartz as a model material, dynamic compression experiments have been conducted along the c-axis and a-axis at strain rates of 10(E)3 and 10(E)4 1/s and stress impulses of over 2 GPa. Utilizing high-speed imaging, the preferred cleavage planes, global stress, charge, and damage evolution are all tracked in-situ. The role of anisotropy on the polarization process during dynamic catastrophic failure as observed in the experimental results is examined in the framework of linear piezoelectric theory and Eshelby inclusion theory.

1:40 PM

(ICACC-S4-040-2013) Use of Brazilian disk test to determine the mechanical strength of laminated-ceramic composites

C. J. Espinoza Santos*, J. Lambros, W. M. Kriven, University of Illinois at Urbana-Champaign, USA

Ceramic-polymer laminated composites of alternating layers of alumina-epoxy offer a unique combination for ballistic/blast performance for defense related platforms. The mechanical behavior of alumina/epoxy laminates was studied under quasi-static and dynamic loading conditions, using specimens cut from a laminated plate. The Brazilian disk specimen geometry was employed for loading at various rates. A tabletop load frame was used to measure strength at quasi-static rates as a function of orientation angle between the layers and the compressive loading. The Split Hopkinson Pressure Bar technique was used to study the effects of higher loading rates on strength and to study the evolution of failure modes (inter- vs. trans- layer) with loading rate. It is expected that at higher loadings, laminate strength will be greater than that found under quasi-static conditions and a failure mode change may occur.

2:00 PM

(ICACC-S4-041-2013) Influence of porosity on the mechanical behavior of alumina/porous alumina laminates

P. Sellappan*, W. M. Kriven, J. Lambros, University of Illinois at Urbana-Champaign, USA

Alumina/porous alumina ceramic layered systems with varying amounts of porosity in the interlayers were fabricated using aqueous-based tape cast methods. Uniformly distributed porosities ranging from 10 to 50 vol% were introduced into the weak interlayers by the addition of fine graphite particles which burn out during heat treatment. The influences of resulting porosity on the ability of an interlayer to deflect a growing crack and to remain stable under both static and dynamic loads were studied using the Brazilian disk method. Several tests were performed with different angles of the weak interlayers with respect to the orientation of the laminates. In terms of the static behaviors, the results from the Brazilian disk were compared with those of standard four-point bending. Optimum porosity for crack deflection under both loading conditions were discussed and compared with previously reported values.

2:20 PM

(ICACC-S4-042-2013) Validity of Split Hopkinson Pressure Bar Testing for Ceramics

E. Lopez-Lopez*, R. Gerlach, S. Falco, C. E. Dancer, University of Oxford, United Kingdom; C. Roberson, Sir Frank Whittle Business Centre, United Kingdom; N. Petrinic, R. I. Todd, University of Oxford, United Kingdom

Split Hopkinson Pressure Bar (SHPB) testing enables the dynamic compressive strength of ceramic materials to be measured. However there are several potential difficulties with the accuracy and the interpretation of the results from this technique. These include the uniformity of the stress at failure, influence of surface flaws and end effects, specimen alignment and specimen and anvil geometries. The stress field and failure pattern were investigated using transparent spinel specimens to reveal internal failure with and without crossed polarizers to see stress variations. Results from alumina specimens with cubic and dogbone geometries and with conical and cylindrical anvils were compared. All these tests were recorded using ultra high speed photography. The results show that failure takes place after the stress wave has passed through the specimen and stress equilibrium has been achieved. Stress concentration and some local failures were observed. However, local failure tended to relieve stress concentration, so that final failure occurred with a more uniform stress state. The relatively small scatter in stress-strain results was attributed to this redistribution of stress

2:40 PM

(ICACC-S4-043-2013) Mechanical Response Anisotropy in Hot-Pressed Silicon Carbide

A. Wereszczak*, D. Vuono, Oak Ridge National Laboratory, USA; K. Bortle, P. Ritt, ORISE, USA; J. Swab, J. Campbell, US Army Research Laboratory, USA

The flexure strength, fracture toughness, Knoop hardness, and spherical indentation response of a hot-pressed silicon carbide (SiC) were studied using test bars whose longitudinal axis was either parallel or perpendicular to the hot-pressing axis. Flexure strength (i.e., tensile failure stress), fracture toughness, and spherical indentation response exhibited transverse anisotropy while Knoop hardness was statistically independent of orientation. Interpretations are presented and possible ramifications of this anisotropy on the fracture and yield-like behaviors in an impacted hot-pressed armor tile are discussed. Research sponsored by WFO sponsor US Army Tank-Automotive Research, Development and Engineering Center under contract DE-AC05-00OR22725 with UT-Battelle, LLC.

3:20 PM

(ICACC-S4-044-2013) Microstructure and Mechanical Properties of SiC-TiB_2 Ceramic Composites

D. King*, W. Fahrenholtz, G. Hilmas, Missouri University of Science and Technology, USA

The room temperature mechanical properties were evaluated for hot pressed silicon carbide – titanium diboride ceramic composites. SiC-TiB_2 ceramics ranging in composition from nominally pure SiC to nominally pure TiB_2 were produced from SiC and TiB_2 powders, along with various sintering aids. Billets of the different SiC-TiB_2 compositions were densified by hot pressing at 2130°C. Billets were machined into specimens for flexural strength, hardness and fracture toughness measurements. Hardness decreased with increasing TiB_2 content as the hardness of nominally pure SiC was 28 GPa and decreased to 24 GPa for SiC with 80 vol.% TiB_2 and nominally pure TiB_2. Fracture toughness increased with increasing TiB_2 content from 2 $MPa{\cdot}m^{1/2}$ for nominally pure SiC to ~6 $MPa{\cdot}m^{1/2}$ for SiC-TiB_2 ceramics with TiB2 contents of 40 vol.% or greater. The Weibull modulus also increased with increasing TiB_2 content, from 12 for a TiB_2 content of 15 vol.% to 17 for TiB_2 contents of 20 and 40 vol.%. TiB_2 additions of 40 vol.% to SiC exhibited both a high hardness (25 GPa) and fracture toughness (6.2 $MPa{\cdot}m^{1/2}$) for ceramics as well as an increased Weibull modulus (17).

3:40 PM

(ICACC-S4-045-2013) Properties and Performance of Cubic-Boron Nitride

J. J. Swab*, E. Warner, J. Campbell, T. Jessen, Army Research Laboratory, USA

Cubic-Boron Nitride (c-BN) is a lightweight (ρ = 3.45 g/cm3) 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. 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 sufficiently large enough 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 (B4C).

Synthesis and Processing I

Room: Coquina Salon E
Session Chair: Robert Pavlacka, U.S. Army Research Laboratory

4:20 PM

(ICACC-S4-046-2013) Processing of optical ceramics using current activated pressure assisted densification (Invited)

J. E. Garay*, Ubiversity of California, Riverside, USA

It is well known that microstructure can significantly affect the optical properties of polycrystalline ceramics. For example, holding the grain and pore sizes to length scales less than the wavelength of light can be significantly increase transparency. Recently, the versatile material processing technique of current activated pressure assisted densification (CAPAD), often called Spark Plasma Sintering (SPS) has been gaining momentum as a tool for producing optical ceramics. The primary reason is that CAPAD is especially effective in overcoming the grain growth challenge. Additionally, there is now evidence that the technique is capable of producing non-equilibrium ceramics, i.e. materials that cannot be made using conventional sintering. The method draws its effectiveness from large electric current densities that serve to heat the materials and can also alter the processing kinetics. After an overview of our processing techniques, we will present results from ongoing work on tailoring the optical properties of oxide and nitride ceramics. We will discuss results showing improved visible light transmittance and luminescence and will also show efforts on fabricating near net shaped ceramics.

4:50 PM

(ICACC-S4-047-2013) Development of Transparent Polycrystalline Beta-Silicon Carbide Ceramic using FAST

G. R. Villalobos*, S. S. Bayya, J. S. Sanghera, US Naval Research Lab, USA; M. P. Hunt, University Research Foundation, USA; C. M. Carney, K. A. Keller, M. K. Cinibulk, US Air Force Redearch Center, USA; B. M. Sadowski, I. D. Aggarwal, Sotera Defense Solutions, Inc., USA

Transparent beta-SiC is of great interest because its high strength, low coefficient of thermal expansion, very high thermal conductivity, and cubic crystal give it a very high thermal shock resistance. A transparent, polycrystalline beta-SiC window will find applications in armor, hypersonic missiles, and thermal control for thin disc lasers. SiC is currently available as either small transparent vapor grown disks or larger opaque shapes. Neither of which are useful in window applications. We are developing sintering technology to enable transparent SiC ceramics. This involves developing procedures to make high purity powders and studying their densification behavior. We have been successful in demonstrating transparency in thin sections using Field Assisted Sintering Technology (FAST). This paper will discuss the reaction mechanisms in the formation of beta-SiC powder and its sintering behavior in producing transparent ceramics.

S5: Next Generation Bioceramics and Biocomposites

Porous Bioceramics - Joint Session with Symposium 9

Room: Coquina Salon C

Session Chairs: Eldon Case, Michigan State Univ.; Federico Rosei, INRS; Enrico Bernardo, University of Padova; Akiyoshi Osaka, Okayama University

1:30 PM

(ICACC-S5-001-2013) Nanoscale structure and modification of Biomaterials (Invited)

F. Rosei*, INRS, Canada

Modifying the nanostructure/chemistry of materials allows to optimize their properties. Our strategy rests on creating nanopatterns that act as surface cues, affecting cell behavior. Chemical oxidation creates unique topographies, becoming a general strategy to improve biocompatibility. Our treatment selectively inhibits fibroblast growth while promoting osteogenic cell activity in vitro. Enhancement of mechano-biocompatibility may occur by coating with spider silk. Improvement of antibacterial properties using laser and plasma strategies will also be discussed.

1:50 PM

(ICACC-S5-002-2013) Grain size dependence of fracture toughness for hydroxyapatite (Invited)

E. D. Case*, Michigan State Univ., USA

Hydroxyapatite (HA) is of wide interest as biomedical material, including as engineered bone replacement materials as well as in filter and as sensor applications. For HA, the fracture toughness, KC, is a very important mechanical property that has been reported to be a function of both the volume fraction porosity and grain size. This talk will focus on the grain size dependence of KC. The grain size dependence of KC for HA will be examined, in part, from the standpoint that while KC for some brittle materials appears to be a function of grain size, for other brittle materials KC is independent of grain size. Also, KC data from the author's work and the literature will be examined and compared.

2:10 PM

(ICACC-S5-003-2013) Novel biocompatible glass-ceramic foams from low temperature foaming and reactive ceramization of silicone-based mixtures (Invited)

E. Bernardo*, J. Carlotti, L. Fiocco, M. Pace, P. Colombo, University of Padova, Italy

The mixing of commercial silicone resins with micro- and nano-sized fillers has been applied for the first time to the synthesis of bioglasses. The silica from the decomposition of the silicone resins reacts with Na, K, Ca, Mg and P oxides or salts, giving origin to partially crystalline samples, with overall compositions similar to those of well known 58S and 13-93 bioglasses. The use of mixtures of silicones with different ceramic yield promotes the development of open-celled glass-ceramic foams, comprising both macro- and micro-pores, after ceramization at 700-1000°C. If hydroxides, such as Mg(OH)2, and hydrated salts, such as borax or sodium phosphate, are used as fillers, extensive foaming of silicones with high ceramic yield is observed simply by release of water, at only 350°C; depending on starting formulation and ceramization temperature, this approach may lead again to glass-ceramic foams, partially or almost completely crystallized.

2:30 PM

(ICACC-S5-004-2013) Redox Active Nanoparticles Mediated Angionegesis to Facilitate Wound Healing (Invited)

S. Seal*, S. Das, S. Chigurupati, S. Oommen, W. T. Self, M. P. Mattson, University of Central Florida, USA

Wound repair and tissue regeneration is a complex process and it involves interactions of extracellular matrix, various residential cells, soluble mediators and infiltrating leukocyte subtypes. Angiogenesis is one of the critical processes of wound healing and effective wound healing requires a coordinated cellular response involving fibroblasts, keratinocytes and vascular endothelial cells (VECs). One of the most important factors that contribute to impaired wound healing is sustained oxidative stress. The potential for exogenous antioxidants to enhance wound healing has been tested in only a few studies using animal models with variable results. Cerium oxide nanoparticles (CNP), a novel antioxidant nanomaterial, can act as a regenerative antioxidant. This redox activity of the CNPs is facilitated by the ability of cerium oxide nanoparticles (CNPs) to mediate its oxidation state between 3+ and 4+ oxidation states. In this study, we have report pro-angiogenic property of CNPs and application which accelerates the healing of full-thickness dermal wounds in mice. Interestingly, we have also found that increase in surface 3+ oxidation state facilitate the angiogenesis process. The ability to facilitate wound healing of CNPs may provide a motivation to develop this technology for use in humans affected by traumatic injury, diabetes and/or burns.

3:20 PM

(ICACC-S5-005-2013) Increasing Mechanical Strength of Carbonate Apatite Block by Ca Salt Introduction

J. Harland*, K. Tsuru, Kyushu University, Japan; M. Maruta, Fukuoka Dental College, Japan; G. Kawachi, K. Ishikawa, Kyushu University, Japan

Carbonate apatite (CO3Ap) is an ideal bone substitute as it has excellent osteoconductivity and bioresorbability. Research has shown that CO3Ap block can be fabricated using calcium carbonate (calcite: CaCO3) block as a precursor, based on the dissolution-precipitation reaction, and the mechanical strength of CO3Ap block was increased by introduction of calcium lactate. However, the resultant CO3Ap block still needs improvement, as higher mechanical strength is desirable for clinical use in load-bearing sites. The objectives of this study were to investigate the feasibility of using calcium acetate in the Ca salt introduction method and examine the effect of reducing porosity, by the addition of extra CO3Ap crystals, on the mechanical strength of CO3Ap block. Calcium acetate (1 M) was introduced into the micropores of CO3Ap block under vacuum at room temperature. Next, the CO3Ap block was exposed to carbon dioxide (CO2) gas under atmospheric pressure for 14 days to carbonate the calcium salt to calcite. Finally, the CO3Ap block was immersed in 1 M disodium hydrogen phosphate (Na2HPO4) aqueous solution at 60°C for 14 days to transform the calcite into CO3Ap. Results suggest that the Ca salt introduction method enables fabrication of reinforced CO3Ap block with greater mechanical strength than the original CO3Ap block and sufficient strength to be a promising bone substitute in load-bearing areas.

3:40 PM

(ICACC-S5-006-2013) Bioactive Ceramic Foams for Bone Tissue Engineering

B. A. Mound*, J. P. Ball, J. B. Allen, F. Barrie, M. V. Manuel, J. C. Nino, University of Florida, USA

The development of bioactive materials for tissue regeneration and implants is of interest for the tissue engineering scientific community. Improvements in current polymeric materials for tissue regeneration and metals for implants are needed and it is clear that bioceramics can offer a path towards enhanced performance. We report the manufacturing of bioactive ceramic scaffolds with potential for orthopedic tissue engineering applications utilizing a direct foaming method. The direct foaming process allows for the control of the overall porosity, pore dimensions, and pore connectivity of the bioceramics. To investigate the potential of the scaffolds for tissue engineering applications, an assessment of the biocompatibility of the material systems and their mechanical properties is presented. The biocompatibility of ceramic foams made of ceria, known for its free radical scavenging ability, and of barium titanate, a piezoelectric material, will be discussed. The ability for bone specific cell types to attach and proliferate on these materials with no significant toxic effects will be demonstrated. The macro-, meso-, and microstructure of the ceramic foams will be presented and its effect on the mechanical properties. Finally, towards a meaningful comparison and assessment of the extended recent work in ceramics foams, the need for the development of standards for mechanical property testing of ceramic foams will be argued.

4:00 PM

(ICACC-S5-008-2013) Hydrothermal conversion of calcite foam to carbonate apatite

T. X. Nguyen*, Kyushu university, Japan; M. Michito, Fukuoka Dental College, Japan; T. Kanji, Kyushu university, Japan; M. Shigeki, Fukuoka Dental College, Japan; I. Kunio, Kyushu university, Japan

We have previously reported an inverse ceramic foam method aiming to improve mechanical strength of calcite foam that has interconnected porous structure. The modified foam was obtained by multiple polyurethane coating. In this study, calcium hydroxide (Ca(OH)2) slurry was poured into the foam. After drying, the foam was burnt out to remove polyurethane and to carbonate Ca(OH)2 under mixed O2-CO2 atmosphere. Ca(OH)2 was completely converted to calcite. Those calcite foams are the useful precursors for the preparation of the three-dimensional (3D) interconnected porous carbonate apatite (CO3Ap) foam. Therefore, we investigated the hydrothermal treatment of calcite foam to CO3Ap foam in phosphate solution. The results indicated that the conversion ratio depends on the degree of porosity of calcite precursor and calcite foam was completely transformed to CO3Ap foam at 200°C for 24 hours. The CO3Ap foam showed the increase in the compressive strength compared to conventional method. So, it is concluded that CO3Ap foam fabricated in this study could be a good candidate for the bone replacement material in clinical application.

4:20 PM

(ICACC-S5-007-2013) Collagen coatings on 45S5 Bioglass® scaffolds

J. Hum*, A. R. Boccaccini, University of Erlangen-Nuremberg, Institute of Biomaterials, Germany

Due to its excellent bioactivity, 45S5 Bioglass® is being highly considered for bone tissue engineering scaffold development. To enhance vascularisation and tissue in growth, these scaffolds must exhibit a highly porous structure with porosity between 80 and 90%. 45S5 Bioglass® scaffolds with a highly interconnected porous structure were fabricated by the polymer replica technique. To enhance the attachment and metabolism of osteoblasts, as well as the mechanical properties, collagen was used as coating material due to its biological properties. Immersion tests in simulated body fluid (SBF) were carried out to evaluate the impact of the presence of the coating on hydroxyapatite (HA) formation on the scaffolds. In addition, protein release as well as degradation behavior of the scaffolds were assessed in SBF solution.

S7: 7th International Symposium on Nanostructured Materials and Nanocomposites

Bio-active Nanomaterials and Nanostructured Materials for Bio-medical Applications

Room: Coquina Salon B
Session Chairs: Mufit Akinc, Iowa State Univ; Yoon-Bong Hahn, Chonbuk National University; Donglu Shi, University of Cincinnati

1:30 PM

(ICACC-S7-039-2013) Impact of the Physicochemical Properties of Engineered Nanomaterials on their Cellular Uptake and Potential Toxicity (Invited)

P. Dutta*, The Ohio State University, USA

Nanomaterials are expected to be increasingly incorporated into food ingredients and food packaging. The unique chemical and physical properties of nanoparticles that make it attractive for use in the food industry include surface characteristics, optical properties, guest molecule stabilization, and targeted delivery. Issues of nanoparticle stability, long-term storage and costs are also critical to the food industry, and so is the issue of nanoparticle toxicity. In a collaborative effort between chemists , chemical engineer and pathologists , we are examining how the physicochemical properties of commercially available nanoparticles influence the interactions with intestinal epithelial cells, with particular focus on toxicity, bioavailability and tissue distribution. We are also developing methodology to track the routes of distribution and sites of accumulation of ingested food-relevant nanoparticles in vivo. Nanoparticles of interest are zinc oxide, silica, titania, silver, and lycophene.

2:00 PM

(ICACC-S7-041-2013) Biocide activity of copper nanoparticles supported on biogenic silica

B. Cabal*, M. Miranda, M. Suárez, Nanomaterials and Nanotechnology Research Center (CINN), Spain; F. Rojo, F. Malpartida, National Center for Biotechnology (CNB-CSIC), Spain; R. Torrecillas, Nanomaterials and Nanotechnology Research Center (CINN), Spain; J. S. Moya, Materials Science Institute of Madrid (ICMM-CSIC), Spain

There is a significant need for improved materials with antimicrobial properties. The emergence of nanoscience and nanotechnology in the last decade presents opportunities for exploring the bactericidal effect of metal nanoparticles. The antimicrobial properties of copper nanoparticle are well-established. The present work reports on the synthesis, chemical, structural and morphological characterization of copper nanoparticles supported on biogenic silica. Samples of various copper loading levels from 1 to 20 % were obtained via a precipitation method followed by a chemical reduction. Commercial diatoms were used as starting materials. The antimicrobial activity of the obtained materials was screened against Gram positive and negative bacteria, and yeast.

2:20 PM

(ICACC-S7-042-2013) Investigation of surface properties of nano-structured TiO2 for dental implants design

S. Issa*, P. Cenedese, IICMPE-MCMC, CNRS UMR 7182, 2-8, rue Henri Dunant, 94320 THIAIS, France; C. Azevedo, U.F.R. Odontologie, France; P. Dubot, IICMPE-MCMC, CNRS UMR 7182, 2-8, rue Henri Dunant, 94320 THIAIS, France

The objective of this work is to study the influence of physico-chemical characteristics of TiO2 nanotubes on their interaction with biological molecules or cells, and study specific adsorption properties of these nanostructures which may optimize the osteointegration process of the dental implants. Titanium nanotubes were fabricated by anodic oxidation of Ti samples in a fluoride-based solution. TiO2 nanotubes surfaces were functionalized with hydroxyapatite Ca10(PO4)6(OH)2 and doped hydroxyapatite by Stontium using pulsed electrodeposition. Samples were characterized by IR,XPS DRX and SEM. The ability of such surfaces to adsorb biomolecules (Amino acids and larger biomolecules) at solid-liquid interface have been studied by FTIR spectroscopy. We found that nanostructuring of TiO2 surfaces can be optimized by chemical and electochemical treatment and create new surface sites which allow to get specific reactive sites on TiO2 nanostructured surfaces. These sites are points of "attachment" to a privileged bioactive coating formed of hydroxyapatite. A partial substitution of Ca2+ doped by Sr2+ was used to increase the cell growth mechanism, with a perspective study of a biological test of cells growth on TiO2. Ongoing studies allow us to disover the influence of creating controlled surfaces on the adsoprtion of biomolecules (amino acids, proteins) and cells for optimal osteointegration.

2:40 PM

(ICACC-S7-043-2013) High Performance Glucose and Cholesterol Biosensors Based on Zinc Oxide Nanostructures (Invited)

Y. Hahn*, Chonbuk National University, Republic of Korea

Zinc oxide (ZnO) is one of most exciting contenders for the fabrication of glucose and cholesterol biosensors. Especially, ZnO nanoscale structures have aroused a substantial interest for their applications as a biosensor due to large surface area to volume ratio, extraordinary electrochemical and thermal stabilities, nontoxic and biological size-compatible characteristics. However, most of the research groups not only used expensive gold or platinum electrodes, but also synthesized nanostructures on substrates then transferred and coated them onto electrodes, which needs additional processes such as preparation of nanostructures-containing solution, coating, network-forming for tight adhesion, and drying. More importantly, the reported cholesterol biosensors showed a low linear range of detection. In this lecture, we report a simple technique for the fabrication of highly selective, ultrafast, reliable and wide linear-range detecting glucose and cholesterol biosensors based on the aspect ratio-controlled ZnO NRs, grown directly on Si/Ag electrodes in solution. We found that the degree of enzyme immobilization on mediators is a crucial factor for the development of high performance glucose and cholesterol sensors which can detect in wide linear range with high selectivity and fast sensitivity.

3:10 PM

(ICACC-S7-044-2013) Nano-hydroxyapatite composites for medical applications

K. Balazsi, I. Lukacs, G. Gergely, Hungarian Academy of Sciences, Hungary; C. Chae, Hallym University, Republic of Korea; P. Gouma, State University of New York at Stony Brook, USA; S. Kim, Gangneung-Wonju National University, Republic of Korea; C. Balazsi*, Hungarian Academy of Sciences, Hungary

Hydroxyapatite, (Hap, Ca10(PO4)6(OH)2) is chemically similar to the mineral component of bones and teeth. HAp is among of the few materials that are classified as bioactive, meaning that it will support bone ingrowth and osseointegration when used in orthopaedic, dental and maxillofacial applications. In this work, nano- hydroxyapatite (nHA) was successfully produced by using recycled eggshell and phosphoric acid. nHA bioactivity was evaluated in animal (rabbit and mouse) models. Sixteen-4-month-old New Zealand white rabbits with an average weight of 2.8kg (range 2.5-3.0kg) were used in experiments. After bilateral parietal bony defects formation (diameter: 8.0mm), nHA was grafted. The control was unfilled defect. The bone regeneration was evaluated by micro-computerized tomograms (μCT) and histomorphometric analysis at 4 and 8 weeks. nHA-cellulose acetate hybrid composites realized by electrospinning and their microstructural, mechanical and biological characterization will be also presented. In conclusion, nHA from eggshell showed much more bone formation compared to unfilled control group in both μCT analysis and histomorphometric analysis. Considering that the eggshell is easily available and cheap, nHA from the eggshell can be good calcium source in tissue engineering.

3:30 PM

(ICACC-S7-045-2013) Bottom up Approach to Design of Nanostructured Materials: Biomimicking and Bioinspiration (Invited)

M. Akinc*, Y. Hu, Y. Yusufoglu, X. Liu, K. Schimdt-Rohr, S. Mallapragada, Iowa State Univ, USA

In order to understand and mimic the extracellular matrix of natural bone, block copolymers based on the nonionic, zwitterionic, anionic, peptide-conjugated polymers, diblock co-polypepttides, and polysaccharides were employed as templates for the growth of calcium phosphate, and zirconia from aqueous solutions. All block polymers used in this study were thermoreversibly gelling at or above room temperature. Depending on the experimental conditions, in particular pH of the solution, calcium phosphate formed as crystalline hydroxyapatite or Brushite whereas zirconium precipitated as amorphous hydroxide. Nanocomposites were characterized by solid state NMR, TGA, FTIR, and X-ray scattering techniques. Nanocomposite formation was confirmed by solid state NMR. Inorganic content of the nanocomposite depends on the critical gelling concentration, ionic nature of the polymer matrix employed as well as the pH of the solution. Hydroxyapatite was shown to grow in the form of thin, elongated crystallites as evidenced by TEM and SAXS. For zirconia, crystallization by heat treatment leads to formation of tetragonal ZrO_2 around 400 °C. Zirconia templated on agarose followed by freeze drying led to high surface area, porous ZrO_2. Porosity was retained up to 900 °C. The present work offers aqueous solution routes for bioinspired bottom-up approaches for synthesis of novel nanocomposites.

4:00 PM

(ICACC-S7-046-2013) Design of Multifunctional "Plug and Play" Nano-Carriers for Biomedical Applications (Invited)

H. Dong, Y. Li, Tongji University, China; D. Shi*, University of Cincinnati, USA

For biomedical applications, several multifunctional nano carriers are designed and developed for drug delivery, fluorescence imaging, and cell targeting. The design of one of the versatile nano-assemblies is based on the concept of "plug and play." The system is engineered on a nanoscaled graphene nano-sheet (GNS) platform via host-guest chemistry between the hybrid and functional payloads. Cyclodextrin (CD), an oligosaccharide consisting of six, seven or eight glucose units (α, β, or γ-CD, respectively), is utilized as the "host" molecule. This cone-shaped cavity of CDs can serve as hosts for a great variety of functional or biological "guest" molecules by taking advantage of its geometric compatibility and hydrophobic interactions between the CDs and the guest molecules. The nanohybird GNS/β-CD is fully capable of selectively accommodating/releasing various biological and functional agents, in a controlled fashion, including antivirus drug amantadine, fluorescent dye (5(6)-Carboxyfluorescein), and the RGD targeting ligands. The loading capability of 5(6)-carboxyfluorescein reaches as high as 110 % with a drug concentration of 0.45 mg/mL. The cyclic RGD is found to exhibit remarkable targeting effect for the HeLa cells.

4:30 PM

(ICACC-S7-047-2013) Self-Assembly of Nanomaterials: Ammonium Hydrogen Phosphate Crystals, Zeolite Crystals, and Lysozyme Fibers Characteristic of Alzheimer's Disease

K. Hari, Y. Lin, L. M. Cole-Burnett, B. J. Burnett, S. Xu, J. R. Brenner*, Florida Tech, USA

Self-assembly of nanoparticles is a naturally occurring process controlled by temperature, concentration, and time. Aggregation leading to bigger particles is common in organic and inorganic materials. Ammonium hydrogen phosphate, zeolites, and chicken egg lysozyme represent three different classes of materials whose aggregation was tracked using scanning electron microscopy (SEM) or atomic force microscopy (AFM) with time. The three materials followed different pathways in forming the aggregates. Ammonium hydrogen phosphate formed fractal intermediates, whereas lysozyme formed rod-like and circular intermediates. It was found that zeolites' organic framework, which can be completely removed via the high dilution factors common to most microscopies, plays a major role in the aggregation of zeolites. All the samples started out as monodispersed particles and ended up as either bimodal or even trimodal distributions. The shape and the path of aggregation were different for each class of materials; tracking these aggregation pathways is now part of a novel laboratory-based curriculum made possible by NSF Nanotechnology Undergraduate Education Grant #0939355.

4:50 PM

(ICACC-S7-048-2013) Controlling the Growth of Biofilms on Ceramics using Nanoparticle Coatings

C. Larimer, M. Islam, A. Ojha, I. Nettleship*, University of Pittsburgh, USA

Some opportunistic human pathogens in the mycobacteria genus have recently been discovered to be concentrated in showerhead biofilms. This is thought to correlate with the increasing incidence of infections derived from the use of domestic showers and demonstrates the need for durable surface protection strategies for domestic appliances and medical instruments that use water. Antibacterial nanoparticles have been proposed for such applications. Unfortunately, nanoparticle efficacy is generally evaluated in the free swimming planktonic state rather than the more resistant biofilm stage of the bacterium lifecycle. This presentation will describe the effect of silver nanoparticles coatings on mycobacteria biofilms grown on the types of ceramic and polymer membranes used in ultrafiltration. Silver nanoparticles coatings were found to inhibit biofilm growth but not completely prevent biofilm formation. Unique flow cell experiments were also performed to examine the effect of liquid flow conditions on biofilm development on ceramic materials. Again silver nanoparticles were able to slow the growth of biofilm but not entirely prevent it. The effect of these findings on the design and implementation of antibacterial nanoparticle coating will be discussed.

5:10 PM

(ICACC-S7-040-2013) A Green Chemical Approach for Highly Water-Soluble and Biocompatible Superparamagnetic Magnetite Nanoparticles for Enhanced MRI

S. Mathur, L. Xiao*, University of Cologne, Germany

Ultrasmall superparamagnetic iron oxide nanoparticles (USPIONs) were synthesized by a simple green chemical approach, in which a natural nutrient of vitamin C was used as reducing agent and its oxidized product was further played a role as capping agent. The as-prepared USPIONs have an average core size of 5.1 nm and exhibit good crystallinity and high magnetization saturation value (47 emu.g-1). The strong capping effects of oxidized vitamin C on the surface of the particles impart to the USPIONs an excellent solubility and stability in water, PBS buffer and cell culture media, as well as a remarkable biocompatibility as determined using primary human immune-competent cells and the zebra fish embryo tests. Detailed NMR analysis of the suspensions provides insight into the magnetic order within the colloid and demonstrates the suitability of the materials as negative contrast agents for MRI. Phantom experiments on the contrast agent (clinical 3 T MRI scanner) reveal an enhanced r2/r1 ratio of 36.4 (r1= 5 s-1mM-1 and r2= 182 s-1mM-1) by comparing with the clinically approved SPIOs and USPIOs, which implies the DHAA-Fe3O4 NPs suspensions are expected to be a promising candidate for negative contrast applications. The cellular uptake studies showed that NIH 3T3 cells have much higher uptake of the DHAA-Fe3O4 NPs than Sinerem@.

S8: 7th International Symposium on Advanced Processing and Manufacturing Technologies for Structural and Multifunctional Materials and Systems (APMT)

Joint S8 & S9: Rapid Prototyping of Porous Ceramics

Room: Coquina Salon A
Session Chair: Paolo Colombo, University of Padova

1:30 PM

(ICACC-S9-040-2013) Commercialization of Robocasting for the Production of Porous Structures (Invited)

J. Cesarano*, Robocasting Enterprises LLC, USA

Robocasting is a versatile layered-manufacturing technique which uses CNC methods to extrude (or "print") concentrated colloidal pastes containing a solvent carrier. Post deposition, removal of the solvent transforms the paste into a solid-like state thereby "curing" the structure and facilitating the creation of components without the need for support materials or sacrificial molds. Robocasting was originally conceived and developed at Sandia National Labs in 1996. Since then, the technology has been successfully spun-off into a private entity, Robocasting Enterprises LLC, and commercial viability for the manufacturing of porous structures is being realized. Robocasting is particularly suited for the creation of lattice structures comprised of cross-hatched layers of struts. This presentation will be used to review robocasting from both engineering and commercial perspectives. From an engineering perspective, the fundamentals of manipulating inter-particle forces in concentrated colloidal pastes for the explicit utility of robocasting ceramics and composites will be discussed. Furthermore, the character and performance of lattices for filtration, catalyst supports, and load-bearing hydroxyapatite bone scaffolds will be reviewed. From a commercial perspective, niche opportunities and the realities of transitioning from scientist to small-business president will be summarized.

2:00 PM

(ICACC-S9-041-2013) 3D printing of Porous Polymer-Derived-Ceramics

A. Zocca*, C. M. Gomes, J. Guenster, BAM Federal Institute for Materials Research and Testing, Germany; P. Colombo, E. Bernardo, University of Padova, Italy

Purpose of this study is to explore a novel application of 3D-printing to preceramic polymers, in order to produce porous Polymer-Derived-Ceramics. One of the main advantages of polymer-derived ceramics, besides their unique structure and properties, is the versatility of the shaping process, which take advantage of the fact that the starting material is a polymer. Preceramic polymers can be shaped using most of the plastic forming technologies (extrusion, injection molding, warm pressing, etc.) and converted to ceramic at a relatively low temperature (1100-1300°C). Selective laser curing has already been successfully applied to preceramic polymers, opening new possibilities for the free-form shaping of complex geometries by additive manufacturing. A new approach for the production of porous polymer-derived by additive manufacturing will be discussed, which is the application of 3D (indirect) printing to preceramic polymers followed by pyrolysis and thus ceramization. The polymeric nature of the material is exploited, since the preceramic powder can be selectively bound by means of an organic solvent, therefore enabling the building of complex architectures starting from a preceramic powder bed. A description of the influence of the main parameters involved in the process will be given, with a presentation of the results achieved so far.

2:20 PM

(ICACC-S9-042-2013) Cellular Si-SiC ceramics by indirect rapid prototyping

C. D'Angelo*, A. Ortona, SUPSI, Switzerland; D. Gaia, S. Gianella, Erbicol, Switzerland

Cellular ceramics have been produced by well established rapid prototyping techniques such stereolihography followed by heat treatments or selective laser sintering. In this work we propose a novel hybrid methodology to produce cellular ceramics of any morphology, combining 3D polymer ink printing and replica. This method overcomes surface finish limitations of the current RP techniques by manufacturing ceramic structures with fine microstructures smooth surfaces. RP structures showed higher strength capability under compression compared to commercial reticulated ceramics produced with the same technique.

2:40 PM

(ICACC-S9-043-2013) Highly-porous LAS glass-ceramics by 3D Printing

C. M. Gomes*, A. Zocca, J. Guenster, BAM Federal Institute for Materials Research and Testing, Germany; P. Colombo, University of Padova, Italy

Aim of this work is the production and optimization of highly porous ordered LAS glass-ceramics with remarkable mechanical properties by indirect 3D printing. Precursor glass powders were printed into 3D ordered structures and heat treated to sinter and crystallization. The final strength and porosity were dependent on the chosen periodic unit cell, the strut morphology and the thermal treatment. Two geometries for the repeated unit cell have been elected: the so-called tetrakaidecahedron and also a diamante-like structure. Parts showing an open porosity of circa 60% achieved values of compressive strength of circa 15 MPa. The crystalline phases on the final porous glass-ceramic were mainly β-spodumene solid solution and a secondary phase of lithium disilicate. The precision of the printed geometry and the density of the struts in the parts were depended on several processing parameters (e.g. powder size, powder packing ratio, flowability and layer thickness) and also from the sintering process.

Prototyping, Patterning and Shaping

Room: Coquina Salon A
Session Chairs: Nahum Travitzky, University of Erlangen-Nuremberg; Soshu Kirihara, Osaka University

3:20 PM

(ICACC-S8-042-2013) Creation of Surface Geometric Structures by Thermal Micro-lines Patterning Techniques

S. Kirihara*, Y. Itakura, S. Tasaki, Osaka University, Japan

Thermal micro-lines patterning were newly developed as novel technologies to create geometrical intermetallics patterns for mechanical properties modulations of steel substrates. pure aluminium particles were dispersed into the photo solidified liquid resins at 40 % in volume fraction, and the slurry were spread on the stainless steel substrates with 50 μm in layer thickness. On the steels substrates, micro patterns with fractal structures were drawn and fixed by an ultra violet laser scanning of 100 μm in spot size. The patterned pure metal particles were heated by the argon arc plasma spraying, and the intermetallic or alloy phases with high hardness were created through reaction diffusions. The mechanical properties and surface stress distributions were measured and simulated by a tensile stress test and finite element method.

3:40 PM

(ICACC-S8-043-2013) Mechanical Properties and Cracking Behavior of 3D Printed Refractory Ceramics

J. F. Bredt*, Massachusetts Institute of Technology, USA

Samples built from alumina-silica refractory media, developed for 3D Printing by Viridis 3D, were measured for dimensional change over the course of processing and tested for strength at different temperatures. In addition, the build process and post-build treatment of 3D printed parts were examined to identify variables contributing to preuse failure by cracking. The flexibility of 3D Printing enabled the design of test parts with variable fragility, with which cracking tendency could be measured. Dog-bone samples were printed in three compositions, using two media (Virishell V18 and Virifrax). After determining the degree of shrinkage and geometric distortion over the course of processing, the samples were subjected to uniaxial tension to failure by Instron, at 20 and 700°C. The composition with the most consistency in robustness and geometry was then used to examine cracking tendency. The strongest material had a UTS of 4.5 ± 1.0 MPa, but exhibited much distortion (7-14 vol% shrinkage). The most geometrically consistent material (1.5% shrinkage) had a UTS of 1.4 ± 0.5 MPa, with no temperature dependence. This material was used to print a series of identical parts to study cracking phenomena. 3D Printed Virifrax parts are about as strong as traditional refractory ceramics, while allowing for greater flexibility of part design. A relation between drying rate and cracking tendency was measured.

4:00 PM

(ICACC-S8-044-2013) Optimized Shaping Process for Transparent Spinel Ceramic

A. Kaiser*, LAEIS GmbH, Luxembourg; T. Hutzler, Fraunhofer Institute for Ceramic Technologies and Systems, Germany; A. Krell, Fraunhofer Institute for Ceramic Technologies and Systems, Germany; R. Kremer, ALPHA CERAMICS GmbH, Germany

Bulky transparent ceramic, especially spinel ($MgAl_2O_4$), can be used for applications such as high-energy laser windows and lightweight armor. One of the traditional routes to manufacture transparent spinel plates includes the steps of material preparation, uniaxial pressing, cold isostatic pressing (CIP), de-bindering and hot isostatic pressing (HIP). When larger sizes are required, CIP can become one of the bottlenecks of the process chain. The paper shows, how an optimized uniaxial hydraulic pressing process allows to avoid the cold isostatic pressing completely. The process is described and the first results of the investigation of transparent spinel properties are discussed. This simplified process will allow to reduce the manufacturing costs for larger sized transparent spinel significantly and/or improve the production capacity.

4:20 PM

(ICACC-S8-045-2013) Fabricating complex-shaped ceramic components by injection molding ceramic suspension gels at room temperature

V. L. Wiesner*, J. P. Youngblood, R. W. Trice, Purdue University, USA

Room-temperature injection molding of ceramic suspension gels (CeraSGels) is proposed as a novel, low-cost and energy efficient processing method capable of forming dense ceramic components with complex geometries. CeraSGels are highly loaded with ceramic (>50 vol.%) and have a minimal amount of polymer carrier (<5 vol.%) dispersed in water. Rheological studies using parallel plate rheometry of alumina CeraSGels revealed that suspensions containing PVP as a viscosity modifier behaved like yield-pseudoplastic fluids at room temperature. Alumina samples have been fabricated with high green body strength and are machinable in the green state despite their low polymer content. After binder burnout and sintering, bulk density of sintered samples using the Archimedes technique was found to reach >98% theoretical density with linear shrinkage of <16%. SEM revealed minimal pore formation within sintered samples. Ultimate strength of the sintered alumina samples was determined using the ASTM C1323-96 compressive C-ring test.

4:40 PM

(ICACC-S8-041-2013) Utilization of Nano-Constituents in Thermoplastics for High Strength, Low Loss Tangent Fused Deposition Three-Dimensionally Printed Structures

Z. J. Larimore*, United States Army Research Labs, USA

Additive Manufacturing (AM) (3-D printing, rapid prototyping, etc.) techniques have made significant advances in the past 25 years. The development of AM systems is constantly yielding higher fidelity systems with larger throughput volumes and decreased initial cost investment. However, advances in materials development for these systems have lagged considerably behind the development of new printing technologies. One AM process that has become increasingly prevalent is Fused Deposition Modeling (FDM); which utilizes the extrusion of thermoplastics through a deposition nozzle. It has previously been shown that mechanical and electrical properties of thermoplastics can be enhanced through the addition of nano-constituents. For this experiment, nano-constituents such as carbon nano-tubes (CNT), graphitic oxides, and ferrite magnetic nano-particles were compounded into traditional FDM materials. These nano-loaded materials were then printed into three dimensional structures and tested to determine variations in mechanical and electrical properties versus the non-loaded base materials.

S10: Virtual Materials (Computational) Design and Ceramic Genome

Virtual Materials Design and Modeling

Room: Oceanview

Session Chairs: Jian Luo, UCSD; Paul Rulis, University of Missouri - Kansas City

1:30 PM

(ICACC-S10-028-2013) Multiscale Modeling of Ablative Composites for Atmospheric Entry Applications (Invited)

J. W. Lawson*, C. W. Bauschlicher, T. H. Squire, J. D. Monk, NASA Ames Research Center, USA

Atmospheric entries of space vehicles represent some of the most extreme application environments experienced by modern materials. NASA has a variety of missions with different vehicles, different planets, and different entry trajectories. Each scenario can have specific material requirements for the thermal protection system (TPS). Entry TPS materials are usually ablative composites consisting of carbon fiber reinforcement and a phenolic polymer matrix. These materials and their performance in these extreme environments are inherently multi scale systems. We illustrate this fact with several examples of computational material modeling at different length scales. First, we perform ab initio calculations to obtain the optical spectra of the carbon char layer that forms on the surface of the TPS. The optical response of char determines the impact of shock layer radiation and also the efficiency of thermal radiation. Second, we perform atomistic simulation of the pyrolysis of the phenolic matrix. Pyrolysis is an endothermic process and obtaining a high char yield is fundamental to the performance of these materials. Third, we perform imaged-based, finite element method (FEM) computations of the thermal conductivity of fibrous carbon materials. FEM meshes are constructed on 3D X-ray CT images. From these computations, the effective thermal conductivity of the material can be obtained.

2:00 PM

(ICACC-S10-029-2013) Thermomechanical simulation of C/C composites from X-ray CMT images (Invited)

G. L. Vignoles*, O. Caty, University Bordeaux, France; G. Couégnat, CNRS, France; M. Charron, T. Agulhon, University Bordeaux, France

One of the most important properties of dense C/C composites intended for ultra-high-temperature applications is their thermal expansion. This quantity is difficult to estimate by “virtual material” models in the case of complex fibrous architectures involving weavings and needlings. We present here a technique based on the processing of medium-resolution X-ray CMT scans of “2.5D” C/C composites. The local orientation of the fiber bundles is detected throughout the sample; then, local thermal and mechanical properties are affected to every voxel accounting for this fiber orientation. A finite-element solver is used for a thermoelastic problem resolution in the image, in a “voxel-element” approach. Preliminary results and validations are shown and discussed.

2:30 PM

(ICACC-S10-030-2013) Inelastic Design of MMCs with Lamellar Microstructure

R. Piat*, Y. Sinchuk, Karlsruhe Inst of Technology, Germany

The purposes of this paper are the optimal design and modeling of inelastic behavior of MMCs with lamellar microstructure. The material under consideration consists of the two phases: ceramics (Al2O3) and aluminum alloy (Al12Si) phases. For modeling of the elasto-plastic behavior of the metal the J2 flow theory was used. The brittle damage model was used for modeling of the failure of the ceramics. Single domain of this material with preferred orientation of lamella was modeled using FE-model and homogenization procedure. Results of the modeling were verified by comparing with experimental data and good corresponding between obtained results was observed. The optimization problem for determination of the sample microstructure with minimal compliance was formulated. The design variables of the posed problem are local orientation of the lamellar domains and the volume fraction of the ceramics in the domain. Solution of the optimization problem is carried out for prescribed volume of the ceramics in the whole specimen. Resulting optimal microstructure were obtained for different geometries of the specimen and for different loading cases. Obtained results show that the microstructure design obtained using inelastic model is partially different from the elastic one.

3:20 PM

(ICACC-S10-031-2013) Explicit modelling of crack initiation and propagation in the microstructure of a ceramic material generated with Voronoi tessellation

S. Falco*, N. A. Yahya, R. I. Todd, N. Petrinic, University of Oxford, United Kingdom

Ceramic materials are currently used for protection of both vehicle and personnel armour since they can be very effective in stopping ballistic projectiles by fragmenting and/or eroding them. However, such armour is generally fairly heavy and does not have multihit capability, mainly due to excessive fragmentation during impact. The development of new ceramics for armour is further hindered by the limited understanding of the intrinsic deformation mechanisms caused by impact loading. In this paper the focus is on the initiation and propagation of cracks in ceramic microstructures, as in different armour ceramics (e.g alumina) the main cause of failure is the inter-granular crack propagation. To simulate this phenomenon the mesh of a polycrystalline aggregate is first created and then crack initiation and propagation along grain boundaries is modelled. A method to generate three-dimensional meshes of polycrystalline aggregates based on Hardcore Voronoi tessellation of random points distribution is presented. The mesh created is enriched with zero-thickness cohesive elements along the grain boundaries to simulate explicitly the propagation of inter-granular cracks. Finally, the numerical results are compared with micro-cantilever beam tests.

3:40 PM

(ICACC-S10-032-2013) Multi-scale modeling of textile reinforced ceramic composites

M. Sejnoha*, J. Vorel, CTU in Prague, Faculty of Civil Engineering, Czech Republic

The present paper describes a two-step homogenization for the evaluation of effective elastic properties of textile reinforced ceramic composites. Attention is devoted to polysiloxane matrix based composites reinforced by plain weave textile fabrics. Glass, basalt and carbon reinforcements are considered. X-ray microtomography as well as standard image analysis are adopted to estimate the volume fraction, shape and distribution of major porosity, considerably influencing the resulting macroscopic response. The numerical procedure effectively combines the Mori-Tanaka averaging scheme and finite element simulation carried out on a suitable statistically equivalent periodic unit cell. The computational strategy employs the popular extended finite element method to avoid difficulties associated with meshing relatively complex geometries on the meso-scale. Comparison with the results obtained directly from the finite element simulations of available Micro-CT scans is also provided.

4:00 PM

(ICACC-S10-033-2013) The self-healing matrix composites: Numerical approach of dynamic behavior of a self-healing fluid and the composite in a rotational system

L. Benazzouk*, E. Arquis, N. Bertrand, University of Bordeaux 1, France; C. Descamps, Snecma, France; M. Valat, University of Bordeaux 1, France

Self-healing matrix composites are currently in full development their use in the aerospace field is mainly due to their remarkable physical and chemical properties. Microscopic cracks are however inherent in the process of developing and are aggravated by the conditions of the use of composite parts. The self-healing matrix has a feature to allow the formation of viscous glasses in a crack by chemical reaction between the constituent elements of the matrix and oxygen. This glass by filling out the crack protects the fiber reinforcement and extends the life of the composite. To begin with, we focus on dynamic behavior of glass drops formed in a crack model by studying their growth and coalescence. These cases of coalescence lead, either to the formation of a liquid film or to the formation of a bridge. These phenomena are modeled using Thetis software developed by I2M to track the evolution of the glass in the crack when the composite material is subjected to an oxidizing environment as well as intense external mechanical stresses such as rotation. Then the experimental studies are carried to study the wettability of various glasses on a mixed substrate, representative of the multilayer self-healing matrix. Finally, numerical simulations of these experiments are conceivable to compare simulation results with those obtained experimentally.

4:20 PM

(ICACC-S10-034-2013) Numerical estimation of the infiltrability of woven CMC preforms

G. L. Vignoles*, W. Ros, C. Germain, University Bordeaux, France

Preforms made of two different arrangements of woven SiC fibers were examined under the angle of their ease to infiltrate by chemical vapor infiltration (CVI) for the preparation of SiC/SiC composites after a first slurry impregnation/pyrolysis step. Based on X-ray CMT scans, numerical infiltration tools – previously validated on the CVI of pyrocarbon [1] - were used to illustrate and to quantify the differences of infiltration behavior between these two samples. [1] G. L. Vignoles, W. Ros, G. Chollon, F. Langlais, C. Germain, Quantitative validation of a multi-scale model of pyrocarbon chemical vapor infiltration from propane, Procs. ICACC 2012 (to appear in Ceram. Eng. Sci. Procs, 2013)

4:40 PM

(ICACC-S10-035-2013) First Principles Calculations of Boron Suboxide

J. S. Dunn*, T. Beudet, Army Research Laboratory, USA; J. R. Smith, University of Michigan, USA

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 large, 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 wetability, 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.

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

Structural Stability under Extreme Environments I

Room: Coquina Salon F
Session Chair: Matthieu Bugnet, McMaster University

1:30 PM

(ICACC-S12-022-2013) Arc-jet testing of LaB6-containing ZrB2-SiC materials under high enthalpy supersonic air flows (Invited)

F. Monteverde*, National Research Council of Italy, Italy

The design of hypersonic vehicles needs leading edge components with sharp profile to improve flight performances. Such components are subject to very stressful heat fluxes in corrosive plasmas from atmosphere, and temperatures exceeding 2300K for several minutes may become a projected service condition. The spectrum of possible material candidates for such extreme conditions is presently grouped within the class of ultra-high temperature ceramics (UHTCs). There has recently been a renewed interest in UHTCs, particularly in the regard of methods for enhancing the resistance to oxidation through the "in-situ" formation and growth (at high temperature) of solid refractory phases. The effects on the resistance to oxidation coming from the addition of LaB6 particulate into hot-pressed ZrB2-SiC matrices were investigated by using an arc-jet testing facility. Differently from oxidizing furnaces or oxyacetylene torches, an arc-jet facility reproduces conditions recalling those experienced during hypersonic re-entry. CFD simulations were essential to first model the test conditions of the free-stream and boundary layer, and thus match the in-situ determinations to material evolution during arc-jet testing. For surface temperature approaching 2300K, the contemporary presence of SiC and LaB6 additives did not bring obvious advantages to improve oxidation resistance of ZrB2-based matrices.

2:00 PM

(ICACC-S12-023-2013) Modelling Damage and Failure in Structural Ceramics at Ultra-High Temperatures

M. Pettina*, F. Biglari, D. D. Jayaseelan, P. Vandeperre, Imperial College London, United Kingdom; P. M. Brown, DSTL Porton Down, United Kingdom; A. Heaton, K. Nikbin, Imperial College London, United Kingdom

Assessment of damage and failure of structural ceramics at extreme temperatures is an area that needs substantial development. In order to develop a robust tool for predictive modelling it is important to assess what material and mechanical properties can be reasonably derived to input in the models. The paper considers the state of the art in both testing and modelling and identifies the material variables that need to be derived for modeling ultra-high temperature ceramics structural failures. It focuses on monolithic ZrB2 ultra-high temperature ceramic for which a reasonable set of test data is available. Relevant properties for this material relating to power law creep deformation mode at temperatures greater than 2000K are used in a remaining multiaxial ductility damage model. In this way the essential properties required to develop predictive damage simulations are investigated, underlining the importance of having accurate materials test data. As an example representative three point bend geometry is modeled to predict damage and cracking for the relevant creep constitutive properties found for ZrB2 at extreme temperatures.

2:20 PM

(ICACC-S12-024-2013) Oxidation behavior of Graphene NanoPlatelets Reinforced Tantalum Carbide composites in High Temperature Plasma Flow

A. Nieto*, D. Lahiri, C. Zhang, A. Agarwal, Florida International University, USA

Tantalum Carbide is an ultra high temperature ceramic (UHTC) with various high temperature applications such as scramjet engines and hypersonic entry vehicles. Graphene NanoPlatelets (GNP) consist of 20-30 sheets of graphene. Graphene Nanoplatelets reinforced Tantalum Carbide composites are consolidated by spark plasma sintering (SPS) in order to improve fracture toughness of TaC. The retention and improvement of TaC oxidation and refractory properties is vital to any UHTC composite as these materials would have application in high temperature, chemically active environments. TaC-GNP composites are exposed to a plasma flow exceeding 2500 °C for 60 seconds. TaC-GNP oxidized microstructure is characterized using scanning electron microscopy (SEM), x-ray diffraction (XRD), energy dispersive spectroscopy (EDS), and micro-raman spectroscopy. The microstructural evolution changes as the content of GNP is changed. The GNP increase the thermal conductivity and suppress the formation of oxides by more than 50%.

2:40 PM

(ICACC-S12-025-2013) Modelling of oxidation effects in the Ultra High Temperature Ceramic structures

M. Pettina*, Imperial College London, United Kingdom; F. Abdi, Alpha STAR Corporation, USA; K. Nikbin, Imperial College London, United Kingdom; Y. Xue, Alpha STAR Corporation, USA

Ultra High Temperature Ceramic (UHTC) composites could see operational temperatures between 1400-2500°C. Material properties and damage mechanisms could substantially vary over this range. In this paper the lower temperature limits are considered where oxidation could play a key role in the degradation of the mechanical properties and hence the lifetime of the ceramic component. The paper considers a combination of analytical and numerical models to describe damage in these materials where oxidation may have an effect. It focuses on the HfB2-SiC and ZrB2-SiC UHTC composites which seem to be the most attractive candidates for UHT applications. The models can aid in the design of robust CMC components, reduce cost and risk, and allow maintenance schedules to be set up. The GENOA code for multi-physics multi-scale durability and damage tolerance (D&DT) assessment was enhanced by implementing key elements of environmental degradation mechanics and can be used to predict long-term environmental effects of CMC components. Prediction of recession, global oxidation (oxide build up), crack density formation, discrete oxidation, fiber rupture (creep) behaviour, low cycle fatigue and interphase mechanics can be computed for CMC. Simulations are made with available data for the candidate HfB2- and ZrB2-based CMC materials. The preliminary results are presented with the view of developing the models further.

Structural Stability under Extreme Environments II

Room: Coquina Salon F
Session Chair: Shaoming Dong, Shanghai Institute of Ceramics, CAS

3:20 PM

(ICACC-S12-026-2013) Behavior of MAX phase thin films under ion irradiation (Invited)

M. Bugnet*, CNRS-Université de Poitiers-ENSMA, France, CNRS-Université de Poitiers-ENSMA, FranceMcMaster University, Canada; V. Mauchamp, T. Cabioc'h, CNRS-Université de Poitiers-ENSMA, France; E. Oliviero, CNRS-IN2P3-Université Paris-Sud, France; F. Mortreuil, CNRS-Université de Poitiers-ENSMA, France; P. Eklund, Linköping University, IFM, Sweden; M. Jaouen, CNRS-Université de Poitiers-ENSMA, France

MAX phases are potential candidates for applications as structural materials in future nuclear reactors thanks to their exceptional mechanical and thermal properties, their strong damage tolerance at high temperature and refractoriness. The work presented here aims to shed light on the behavior of these materials under extreme environment such as ion irradiation. Selected Ti-based and Cr-based MAX phase epitaxial thin films were grown by magnetron sputtering and exposed to low energy (150-360 keV) Ar^{2+} and Xe^{2+} beams. The microstructural modifications are investigated by electron energy loss spectroscopy and X-ray absorption spectroscopy, in addition to X-ray diffraction and transmission electron microscopy. The interpretation of spectral features by first principles calculations in Ti_3AlC_2 evidences that Ti_6C octahedra layers are very resistant to irradiation damage. In contrast, Al layers are strongly disordered. Similar behaviors are suggested for Ti_2AlC, Ti_2AlN, and partly for Cr_2AlC. Although Ti-based materials are still crystalline after irradiation at high fluence, Cr-based compounds rapidly amorphize. Of particular interest for nuclear applications, it is evidenced that the initial crystalline structure of most compounds is recovered after post-irradiation annealing. We suggest that the behavior of these materials in irradiative environment can be tuned by the chemical composition and the stacking sequence.

3:50 PM

(ICACC-S12-027-2013) Ultra High Temperature Mechanical Testing of ZrB_2 Based Ceramics

E. W. Neuman*, G. E. Hilmas, W. G. Fahrenholtz, Missouri University of Science and Technology, USA

Mechanical properties of hot pressed zirconium diboride (ZrB_2) and zirconium diboride – silicon carbide (ZrB_2-SiC) composites were tested at room temperature and at elevated temperatures. ZrB_2 with 0.5 wt% C, and ZrB_2-SiC composites with 30 vol% SiC as a dispersed particulate phase, were hot pressed to full density at 2150°C and 1950°C under an applied pressure of 32 MPa in an inert atmosphere. The hot pressed billets were machined to ASTM standard test bars with the tensile surface polished to 1 μm. Four-point bend tests and chevron notch fracture toughness, from room temperature to 1600°C, were performed in air. Four point bend tests and chevron notch fracture toughness were also performed up to 2300°C in a flowing argon atmosphere. The room temperature flexure strength of ZrB_2 was measured to be ~380 MPa. The strength of ZrB2 was determined to be ~220 MPa from 1600°C to 2300°C. The flexure strength of ZrB_2-30SiC at room temperature was ~680 MPa. The strength of ZrB_2-30SiC was determined to be 420 MPa at 1600°C, decreasing 220

MPa at 1800°C, and having a yield strength of ~40 MPa at 2000°C. The influence of microstructure, and testing environment, on the mechanical properties will be discussed.

4:10 PM

(ICACC-S12-029-2013) Thermal Stability of Cr2AlC and Ta4AlC3 in Argon Atmosphere at Elevated Temperature

J. Low*, Curtin University, Australia

The susceptibility of two MAX phases (Cr2AlC and Ta4AlC3) to high-temperature thermal dissociation in argon environment has been investigated using in-situ synchrotron radiation diffraction. In argon, these phases decomposed above 1400°C through the sublimation of Al element, forming a surface coating of binary carbide. The kinetics of isothermal phase decomposition was modelled using the Avrami equation and the Avrami exponent (n) of isothermal decomposition of Cr2AlC and Ta4AlC3 was determined to be 0.65 and 0.21 respectively. The characteristics of thermal stability and phase transitions in Cr2AlC and Ta4AlC3 are compared and discussed.

4:30 PM

(ICACC-S12-028-2013) Hafnia polycrystals with a polymer-derived amorphous HfSiCNO interfacial phase for Ultrahigh Temperature Structural Applications

I. Lisenker*, R. Raj, University of Colorado, USA

Composites of HfO2 and polymer derived ceramic (PDC) SiCN were created by sintering HfO2 powder coated with crosslinked PDC precursor. Efficient coating process appears critical to achieving a functional composite. The PDC and hafnia form an interfacial phase that effectively prevents grain growth up to 1450C and appears to retard it up to at least 1600C. Kinetics of the high temperature oxidation process are explored as reflected in the mechanical properties and evolution of phases of the composite.

S13: Advanced Ceramics and Composites for Sustainable Nuclear Energy and Fusion Energy

Radiation Defects in Ceramics / Codes and Standards

Room: Ponce DeLeon
Session Chairs: Sosuke Kondo, Kyoto University; James Hemrick, Oak Ridge National Laboratory

1:30 PM

(ICACC-S13-001-2013) Defect Stability and Mobility in Nano-engineered Silicon Carbide (Invited)

T. Oda*, University of Tennessee, USA; Y. Zhang, Oak Ridge National Laboratory, USA; W. J. Weber, University of Tennessee, USA

Silicon carbide (SiC) is an important material in a wide range of engineering fields including application in nuclear reactors. Recent research has experimentally revealed that a nano-engineered SiC (NE-SiC), containing nanograins with high-densities of stacking faults, exhibits extraordinary irradiation resistance. In order to gain insights on the underlying mechanisms, the stability and the mobility of intrinsic defects in NE-SiC were studied. We performed classical molecular dynamics simulation (MD) and first-principles calculation based on density functional theory (DFT). Defect structures and migration paths were widely examined using MD, and then were refined and screened using DFT. Three different simulation cells were prepared in order to depict the fundamental nature of the NE-SiC: (1) 3C-SiC single crystal, (2) 3C-SiC with extrinsic stacking faults, and (3) 3C-SiC with intrinsic stacking faults. MD simulations showed that the mobility of interstitial Si was enhanced in NE-SiC, while that of interstitial C and vacancies was largely unchanged. The enhanced mobility of the interstitial Si was attributed to the stacking faults because the mobility depends on stacking-fault density. Defect energies were also changed near stacking faults. Correlation between defect natures and the high radiation resistance in NE-SiC will be discussed.

2:00 PM

(ICACC-S13-002-2013) Off-stoichiometric Sintering of Oxide Fuel and Fuel Surrogates

J. B. Henderson*, Netzsch Instruments North America LLC, USA

Oxide fuel is used in the vast majority of LWRs and is still a focus of research 50 years on. Much of this work has been directed at gaining a more complete understanding of the parameters which control the sinterability and quality of the fuel and hence its ultimate performance. Despite the impressive amount of work done on this subject, many open questions remain. A major player impacting processability is stoichiometry. This is because diffusion is controlled by the defect structure, which in turn is controlled in part by stoichiometry, i.e. oxygen-to-metal ratio (O/M). The purpose of this work was to investigate the interrelationship between O/M, defects and diffusion and their impact on sinterability. The materials investigated were UO_2 and CeO_2 and UO_2-$GdO_{1.5}$ and CeO_2-$GdO_{1.5}$ blends. The measured thermal expansion and O/M data on the single-component systems clearly demonstrate the impact of stoichiometry on sinterability. In the case of the more complex powder blends, the data show that stoichiometry plays an even more important role, because not only is the sintering of the solutionized system O/M dependent, but the diffusion of the gadolinia dopant into the fluorite structure as well. The simultaneous dopant diffusion and sintering create, in some cases, a blocking mechanism which compromises final density and can only be explained with the aid of O/M data. The results of this work will be presented.

2:20 PM

(ICACC-S13-003-2013) Effects of Ionization on Irradiation Damage in Silicate Ceramics

W. J. Weber*, M. Backman, University of Tennessee, USA; Y. Zhang, Oak Ridge National Laboratory, USA; M. Toulemonde, University of Caen, France

The interaction of ions with solids results in energy loss to both atomic nuclei and electrons. At low energies, nuclear energy loss dominates, and irradiation damage occurs primarily by ballistic collisions. At high energies, electronic energy loss dominates, and the intense ionization can lead to latent track formation. At intermediate ion energies, which includes ions generally used to study irradiation damage in nuclear ceramics, nuclear and electronic energy losses are of similar magnitude and can lead to synergistic or competitive processes that affect the evolution of irradiation damage. Experimentally, we have shown that that there is a synergy between nuclear and electronic energy losses on damage production in amorphous SiO_2 at intermediate ion energies. Large scale molecular dynamics simulations, which include ballistic collisions and local heating based on the inelastic thermal spike model, have confirmed the additive effect of nuclear and electronic energy losses on damage production in SiO_2. Similar synergy between ionization and ballistic processes is observed experimentally in $ZrSiO_4$ irradiated with intermediate ion energies; while in $Ca_2La_8(SiO_4)_6O_2$, ionization leads to competitive dynamic recovery processes under irradiation that decrease damage production.

2:40 PM

(ICACC-S13-004-2013) A Hybrid Model on Low Energy Ion Beam Induced Quantum Dot Structuring in GaAs

E. Hernandez*, University of Michigan, USA; V. Tikare, Sandia National Laboratory, USA; L. Wang, University of Michigan, USA

Ion beam nano-structuring, e.g. quantum dots (QDs) and nano-porous structures, of semiconductors has been gaining interest due to their potential applications. Low energy ion beams, in the range of a few to tens of keV, are able to induce the self-assembly of QDs nano-structures. We developed a hybrid model, which integrates kinetic Monte Carlo (kMC) and phase field techniques to simulate low energy ion irradiation of an initially flat surface. This model properly describes the evolution of these QDs under irradiation conditions prescribed by normalized distributions of the damage rate and energy deposition. The kMC, an event-selection algorithm, has been coupled with the Cahn-Hilliard equations to describe the phase evolution behavior. We are able to observe that development of a quasi-liquid phase film and mass redistribution are adequate in describing the formation of the QDs. There is a clear correlation between the system's kinetics and thermodynamics in determining the proper conditions under which these structures form. Sandia Corporation is a wholly owned subsidiary of Lockheed Martin Corporation operated for U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

3:20 PM

(ICACC-S13-005-2013) Test Methods for Hoop Tensile Strength of Ceramic Composite Tubes for Light Water Nuclear Reactor Applications (Invited)

M. G. Jenkins*, Bothell Engineering and Science Technologies, USA; J. A. Salem, 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 ceramic matrix composites (CMC) thereby enhancing fuel performance and accident tolerance of LWRs. Silicon carbide fiber-reinforced silicon carbide-matrix (SiC/SiC) composites demonstrate tolerance to the irradiation and chemical environments of LWRs. Loss of gas tightness and mechanical integrity due to the build-up of internal gas pressure and the swelling of fuel pellets are among the anticipated failure modes for the LWR fuel cladding. Therefore, rigorous determination of the hoop tensile (or equivalent) strength properties is critically important for evaluation of SiC/SiC CMC fuel claddings. Because there are no commonly-accepted design methodologies for advanced composite tubular components, there are almost no mechanical test standards for any properties of CMC tubular components. Therefore, some current and proposed test methods for measuring tensile hoop strength of composite tubes are presented, discussed, and compared for application to CMCs. Test methods are presented in terms of the following experimental issues — test specimen geometries/preparation, test fixtures, test equipment, interferences, testing modes/procedures, data collection, calculations, reporting requirements, precision/bias.

3:40 PM

(ICACC-S13-006-2013) Test Methods for Flexural Strength of Ceramic Composite Tubes for Small Modular Reactor Applications

M. G. Jenkins*, Bothell Engineering and Science Technologies, USA; T. L. Nguyen, Levitas Consultants, USA

US DOE is planning to use advanced materials for the core and the reactor unit components in various advanced Small Modular Reactor (SMR) concepts. Ceramic matrix composites (CMC), in particular silicon carbide (SiC) fiber SiC-matrix (SiC/SiC) composites, could revolutionarily expand the design window for various components in terms of operating temperature, applicable stress, and service life, as compared to heat-resistant metallic alloys, while significantly improving safety margins and accident tolerance. Examples of CMC tubular components include control rod sleeves, control rod joints, and fuel rods. Anticipated failure modes for these components include axial and hoop tension, axial flexure, axial and diametral compression, and axial shear. Because there are no commonly-accepted design methodologies for advanced composite tubular components, there are almost no mechanical test standards for any properties of CMC tubular components. Therefore, some current and proposed test methods for measuring axial-flexure strength of composite tubes are presented, discussed, and compared for application to CMCs. Test methods are presented in terms of the following experimental issues — test specimen geometries/preparation, test fixtures, test equipment, interferences, testing modes/procedures, data collection, calculations, reporting requirements, precision/bias.

4:00 PM

(ICACC-S13-008-2013) New ASTM Committee C28 Material Specifications for Carbon-Carbon and SiC-SiC Composite for Nuclear Applications

S. T. Gonczy*, Gateway Materials Technology, USA; Y. Katoh, Oak Ridge National Laboratory, USA

The ASTM C28 Committee on Advanced Ceramics has developed specification documents for fiber-reinforced carbon-carbon (C-C) and silicon carbide-silicon carbide (SiC-SiC) composites. These ceramic matrix composites (CMCs) are being developed as fuel rod cladding in Light Water Reactors and as structural core components in the Very High Temperature Reactor. The specifications serve as regulatory documents in the design, fabrication, and use of ceramic composites for nuclear applications. The two specifications (one for carbon-carbon composites and one for SiC-SiC composites) consist of two parts – a classification system for designating different types of CMCs and a property specification system with requirements/recommendations for material properties, durability, testing, and fabrication processing. The classification system organizes the CMCs based on fiber type, architecture class, matrix source, physical properties (fiber volume fraction, bulk density, apparent porosity) and priority mechanical properties (tensile strength, and tensile modulus). The specification system defines the chemistry (components, nuclear impurity limits) requirements and the primary physical and mechanical properties of interest. Guidance is also provided on durability specifications and testing, manufacturing process specifications, and quality assurance and testing.

4:20 PM

(ICACC-S13-009-2013) Round-Robin Interlaboratory Study for the Precision of Uniaxial Tensile Testing of Ceramic Composite Tubes

S. T. Gonczy*, Gateway Materials Technology, USA; Y. Katoh, Oak Ridge National Laboratory, USA; M. Jenkins, California State University, USA

The ASTM C28 Committee on Advanced Ceramics has developed a standard test method to evaluate the axial tensile strength of fiber-reinforced carbon-carbon (C-C) and silicon carbide-silicon carbide (SiC-SiC) composite tubes at ambient temperature. As part of the ASTM specification process, a round-robin interlaboratory study has been planned and organized to assess the precision, repeatability, and reproducibility of the uniaxial tensile strength tests of SiC-SiC composite tubes. The round-robin study will conduct tensile tests at ambient temperature on over 80 test specimens at more than five laboratories. The test study procedure will specify a common gripping system, controlled alignment, uniform strain measurement, and specified/measured experimental parameters (loading rates, bending stresses, environmental conditions, etc.). With controlled and measured experimental procedures, the round-robin study will provide data on the inherent variability of test specimens as well as assess the experimental variability between laboratories

4:40 PM

(ICACC-S13-007-2013) Advanced Cladding Inspection Using Innovative Optical Morphological Analysis

J. E. Garnier, M. V. Glazoff, S. Rashkeev, I. J. Van Rooyen, G. W. Griffith, S. Bragg-Sitton*, Idaho National Laboratory, USA

Silicon carbide (SiC) is being investigated as a candidate cladding material in water-cooled reactors that may substitute or modify Zircaloy based cladding. This study uses advanced optical quality assurance analysis to effectively and efficiently characterize composite and metal clad surfaces. Morphological optical analysis results include (i) fuel rods surface quality (before/after) with composite SiC cladding; (ii) analysis of cracks and other structural defects in metal end caps and breached cladding; and, (iii) three-dimensional surface topography analysis. The analysis uses the unique INL "MorphoHawk" software computer platform coupled to an optical imaging system. The analysis approach has the capability to find solutions for two "difficult" classes of informational analysis problems: (1) extracting useful information from images obtained under continuously varying conditions; and, (2) monitoring of known objects (defects) in order to automatically identify the appearance of new "objects" which can be distorted very strongly under extreme conditions of environmental exposure. This unique method of analysis does not depend on the conditions of image registration which also overcomes the fundamental limits of current linear methods used in optical informational analysis.

Engineering Ceramics Summit of the Americas

Ceramics for Human Health

Room: Coquina Salon G
Session Chairs: Mrityunjay Singh, Ohio Aerospace Institute; Jose Varela, University of Sao Carlos

1:30 PM

(ICACC-ECSA-001-2013) Innovative Ceramic Technologies to Transform the World (Invited)

L. Hench*, University of Florida, USA

During June 21-22, 2010 the seminal Ceramic Leadership Summit (CLS) was held in Baltimore, MD, hosted by the American Ceramic Society, to explore the major trends affecting the ceramics materials community world-wide. Throughout the Summit delegates from industry, government and academia heard the latest thinking from noted scientists, leaders, and colleagues on ways that innovative ceramics technologies can transform the world. During the closing session, I attempted to connect the concepts, predictions, and provocations encountered from those thought leaders with input from American Ceramic Society members who participated in a survey about ceramic technologies that are most likely to have a significant impact in the future. I will present an overview of the findings from the first CLS and update the conclusions with his latest personal perspectives on new technical developments, the economic issues, socio-economic factors and feasibility of achieving breakthrough technologies in the years 2013-18. The emphasis will be on the following sectors of business: Energy, Environment and Healthcare. Two critical questions are addressed: 1) What are the most important breakthrough technologies that can produce an economic solution to energy, environment and healthcare issues? 2) What are the scientific, socio-economic or political barriers that must be overcome to make these innovative technologies have an impact world-wide?

2:00 PM

(ICACC-ECSA-002-2013) Novel Calcium Phosphate Silicate Cements for Dentistry: A Case Study of Successful Commercialization of Bioceramics in Canada (Invited)

T. Troczynski*, UBC, Canada

While Calcium Phosphate Cement (CPC) has been a "gold standard" of bioceramic cements for orthopedic uses for more than two decades now, its relatively weak and of neutral pH (~7) during setting, making it less attractive as an endodontic cement for dental root canal treatment. This was addressed by Calcium Silicate Cement (CSC), which is considerably stronger than CPC and sets at pH of about 12, rendering self-sterile conditions in dental applications. We have further improved CSC by making it more bioactive by addition of phosphates, and at the same time further improving its structural behaviour. Such Calcium Phosphate Silicate Cement (CPSC) combines the best properties of both CPC and CSC, and has been recently commercialised for dental root canal sealer applications. This presentation will discuss CPSC development process, including the effects of phosphates on the properties of CPSC after hydration and its final properties

2:30 PM

(ICACC-ECSA-003-2013) New materials for energy and biomedical applications (Invited)

B. Bregadiolli, D. Leite, UNESP, Brazil; A. H. González, P. H. D Alpino, UNIBAN, Brazil; C. F. Graeff*, UNESP, Brazil

Research at the Laboratory of New Materials and Devices (LNMD) includes the synthesis and characterization of ceramic materials for energy technologies and the characterization of bioceramics and composites for dental applications. For these reasons, La0.50Li0.50TiO3 nanoparticles were synthesized by the polymeric precursor method (PPM) for application as cathode in secondary lithium batteries. Electrochemical measurements of reduction/oxidation processes gave evidence of two kinetic processes. Also, nanocrystalline TiO2 and Nb2O5 films for application in hybrid solar cells were synthesized. The particles were prepared from a "sol" solution by microwave assisted hydrothermal synthesis. The films were deposited by painting on ITO substrate and sintered at 450°C. In addition, the preparation of ZrO2 bioceramic by PPM was investigated. Structural characterization by XRD showed that the powders are polycrystalline and secondary phases free. Morphological results revealed a microstructure of spherical grains with homogeneous sizes of 70 nm. Finally, the ability to accurately predict changes in dental composite properties is of critical importance for the industry, researchers, and clinicians. An accelerated aging process has been used to characterize the mechanical, structural and rheological parameters of composites. Results have shown that this process influences most of the parameters when predicting 9 months of aging.

3:20 PM

(ICACC-ECSA-004-2013) Medical Initiatives from the Nuclear Community: Applications of Unique 'Multi-Use Technologies' (Invited)

G. W. Wicks*, Savannah River National Laboratory, USA

The Savannah River Site (SRS) is a 310- square mile nuclear Department of Energy (DOE) facility, located in Aiken SC. It has been operational for more than 50 years providing state of the art research, products and services, primarily in areas of clean energy, environmental remediation, nuclear waste management and national security. In 2004, the laboratory was designated the 12th National Laboratory in the DOE complex and shortly afterwards, an important Memorandum of Understanding (MOU) was signed between the leadership of the Savannah River National Laboratory (SRNL) and the Medical College of Georgia (MCG), which has been periodically updated, to "… foster collaboration… in areas of life sciences, engineering and related technologies….. leverage resources and expertise…… and explore opportunities that benefit both organizations". As a result of these agreements, new collaborations were initiated between scientists and engineers from the national laboratory and those from the medical field, which focus on 'Multi-use Technologies', i.e., often unique or one-of-a-kind technologies developed within the nuclear community and successfully applied to many uses over the years, but generally, within the DOE complex. These special technologies are now being examined by interdisciplinary groups for potential use in other fields, including the medical arena. One important set of goals, are to produce improved, as well as brand new tools, to assist clinicians in their critical tasks of providing the best healthcare possible. About a half-dozen of these joint projects will be discussed in areas of digital radiography, microbiology, sensors, robotics, and in advanced materials and systems, including new ceramics/ glasses that have recently been patented and licensed.

3:50 PM

(ICACC-ECSA-005-2013) Tailoring Ceramic Material Systems for Bioreactors used in Regenerative Medicine (Invited)

I. Nettleship*, University of Pittsburgh, USA

Many regenerative medicine therapies will require readily available supplies of human stem cells. These stem cells will need to be expanded from the limited number of sources available in donated organ tissue. The expansion of stem cells will require in-vitro systems that can both stimulate the stem cells to multiply and then, at the required time, cause differentiation into the required cells which can ultimately be harvested as cell products or stimulated to reorganize into tissue. The systems most suited to this task are bioreactors. This presentation will introduce the different types of bioreactor that are capable of this task and review the use of ceramics in each. The importance of the "stem cell niche" or microenvironment experienced by stem cells in controlling cell behavior will be emphasized in considering the requirement of ceramic cores in direct perfusion reactors and hollow fiber membrane reactors used to manipulate bone marrow stem cells. The effect of these requirements on future processing and manufacturing of new bioreactor systems will then be addressed.

4:20 PM

(ICACC-ECSA-006-2013) Chemiosensor Response of Inorganic Oxides (Invited)

A. A. Felix, P. H. Suman, D. P. Volanti, UNESP- Araraquara, Brazil; H. L. Tuller, Massachusetts Institute of Technology, USA; M. O. Orlandi, J. A. Varela*, UNESP- Araraquara, Brazil

Nanomaterials have attracted the attention of researchers in the last decade due to their interesting properties. Moreover, there is a wide applicability of these materials in several areas of knowledge, for example, chemicals sensors, solar cells and others, and tests have showed that the use of nanomaterials can make devices faster, more sensitive and consume less energy. In this work we will present chemiosensor response of CuO and Tin-based oxides, focusing on the effect of morphology (nano or micro sized) and structure in the sensor response. CuO structures were synthesized by microwave assisted hydrothermal method and results showed that is possible to control the material morphology – nanorods, nanofibers or urchin-like; all of them in pure tenorite phase – by controlling the synthesis precursors. Sensing response showed that CuO materials are more sensitive to reducing gases, which is expected for a p-type semiconductor and the sensor response is discussed based on surface area, exposed planes and interconnectivity of materials. The Tin-based structures studied were obtained by carbothermal reduction process and are 1D materials (i.e., nanobelts) grown in different phases (SnO, SnO2 or Sn3O4) depending on synthesis conditions. Sensor response of belts for reducing and oxidizing gases were studied and discussed. Results show that Sn3O4 material has the best response for NO2 gas while SnO2 is the best material to detect H2.

S3: 10th International Symposium on Solid Oxide Fuel Cells (SOFC): Materials, Science and Technology

S3 Poster Session

Room: Ocean Center

(ICACC-S3-P038-2013) Mechanical Properties of Ni / (Sc2O3)0.1(CeO2)0.01(ZrO2)0.89 Porous Anodes

Y. Chen*, N. Orlovskaya, University of Central Florida, USA; T. Graule, J. Kuebler, Empa, Swiss Federal Laboratories for Materials Science and Technology, Laboratory for High Performance Ceramics, Switzerland

Ni / (Sc2O3)0.1(CeO2)0.01(ZrO2)0.89 (Ni / SCSZ) cermet is one of anode materials with good catalytic activity towards hydrogen oxidation, superior ionic conductivity and low carbon deposition for use in Solid Oxide Fuel Cell (SOFC). The mechanical properties of anode materials play an important role in the reliability and durability of solid oxide fuel cells operating at high temperatures in a reducing environment. Mechanical properties of porous Ni / SCSZ cermet bars reduced from 65wt%NiO-35wt%SCSZ ceramics were tested and characterized. Young's modulus as well as strength and fracture toughness of non-reduced and reduced anodes has been measured, both at room and at high temperatures. High temperature experiments were performed in the reducing environment of forming gas. It is shown that while at 700 °C and 800 °C, the anode specimens exhibited purely brittle deformation, a brittle-to-ductile transition occurred for heating above 800 °C and the anode deformed plastically at 900 °C. Fractographies of the anode specimens were performed to identify the fracture modes of anodes tested at different temperatures.

(ICACC-S3-P039-2013) A Study of the Anelastic Relaxation of Defect Complexes in Oxide Ceramics by Resonant Ultrasound Spectroscopy

P. Gao*, M. Westwick, Texas A&M University, USA; T. Ali, British University in Egypt, Egypt; M. Radovic, Texas A&M University, USA

In this study, a high temperature resonant ultrasound spectroscopy (RUS) was used to quantify the effects of type, concentration and association of point defects (i.e. oxygen vacancies and dopants) on the elastic properties in pure or doped ceria-based and zirconia-based oxides. Elastic moduli of aluminum oxide and pure cerium oxide were found to decrease almost linearly with temperature. However, doped ceria-based oxides shows anomaly in Young's and shear moduli vs. temperature plots, with the saddle region between 100°C and 400°C, depending on the type of dopant. The variation of elastic moduli with temperature was also found to be non-linear for zirconia-based oxides with the minimum values at between 500°C~700°C. In both oxide systems, the resonant spectroscopy peaks were found to be become much broader at the temperatures where elastic anomaly was observed, indicating a high ultrasonic attenuation (or mechanical loss) at those temperatures. Non-linear changes of elastic moduli with temperature and strong attenuation at the elastic anomaly temperature are discussed in more detail in terms of anelastic relaxation of oxygen vacancy – doping cation dipoles.

(ICACC-S3-P040-2013) Preparation of $Ce_{0.9}Sm_{0.1-x}Tb_xO_{2-\delta}$ Films by Using Ultrasonic Spray Pyrolysis

M. Vestli*, M. Maide, E. Anderson, G. Nurk, E. Lust, Institute of Chemistry, University of Tartu, Estonia

The purpose of this work is to study Tb and Sm co-doped ceria film as electrolyte for solid oxide fuel cell. Precursor solution containing metal nitrates in a tetraethylene glycol based solvent was sprayed on heated sapphire substrate by means of ultrasonic atomizing nozzle. Based on previous studies in the field of spray pyrolysis and the thermal stability and decomposition analysis, the deposition conditions were optimized. Crack-free homogenous films with different dopant concentration were deposited and thereafter annealed at temperatures 1000 – 1200°C. $Ce_{0.9}Sm_{0.1-x}Tb_xO_{2-\delta}$ films were analyzed using X-ray diffraction, scanning electron microscopy and atomic force microscopy methods. As Tb dopant concentration was increased from 0 to 0.1 mol%, the mean crystallite size and lattice parameter for $Ce_{0.9}Sm_{0.1-x}Tb_xO_{2-\delta}$ film, annealed at 1200°C, decreased from 32 to 22 nm and from 5.416 to 5.396 Å, respectively. The grain size increased when Tb dopant was added or when the annealing temperature and time were increased. This study shows that Tb as dopant ions influence the crystal structure of co-doped ceria film. Thus the spray pyrolysis method is a convenient way to deposit dense homogenous oxide films varying chemical composition and microstructure. The sintering temperatures can be kept low as 1000° to 1200°C.

(ICACC-S3-P041-2013) Oxygen permeability and phase stability of $SrCoO_{3-\delta}$-based mixed conducting perovskite membrane

T. Nagai*, W. Ito, Nippon Steel Corp., Japan

Stability of the perovskite structure and oxygen permeability was investigated for cation substituted $SrCoO_{3-\delta}$-based mixed conductors. $(La_{0.1}Sr_{0.9})CoO_{3-\delta}$ and $Sr(Co_{0.9}X_{0.1})O_{3-\delta}$ where X was Ni, Cu, Zn, Cr, Fe, Al, Ga, In, Ce, Ti, Zr, Sn, V and Nb were prepared by solid reaction and sintering process and the tendency to transform to the low oxygen permeable 2H–$BaNiO_3$-type phase was tested. Some of the oxides were sintered as dense ceramic disk samples and the oxygen permeability was measured by gas sweep method. The stability of the perovskite structure was found to be enhanced by a rise in the valence of the substitutional cation. Within the measured samples,

$Sr(Co_{0.9}Nb_{0.1})O_{3-\delta}$ (SCNb) exhibited the highest stability of the perovskite structure and the highest oxygen permeability at 900°C with good gas-tightness. Using SCNb, an oxygen separation tube with a composite structure in which a dense membrane was formed on a porous body was fabricated. Using the tube, high-purity oxygen was successfully separated from compressed air. The permeation rate reached 9 $cm^3/min/cm^2$ at an oxygen collection rate of 20% under the condition of 900°C and 10 atm air. The permeability was measured for over a half-year, and the reliability of the fabricated tube was confirmed.

(ICACC-S3-P042-2013) Influence of the Method of Sintering on Phase Assemblage and Electrical Conductivity of Zirconia-Scandia-Ceria Solid Electrolyte

R. L. Grosso, E. N. Muccillo*, Energy and Nuclear Research Institute, Brazil

Scandia-doped zirconia is a candidate material for solid electrolyte in intermediate-temperature solid oxide fuel cells. The main concern is based on the complex nature of its phase composition. Addition of cerium oxide has been proven to be effective for stabilization of the cubic phase at room temperature, and the ternary system has been studied for that purpose so far. In this work, the influence of the sintering method on phase assemblage and electrical conductivity of the ternary system is systematically studied. Several dwell temperatures and times were exploited in both the conventional and the two-stage sintering methods. In the conventional method of sintering, the rhombohedric phase originates for dwell temperatures in the 1150-1300°C range. The content of this phase depends on the dwell time at each specific temperature. At high dwell temperatures and/or longer times the phenomenon of overfiring is observed with consequent degradation of the cubic structure. For the two-stage method of sintering, the choice of temperature and time is critical for phase stabilization. Finally, for a given sintered density the two-stage method gives rise to a ceramic material with fine microstructure with good properties.

(ICACC-S3-P043-2013) Effects of Humidity in Cathode Air on LSM/YSZ Cathodes

J. W. Templeton*, J. S. Hardy, S. W. Jeffry, Pacific Northwest National Laboratory, USA

Two sets of experiments investigating the effects of 3% humidity on LSM/YSZ cathodes were conducted by operating button cells for 1000 hours at temperatures ranging from 800 to 950°C and at operating voltages of 0.7 and 0.8V. The first experiments cycled the air supply to the cathode between dry and moist air, spending approximately 100 hours at each humidity level. All of the fuel cells in the second set of experiments were operated at 0.8V and a third of the cells were tested in each of three conditions. The first and second conditions consisted of dry air and humid air, respectively, being supplied to the cathode throughout the entire 1000 hour test duration while the third consisted of cycling the air between dry and moist, spending approximately 250 hours at each humidity level before switching to the other. Cells exposed to humid air experienced higher degradation rates than those exposed to dry air. Upon every change to humid air, the cell ASR increased by up to nearly 20% and became increasingly pronounced as temperature was decreased. The increase in ASR was at least partially reversible upon reverting back to dry air. Analysis of difference in impedance spectra (ADIS) suggests the same humidity-induced degradation mechanism of the LSM/YSZ cathode at 800 to 950C as has been reported by prior researchers at 750C.

(ICACC-S3-P044-2013) Ionic conductivity in mullite and mullite type compounds

C. H. Rüscher*, F. Kiesel, Leibniz University Hannover, Germany

Mullite type compounds of compositions Bi2-2xSr2xAl4O9-x have attracted attention for possible fuel cell applications due to a suggested high oxygen diffusion. However, more recently it could be shown that the rather high conductivities (up to about 0.3 S/cm at 1073 K) of as prepared ceramics must be related to Sr containing Bi2O3 films segregated on the crystal interfaces. Thus there had been a fundamental misunderstanding concerning the conducting properties of mullite type material. Moreover, a literature survey reveals a significant deficiency in basic investigations on the conducting properties of mullite itself. Here new results based on impedance spectra (1-10^6 Hz) of single crystals and ceramics between 200 and 800°C are presented. A new type of data evaluation including first derivatives of spectra reveal a separation into dielectric response and dc transport behavior related to unsuccessful and successful hops of ions, respectively. The Arrhenius activation energies of the dc conductivity are about 1.2 eV for Bi2Al4O9 and 1.0 eV for Al4.8Si1.2O9.6, showing at 1073 K specific values of about 10^-5 and 10^-7 S/cm, respectively. Including previous diffusion data it is concluded that ionic diffusion must be impurity controlled in case of mullite (Na, Mg, H) whereas in case of Bi2Al4O9 cations could "intrinsically" dominate the conductivity via the formation of Frenkel type defects.

(ICACC-S3-P045-2013) Electrical Properties of Composite YSZ/Al2O3

H. Araujo*, D. F. Souza, PPGCEM- UFSCar, Brazil

In the present work the electrical properties of composite based in yttria stabilized zirconia and alumina ceramics have been investigated. Pellets with alumina content ranging from 0 to 50 vol % were isostaticaly pressed at 200 MPa and sintered at 1550 °C for 2 h. The microstructure was analyzed by scanning electron microscopy and atomic force microscopy. Impedance spectroscopy measurements were realized at 200-600 °C temperature range and 5Hz – 30 MHz frequency range. The impedance data were analyzed by the Z-Plot/Z-View software package. The impedance spectra showed two distinct semi-circles at low and high frequencies. Although the electrical conductivity decreased systematically with alumina addition, for alumina content between 10 and 30 vol.% the decrease rate was less pronounced. Furthermore the behavior of total conductivity was similar to bulk conductivity rather than interface conductivity unlike commonly observed in polycrystalline ceramics. The Bode diagrams showed that the increase of alumina content provides a displacement in the relaxation frequency in low frequency range. These results suggest that the addition of alumina causes a new interface mechanism causing displacement in Bode and Nyquist diagrams and change the electrical conductivity behavior.

(ICACC-S3-P046-2013) Influence of sintering temperature on the electrical properties of GDC/YSZ composites

R. F. Marcomini, D. F. Souza*, Programa de Pós Graduação em Ciência e Engenharia de Materiais, Brazil

It has been analyzed the influence on the electrical properties of the Ce-Zr solid solution formed during sintering of Gadolinia doped-Ceria (GDC)/Yttria Stabilized Zirconia (YSZ) composites. Composites containing 30 vol% YSZ/ 70 vol% GDC and 70 vol% YSZ/ 30 vol% GDC were obtained after homogenizing a suspension of both phases, drying and pressing cilindrical samples at 200 MPa. In order to control the dispersed phase reactivity during sintering, the powders were pre-sintered at different temperatures prior the mixture. Samples were sintered at 1000 –1300 °C temperature range. Impedance spectroscopy was performed in air from 200 °C to 500 °C with platinum electrodes. It was seen that the electrical properties are strongly influenced by the dispersed phase pre-sintering temperature. Although the solid solution was not directly detected by DRX, EDS line mapping identified the diffusion profile of species in the CDG/YSZ interface. It was found that the diffusion profile increases with sintering temperature. It was observed that although higher temperatures yields denser samples, the higher amount of solid solution decreases the total electrical conductivity. It is proposed that the morphology of the solid solution, elongated, distributed at the CDG/YSZ interfaces causes higher disturb on the electrical field then the rounded pores dispersed in the matrix, having a higher blocking effect.

(ICACC-S3-P047-2013) ZnO as sintering aid of Yttrium-doped BaCeO3

F. J. Macambira*, D. F. Souza, PPGCEM-UFSCar, Brazil; C. M. Hosken, UFF, Brazil

Doped perovskite proton conductors have been considered as electrolyte for oxide fuel cells. The proton insertion in perovskite structure occurs through the oxygen vacancies filled by hydroxyl groups during heat treatment in water vapor atmosphere. The technological use of these ceramics is limited by their refractory nature. High densification is achieved only at high temperature resulting in barium deficiency and deleterious yttrium rich second phase. In this work, the mechanism of ZnO effect on the densification of Y-doped BaCeO3 and also on the phases formation reactions have been investigated. ZnO-doped powders were prepared by citrate and oxide mixture processes. Pellets were sintered in air at 1200–1600 °C range during 2-10 h. Pellets from both powders achieved high densification at low temperature, 1300 °C. However highest temperature was necessary to obtain the phase of interest as the majority phase, 1325 and 1600 °C for citrate and oxide mixture process, respectively. XRD and SEM characterization showed that ZnO addition favored liquid phase formation. The impedance spectroscopy measurements showed that the H+ insertion efficiency during heat treatment in a water vapor atmosphere depends on the singular microstructure, mainly the vitreous phase distribution and also the amount and distribution of Ydoped-BaCeO3 perovskite which is the phase responsible for the H+ insertion.

(ICACC-S3-P048-2013) The effect of Co and Zn addition on densification and electrical properties of ceria-based nanopowders

L. A. Villas-Bôas*, D. F. Souza, PPGCEM-UFSCar, Brazil; F. Marques, F. Figueiredo, University of Aveiro, Portugal

Ceria based electrolytes has received great attention for application in Solid Oxide Fuel Cells (SOFC) technology due to their high ionic conductivity with respect to traditional zirconia-based electrolytes. However, ceria-based ceramics prepared with micrometric powders must be sintered at high temperatures which justified a large attention to alternative processing or compositional approaches to avoid this problem. In this work pure, cobalt and zinc doped samples were prepared from Ce0.8Gd0.2O1.9 nanopowder. The ceramic samples were shaped both by powder pressing and slip-casting, and afterwards sintered following a two-step profile. Samples were studied by X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Impedance Spectroscopy (IS) in air. Cobalt and zinc addition was effective as sintering aid allowing peak sintering temperatures in the order of 1000 °C to reach densifications in excess of 95% and showing no evidence for the presence of secondary phases. However, Co doping was deleterious to grain boundary conductivity although it has improved grain conductivity comparing to Co-free samples. IS data from Zn samples showed that Zn-additions have a positive role on sintering without the formation of ion-blocking grain boundaries, thus resembling Co-doped CGO rather than materials based on other sintering additives like Ga.

(ICACC-S3-P049-2013) Numerical Simulation of Electrolyte-Supported Planar Button Solid Oxide Fuel Cell (SOFC)

A. Aman*, R. Gentile, Y. Chen, Y. Xu, University of Central Florida, USA; X. Huang, University of South Carolina, USA; N. Orlovskaya, University of Central Florida, USA

The use of electrolyte materials with higher ionic conductivity will improve the maximum power density produced by the SOFC. 10 mol% SC2O3-1 mol% CeO2-ZrO2 [SCSZ] has a significantly higher ionic conductivity than 8 mol% Y2O3 stabilized ZrO2 [YSZ]. But, SCSZ undergoes phase transition while YSZ maintains its phase stability during the SOFC operation. To use advantages from both materials, SCSZ layers are placed within two outer layers of YSZ. Each layer has a thickness of 30μm. A total of nine electrolyte designs were developed and tested: 3-, 4-, and 6-layered designs of YSZ, SCSZ, and the layered combination YSZ-xSCSZ-YSZ, where x=1, 2 or 4. An electrolyte-supported planar button cell is modeled using COMSOL Multiphysics 4.3. The main governing equations include Maxwell-Stefan diffusion model, Butler-Volmer and Brinkman equations. The anode [Ni-YSZ] and cathode [(La0.6Sr0.4)0.95-0.99Co0.2Fe0.8O3] materials and operating conditions were kept constant while the electrolyte material was changed. Model validation was done against experimental results of another planar SOFC. The results show that SOFC with 3-layered SCSZ electrolyte produced the highest power density; the cell with 6-layered YSZ electrolyte produced the least power density. The SOFC with YSZ-xSCSZ-YSZ electrolyte performs better than the SOFC with YSZ, and has a better stability compared to the SOFC with SCSZ.

(ICACC-S3-P050-2013) Structural Stability and Conductivity of $La_{0.8}Ca_{0.2}Fe_{1-X}Co_{XO}3$(x=0~0.4) Perovskite in Reducing Atmosphere

K. Fung*, H. Liu, C. Liu, National Cheng Kung University, Taiwan

$LaFeO_3$ perovskite is a mixed ionic/electronic conductor exhibits good stability with low conductivity. The addition of aliovalent dopants is an effective way to enhance the conductivity of perovskite oxides. The objective of this work is to enhance the conductivity of $LaFeO_3$ by using double doping in perovskite's cation sublattices. For instance, Ca/Co ion was added into A/B-site cation sublattice for substitution of La/Fe ions. The samples were prepared using solid state reaction method based on the formula of $La_{0.8}Ca_{0.2}Fe_{1-X}Co_XO_3$(x=0~0.4). After sintering at 1300°C, the powder compacts with various compositions were densified. All the samples showed typical p-type semiconducting behavior. The addition of Co tends to enhance the conductivity of $La_{0.8}Ca_{0.2}Fe_{1-X}Co_XO_3$. When 40% of B-site cation sublattice was replaced by Co ions, the conductivity of $La_{0.8}Ca_{0.2}Fe_{1-X}Co_XO_3$ was enhanced from 90 S/cm to 255 S/cm. However, the stability of $La_{0.8}Ca_{0.2}Fe_{1-X}Co_XO_3$ tends to decrease with increasing amount of Co addition. For instance, 40% Co-doped $La_{0.8}Ca_{0.2}Fe_{1-X}Co_XO_3$ was found to decompose into La_2O_3,and metallic Co, Fe when the sample was heat-treated with 10%H_2 at 800°C. The enhancement in conductivity and structural instability of perovskite will be rationalized in light of defect chemistry and bond strength between the transition metal and oxygen ions.

(ICACC-S3-P051-2013) Structural and conductivity studies of doped lanthanum gallate

K. Sood*, K. Singh, O. P. Pandey, Thapar University, India

Ba doped lanthanum gallate has been prepared by conventional solid state reaction method. The calcined sample has been isostatically pressed into pellets at a load of 12 kN cm-2 and then sintered at 1400 C for 12h. The crystalline phase formation and composition has been confirmed by X-ray diffraction (XRD) method and energy dispersive spectroscopy (EDS) analysis respectively. Sintered sample is found to be orthorhombic perovskite phase with density around 90 % is achieved. The ac conductivity of the sample was studied from room temperature to 600 C and frequency range of 1-106 Hz. The bulk and grain boundary contribution with frequency has been studied using impedance plots. The impedance study revealed the higher grain boundary contribution to total conductivity. The activation energy has been found in the range of Ea = 0.95 eV which indicates that the prepared samples is essentially ionic conductor.

(ICACC-S3-P052-2013) Mixed Protonic-Anionic Conducting Ceramics For Dual Membrane Fuel Cells

M. Viviani, S. Presto, V. Buscaglia*, G. Canu, National Research Council, Italy; A. Barbucci, P. Carpanese, University of Genoa, Italy; Z. Stoynov, D. Vladikova, Bulgarian Academy of Sciences, Bulgaria; A. Thorel, Mines-ParisTech, France; Z. Ilhan, DLR, Germany

The Dual Membrane Cell (DM-Cell) is an innovative concept for solid state fuel cells operating in the temperature range 600-700°C. It is based on a junction between the cathode part of a Solid Oxide Fuel Cell (SOFC) and the anode part of a protonic SOFC (pSOFC) via a mixed H+ and O2- conducting porous ceramic membrane. The key feature of the DM-Cell architecture is the presence of a third gas compartment for water vapour formation. The DM-cell concept makes it possible to separate the compartment for water formation from both fuel and oxidant chambers. Such a three-chambers configuration gives many advantages related to fuel dilution, materials corrosion and reversibility between fuel cell and electrolyzer operational modes (SOFC/SOEC). Dual conductivity (protonic-anionic) can be achieved by mixing BaCe0.85Y0.15O3 (BCY) and Ce0.85Y0.15O2 (YDC). Alternatively, as the proton conduction mechanism involves the same sites used for oxide ions migration, i.e. lattice oxygen vacancies, the dual conductivity can also be obtained in single BCY layers. The conductivity of BCY was measured by electrochemical impedance spectroscopy in wet hydrogen and in air. Preliminary tests of the material in the new cell design were successfully performed. The fabrication route, the microstructural and electrochemical testing results on different types of DM-cells are reported in this work.

(ICACC-S3-P174-2013) Effect of Pore-Formers of Anode-Support Microstructure on the Performance of Micro-Tubular Solid Oxide Fuel Cells

H. Kim*, POSTECH, Republic of Korea; J. Lee, T. Lim, S. Lee, S. Park, R. Song, D. Shin, Korea Institute of Energy Research, Republic of Korea; N. Sammes, POSTECH, Republic of Korea

Micro-tubular solid oxide fuel cells (SOFCs) have been developed in recent years mainly due to their high specific surface area, high volumetric power density, lower temperature and fast start-up. However, due to the small diameter of the anode-support, it is potentially damaged when fabricating the cells and rapidly increasing the temperature. Therefore improvement in the mechanical properties is required. Initially, this work examined the effect of activated carbon and carbon black as pore-formers on the microstructure, porosity, gas permeability and mechanical properties of the anode-support of micro-tubular SOFCs. It was found that activated carbon showed high porosity and irregular pore shapes while carbon black showed low porosity, spherical pore shapes and high fracture strength (e.g. activated carbon: 22.3 MPa, carbon black: 57.9 MPa). The unit cell of micro-tubular SOFCs was fabricated with outer diameter of 6 mm and wall thickness of 1 mm. The maximum power density of SOFCs using activated carbon and carbon black on hydrogen flow rate of 150 cc/min. showed 371 mW/cm2, 251 mW/cm2 at 750 °C respectively. The effects on cell performance will be also described in this paper.

(ICACC-S3-P175-2013) Solid Oxide Fuel Cell Combined with Supercritical Water Oxidation on Using Biomass Gas

H. Kim*, A. Parfitt, Y. Chung, N. Sammes, POSTECH, Republic of Korea

Solid oxide fuel cells (SOFCs) have many desirable advantages compared to other fuel cell applications. The advantages of SOFC's are that they do not require expensive precious metal, and thus they can use a variety of fuel sources. Supercritical water oxidation (SCWO) has attracted attention because it can easily produce the product gas and store high pressure hydrogen due to the reaction medium of the SCW. The produce gas (i.e. hydrogen, carbon dioxide, carbon monoxide and methane) can be used as a fuel for SOFCs. In this study, SCW-SOFCs system will be described when the anode/electrolyte is exposed to the pressure and chemical milieu of the SUWOX reactor. The effect of reaction temperature, and amount of water and oxygen fed into supercritical water reactor under SCW conditions will be studied. The effects on electrical performance will be also described in this paper. Preliminary results on a number of feed stocks, for example pectin, are also described.

(ICACC-S3-P176-2013) SOFC Anode Coking Mechanisms and Potential Solutions

Y. Chung*, H. Kim, N. Sammes, POSTECH, Republic of Korea

The Solid Oxide Fuel Cell (SOFC) is an energy generating device with high efficiency and fuel diversity. It can be operated on hydrocarbons, although carbon is deposited on the Ni based anode causing performance drop and eventually cracking. In this paper, the behavior of Ni-YSZ cermet anode, under dry methane conditions, is studied, and the carbon deposition mechanism is analyzed. Further, carbon resistive anodes are also being studied. A Ni-YSZ anode support button-cell was fabricated by pelletizing, while YSZ was used as the electrolyte and LSM as the cathode which were screen printed on the cell. Various dopants were doped on Ni, and the coking behavior under different operating conditions was examined; temperature, S/C ratio and voltage. Microstructure of the anode was analyzed, and carbon deposition rate and the amount of deposited carbon were analyzed. When the cell was operated under methane, carbon crystals grew in nano-tubular form and the cell eventually cracked. Under dry methane conditions the trend of carbon deposition speed, as a function of temperature was different from the known result of operation under wet methane. Mo, Mn and a ceria-based layer were applied as potential coking resistive materials, and they lowered the amount of coking formed on the surface of the Ni anode.

(ICACC-S3-P177-2013) Thermodynamic, electrical, and electrochemical properties of $Sm_{0.5}Sr_{0.5}Co_{1-x}Nb_xO_{3-\delta}$ (x = 0, 0.05, and 0.1) as cathode materials in IT-SOFCs

S. Yoo, UNIST, Republic of Korea; J. Shin, Dong-Eui University, Republic of Korea; G. Kim*, UNIST, Republic of Korea

The perovskite-oxides, such as (La,Sr)CoO_3 and (Ba,Sr)CoO_3, have received much attention in recent years as cathode materials for intermediate temperature-solid oxide fuel cells (IT-SOFCs). In this study, we have investigated the structural, electrical, electrochemical, and redox properties of $Sm_{0.5}Sr_{0.5}Co_{1-x}Nb_xO_{3-\delta}$(SSC-Nbx) cathodes under conditions relevant to IT-SOFC operation.The SSCNbx (x = 0, 0.05, and 0.1) oxides show gradually decreasing electrical conductivity with increasing Nb contents at the same temperature. The maximum power density of SSCNbx (x = 0.05, 0.1) is lower than that of SSC; however, SSCNbx (x = 0.1) is more stable than SSC considering the thermodynamic behaviour, as determined through redox isotherms. These results suggest that a Nb doped SSC perovskite is suitable, considering its high power density and reasonable redox stability, as an IT-SOFC cathode material.

S5: Next Generation Bioceramics and Biocomposites

S5 Poster Session

Room: Ocean Center

(ICACC-S5-P078-2013) Friction and Wear Behavior of Ceramic (Used for Head of Total Hip Replacement)

F. Mamoun*, L. Mohammed, laboratory of metallurgy and materials engineering, Algeria

The problems of friction and wear in the prosthesis for substitution of hip joints and knees have been addressed by many authors due to its crucial importance in the performance of these devices .The choice of the materials for the head and the cup takes into consideration not only properties such as mechanical resistance, friction and wear, but also biocompatibility and corrosion resistance. The consideration of pro's and contra's led to the conclusion that among the best combinations are ultra high molecular weight polyethylene (UHMWPE) for the cup and alumina, stainless steel or CoCrMo alloy for the head.

(ICACC-S5-P079-2013) Effect of sintering additives on Mechanical Properties and Bioactivity of Hydroxyapatite/β-Tricalcium Phosphate Composites

S. Kobayashi*, T. Murakoshi, Tokyo Metropolitan University, Japan

Bioactive ceramics attracts attentions as materials of the bone implant, because of their high biocompatibility. For example, hydroxyapatite (HA) has bone-bonding ability through the bone like apatite layer, and β-tricalcium phosphate (β-TCP) has a high bioresorbability in body environment. In this study, HA/β-TCP composites with different content of β-TCP (0, 10, 20 and 30wt%) were prepared by wet mixing of HA and β-TCP powder, compaction of the powders and sintering. Bending strength of HA/β-TCP composites was measured before and after soaking in the simulated body fluid (SBF). The bioactivity of HA/β-TCP composites was also evaluated by soaking in SBF. To improve mechanical properties, the effect of additive of SiO2 and MgO were also investigated. It was found that the several mechanical properties and ability of apatite formation decreased as content percentage of β-TCP increased. It was also found that the change in bending strength after soaking depended on its surface reaction in SBF and its porosity. Additive of SiO2 didn't improve mechanical properties. On the other hand, additive of MgO improved several mechanical properties. It is confirmed that MgO improves the sinterability of only β-TCP. Furthermore, it is also confirmed that the addition of 3wt% MgO for β-TCP is the best ratio for sinterability.

(ICACC-S5-P080-2013) Synthesis of doped calcium phosphate nanorods

T. S. Eufrásio, A. G. Prette, V. M. Sglavo*, University of Trento, Italy

The use of calcium phosphates based-nanomaterials is as an emerging field in biomedicine thanks to the unique physical and chemical achievable properties rarely paralleled with other man-made materials. In the present work the precipitation method was used to produce calcium phosphate nanorods. The Ca precursor solution was added to the P solution to keep a Ca/P ratio equal to 1.67 like in pure hydroxyapatite. Different Ca precursor were used: $Ca(NO_3)_2.4H_2O$ and $Ca(OH)_2$. The solution was kept at constant pH (8.5 or 10). During the whole synthesis, the suspension was continuously stirred and kept at 75°C. Then the solution was aged for 24 h at 75°C. The precipitate formed from the solution was filtered and washed, kept at 75°C for additional 24 h and calcined in air at different temperatures between 650°C and 900°C for 30 min. The synthesis of calcium phosphates doped with metallic ions was also carried out to obtain specific magnetic and, therefore, therapeutic properties. Additional reagents containing the metallic ions were added to the starting Ca and P precursors-containing solution. The metallic ions used in this study were Zn and Co with maximum concentration of 5 mol% with respect to hydroxyapatite. The produced nanomaterials were characterized by TEM, XRD and ICP-AES. It is shown that the use of $Ca(OH)_2$ as Ca precursor allows the production of hydroxyapatite nanorods with aspect ratio larger than five.

(ICACC-S5-P081-2013) Electrospinning vs. Three-Dimensional (3D) Rapid Prototype Bioprinting

M. Hansen, J. R. Brenner*, Florida Tech, USA

Printing of scaffolds for tissue engineering is commonly done via electrospinning of polymer fibers at high voltages (15-30 kV) and currents < 1 mA. In the last several years, three-dimensional rapid prototyping printers have gone down in price from $20-30 K to about $2000 for Cornell University's Fab@Home printers and even as low as $600 for the Prusa Mandlebot. This dramatic cost reduction was made possible via open sourcing of both the Prusa hardware and software technology via reprap.org. The Prusa automatically converts either Pro-Engineer or SolidWorks inputs into solid freeform (.sff) format and operates using Python-based computer code. The Fab@Home and Prusa technologies print with approximately 2 μm and 10 μm precision, compared to 100 nm for electrospinning. Thus, our group is working towards printing poly(lactic acid) (PLA) scaffolding with the rapid prototyping printers, with the goal of first printing cartilage-like objects, then synthetic bone from gelatinous suspensions containing nanoparticulate hydroxyapatite, and ultimately combining the precision of electrospinning with the cost of rapid open source prototyping and printing. We will demonstrate printing with the Prusa at the poster session.

S7: 7th International Symposium on Nanostructured Materials and Nanocomposites

S7 Poster Session

Room: Ocean Center

(ICACC-S7-P091-2013) Sol-Gel Approach to the Calcium Phosphate Nanocomposites

A. Beganskiene*, Z. Stankeviciute, M. Malakauskaite, I. Bogdanoviciene, Vilnius University, Lithuania; K. Tõnsuaadu, Tallinn University of Technology, Estonia; A. Kareiva, Vilnius University, Lithuania

Calcium phosphate and calcium hydroxyapatite composites are calcium phosphate based bioceramics which make up the majority of the inorganic components of human bones and teeth. Synthetic calcium phosphate/hydroxyapatite composite is known to be one of most important implantable materials due to its biocompatibility and osteoconductivity. The specific chemical, structural and morphological properties of this bioceramics are highly sensitive, however, to the changes in chemical composition and processing conditions. The sol-gel chemistry route has been developed to prepare Ca-P-O gels samples. In the sol-gel process 1,2-ethanediol and EDTA were used as complexing agents. Additionally, triethanolamine and polyvinyl alcohol were used as gel network forming materials. Calcium phosphate/hydroxyapatite thin films were obtained on silicon and titanium substrates by dip-coating technique. The final nanocomposites were obtained by calcination of coatings for different time at 1000 °C. It was shown that adjustment of heating time and dip-coating conditions can be used to control the process of synthesis, phase purity and morphology of thin films. It was concluded, that the formation of calcium phosphate/hydroxyapatite composites in some cases is promoted by dipping time. However, the formation of calcium hydroxyapatite phase on the titanium substrate using an aqueous sol-gel processing route was found to be problematic.

(ICACC-S7-P092-2013) Surface modification of SnO2 nanoparticles by Ti4+

J. Miagava*, D. Gouvea, Universidade de Sao Paulo, Brazil; A. Navrotsky, R. Castro, University of California - Davis, USA; A. Rubbens, P. Roussel, Universite de Lille, France

SnO2-TiO2 system has attracted considerable attention due to its potential application as gas sensor and as photocatalyst. In both cases, the device performance is strongly related to the surface energetics of SnO2-TiO2 materials. In this work, TixSn1-xO2 (0.00 ≤ x ≤ 0.50) nanoparticles were synthesized by Pechini method at 500 °C for 15 h. XRD patterns and Raman spectra show a rutile solid solution structure in all samples. Increasing the Ti4+ content, both crystallite size determined by XRD and particle size determined by N2 adsorption decrease. A possible cause for this phenomenon is the segregation of Ti4+ in the SnO2 surface. Surface segregation has already been observed for other oxide systems such as SnO2-MgO and SnO2-CrO2. Rutile TiO2 and SnO2 present similar structures, ionic radii and valences. This fact indicates that the driving force for nanoparticle stabilization in this work may be the surface energy. High temperature oxide melt solution calorimetry is being done in order to evaluate the energetics of TixSn1-xO2 nanoparticles.

(ICACC-S7-P093-2013) Preparation and Photoelectric Properties of ZnO/a-$Si_{1-x}C_x$:H Heterojunctions

T. Zhao*, Y. Qin, J. Yang, State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, China

ZnO/a-$Si_{1-x}C_x$:H heterojunctions were synthesized via a two-stage process on Si (111) and anodic aluminum oxide (AAO) substrates by plasma enhanced chemical vapor deposition (PECVD) for a-$Si_{1-x}C_x$:H layer and atomic layer (ALD) deposition for ZnO layer, respectively. The experimental results clearly show that Si quantum dots (QDs) with a size of 5–6 nm embedded in a hydrogenated amorphous

SiC (a-SiC:H) matrix were formed in a-$Si_{1-x}C_x$:H layers of ZnO/a-$Si_{1-x}C_x$:H/Si heterojunction and molecular sieve structures were also found in a-$Si_{1-x}C_x$:H layers of ZnO/a-$Si_{1-x}C_x$:H/AAO heterojunctions, in which the structure of ZnO layers are polycrystal nanorods. Experimental investigations indicate that I-V, optical band gap and photoluminescence properties of these heterojunctions were strong related to the structures caused by different substrates. This is an important and interesting study for the development of the nanosturctrue cell-based third generation photovoltaic solar cells.

(ICACC-S7-P094-2013) Effect of Incorporation of Clay and Zinc Oxide Nanoparticles on Oxygen Barrier Properties of Polypropylene Films

M. Oner, P. Atayev*, Yildiz Technical University, Turkey

The polyolefin market, which comprises large volume materials such as polyethylene (PE) and polypropylene (PP), has experienced highest growth in recent years due to increased utilization in the automobile, consumer durables, flexible packaging and health industries. Polypropylene (PP) is an attractive candidate material for packaging applications because of its low cost and improved thermal stability compared with polyethylene. This research has concentrated on the development of methods for creating clay and ZnO nanocomposites with polypropylene (PP), for the purpose of improving barrier and other properties. Polymer and nanoparticles are mixed in the twin screw extruder under shear above the softening temperature of the polymer. This method has several advantages over other methods: It doesn't use a solvent, so that makes it more environmentally acceptable. PP/clay and PP/ZnO blends were produced with different compositions to determine the optimum amount of nanoparticles. Physical properties of polypropylene composites were investigated using X-ray diffraction and differential scanning calorimeter. The oxygen barrier properties of the composites were determined at different temperature. The results showed that the filled polypropylene exhibit lower gas permeability compared to the unfilled polypropylene.

(ICACC-S7-P095-2013) Polymeric gels and colloidal route of the sol-gel process -alternatives to produce Fe-ZrSiO4

G. Herrera*, N. Montoya, J. Alarcón, Universidad de Valencia, Spain

The purpose of this work is the preparation of non-aggregated particles of iron–zircon (Fex-ZrSiO4) using mineralizer-free sol–gel techniques. Fex-ZrSiO4 with compositions $0 < x < 0.15$ was prepared by sol-gel via polymeric gels obtained by hydrolysis-condensation of alkoxides and colloidal route. The temperature of zircon formation (determined by differential thermal analysis, DTA) decreases with the use of iron, suggesting a catalytic effect of iron. Thermally annealed gels between 400 oC and 1600 oC were characterized by x-ray diffraction (XRD), infrared, ultraviolet-visible (FT-IR, UV-Vis) and Raman spectroscopies. These results confirmed the formation of Fe-t-ZrO2 preceding the final Fe-ZrSiO4 formation. Transmission electron (TEM) micrographs of non-agglomerated particles show a uniform distribution of particle size and shape in which varies from 40 to 60 nm. The synthesis method generates important differences in microstructure: colloidal gel samples showed nonporous microstructure improving the densification of the material in comparison with specimens prepared by polymeric gels. The lattice parameter variation (refined by Rietveld method using FullProf) and UV-Vis, suggest that the Fe3+ cations inside the zircon are distributed into tetrahedral sites replacing to Si4+.

(ICACC-S7-P096-2013) Eddy Current and Microwave Characterization of Fe-based Alloy Synthesized by Mechanical Alloying

Z. Hamlati*, S. Bergheul, University of Saad Dahleb, Algeria; M. Azzaz, U.S.T.H.B, Algeria

In the present study mechanical alloying has been used to obtain bulk nanocrystalline FeAl intermetallic compound. Nanocrystalline powder of Fe(Al) solid solution was the product of ball milling. The structural effects of mechanical alloying of powders were investigated by X- Ray diffraction analysis, microwaves and eddy current technique. The complete formation of bcc-FeAl solid solution was observed after 4 h of milling. Crystallite size of 10nm was obtained after 24 hours of milling. Experimental results showed that fine nanocrystalline alloy powders prepared by mechanical milling were very promising for microwave applications.

(ICACC-S7-P097-2013) Inkjet Printed Fractal-Connected Electrodes with Silver Nanoparticle Ink

M. Vaseem*, A. Hong, Y. Hahn, Chonbuk National University, Republic of Korea

The development of a simple and reliable method for nanoparticles-based ink in an aqueous solution is still a challenge for its inkjet printing application. Herein, we demonstrate the inkjet printing of fractal-aggregated silver (Ag) electrode lines on substrates. Spherical, monodisperse Ag nanoparticles have been synthesized using silver nitrate as a precursor, ethylene glycol as a reducing agent, and polyvinyl pyrrollidone as a capping agent. As-synthesized pure Ag nanoparticles were well dispersed in water-ethylene glycol mixture, which was directly used as an ink for inkjet printing. Using this ink, the Ag electrodes of fractal-connected lines were printed on Si/SiO2, glass, and polymer substrates. The fractal-connected Ag lines were attributed to the diffusion-limited aggregation of Ag nanoparticles and the effect of annealing on conductivity was also examined.

(ICACC-S7-P098-2013) The Effect of Silicon Carbide Nano-Dispersants on the Hardness and Indentation Size Effect of Alumina/Silicon Carbide Nanocomposites

J. Wade*, H. Wu, Loughborough University, United Kingdom

Silicon carbide nano-dispersants have been well recognised as being capable of interfering with lattice slips when they are activated inside alumina crystallites. Nevertheless, scepticism remains as to whether they are capable of influencing crack initiation and propagation under indentation. In this study, we used Vickers and Berkovich indenters to measure the indentation resistance of alumina-based nanocomposites consisting of variable silicon carbide nano-dispersant volume percentages of 1% up to 20%. Indentation tests were performed under a broad range of loads from millinewtons to tens of Newtons. The data acquired was subsequently analysed across the different models available with a particular focus on the observed indentation size effect (ISE). A comparative study detailing the elastic and plastic deformation behaviour across all compositions was also undertaken and where necessary, cracking patterns around and underneath the impressions were recorded in order to confirm noticeable correlations with the predictions provided by the models. Potential mechanisms by which silicon carbide nano-dispersants influence the hardness and the ISE are also discussed.

(ICACC-S7-P099-2013) Stoichiometry-Controlled Growth of BaxSr1-xTiO3 Nanoparticles and Their Thin Films for Heterojunction Devices Application

D. Liu, A. Hong*, H. Bae, S. Das, Y. Hahn, Chonbuk National University, Republic of Korea

An optimized chemical synthesis route was proposed to obtain BaxSr1-xTiO3 thin films with stoichiometry control. The molar ratios of the precursors were altered to produce cubic phase of SrTiO3, Ba0.5Sr0.5TiO3, Ba0.67Sr0.33TiO3 and tetragonal phase of BaTiO3 thin films on single crystalline p-Si (100) and quartz substrates. The obtained Raman spectra for the BaSrTiO3 thin films on quartz substrates showed characteristic vibration modes at ~303, 515 and 716 cm-1. The active modes of BaTiO3 signify the tetragonal phase, which is important for its various technological advantages. The significant features of these materials were obtained through capacitance-voltage measurements with Pt (or Ag)/BaSrTiO3/p-Si/Pt (or Ag) assemblies, at 1, 10 and 100 kHz. Substantial hysteresis of 315 mV (with Ag) and 219 mV (with Pt) was observed for Ba0.5Sr0.5TiO3, whereas for BaTiO3 and SrTiO3 the obtained hysteresis was 256 mV and 96 mV, respectively. Largest hysteresis of 793 mV was observed for SrTiO3 with Pt electrode. The above findings are important for assessing device compatibility of cost efficient solution processed BaSrTiO3 thin films.

(ICACC-S7-P102-2013) Effect of raw materials and fabrication parameters on the structure and morphology of Nanocrystalline magnesium aluminate spinel powders fabricated by gel combustion method

A. Sedghi*, Imam Khomeini International University, Islamic Republic of Iran; S. Poostian, Azad University, Saveh Branch, Islamic Republic of Iran; P. Sedghi, Azad University, Science and research campus, Islamic Republic of Iran; M. Salmani, Azad University, Saveh Branch, Islamic Republic of Iran

Because of chemical inertness and very good physical and thermo mechanical properties, MgAl2O4 spinel is widely used in the many industrial fields. In many of MgAl2O4 spinel applications, properties such as high surface area, small crystallite size and more active sites is essential which are influenced by the fabrication method. Many Fabrication methods are used for fabrication of this spinel as like as solid state method, spray pyrolysis, mechano-chemical synthesis, co-precipitation, sol–gel synthesis and combustion synthesis but among of them the gel combustion synthesis technique has been regarded as best one due to its convenient processing, significant time-saving and high purity products. Although, in this method many different raw materials and fabrication parameters have been involved which haven't been studied well. Therefore, in this study gel combustion method with different parameters were investigated and based on the structure and morphology of fabricated samples, type of raw materials, their ratios and fabrication parameters were optimized. Results of this study revealed that by choosing the optimum parameters, it's possible to fabricate stoichiometric, very fine and less agglomerated Nanocrystalline magnesium aluminate spinel powders by gel combustion method.

(ICACC-S7-P103-2013) Internal Reduction of Transition Metal Doped Oxides and Perovskites

A. Morrissey*, J. Tong, I. E. Reimanis, Colorado School of Mines, USA; J. R. O'Brien, Quantum Design, Inc., USA

Transition metal (M = Ni, Co, Fe) doped Y_2O_3-stabilized ZrO_2 (YSZ) is widely used in oxygen pumps, oxygen sensors, and solid oxide fuel cells (SOFCs). These electrochemical devices can be operated in reducing and oxidizing environments. In the present study, specimens containing small concentrations of M dopant (0.01 to 1 mol%) dissolved in the YSZ matrix are chemically synthesized using high purity methods. Reduction experiments are conducted in a custom-built, environment-control furnace. The extent of internal reduction which occurs at variable times (up to 500 h) and temperatures is monitored with SQUID VSM magnetometry. The microstructural development of the internal reduction process of each M dopant is confirmed with microscopy techniques. Magnetometry is shown to be useful for distinguishing between M ions present in solution, as a second phase, or as metal particles of various sizes. The investigation is repeated on M doped yttrium-doped barium zirconate (BZY), a proton conducting perovskite.

(ICACC-S7-P104-2013) Boron Nitride Nanotube Growth on SiC Fiber Surfaces

D. Santiago*, J. Hurst, NASA Glenn Research Center, USA

Boron nitride nanotubes are a high temperature-compatible analog of carbon nanotubes. Therefore this makes them a potentially significant reinforcement phase for high temperature ceramic matrix composites such as SiCf/SiCm. Recently, boron nitride nanotube synthesis on silicon carbide fiber surfaces to create "fuzzy fibers" has been demonstrated by the authors to provide improved composite properties in simple BNNT/SiC composites. However a similar concept, CNT grown on carbon fibers, while demonstrating resin composites with improved interlaminar shear strength, has also resulted in reported damage of the carbon fiber surfaces by CNT catalyst particles. While cursory examination of BNNT growth on SiC has not revealed damage in this case, a more detailed investigation is warranted to determine the effects of BNNT growth and processing parameter on surfaces of SiC fibers as well as on the tow strength. Effect of BNNT growth on the strength of SiC fibers will be reported. BNNT structure will be examined by TEM, SEM, and FTIR.

(ICACC-S7-P105-2013) Comparision of thin film WO3 photoanodes prepared by different methods

M. Sarnowska*, P. Barczuk, CeNT, Warsaw University, Poland

One of very promising photoanodic materials able to capture visible light and to resist against phtocorrosion in aqueous solutions is tungsten trioxide (WO3). Basically, this material in its monoclinic crystalline form absorbs blue and green parts of the solar spectrum consistent with the 2.5 eV optical band gap. Because of the indirect nature of the latter optical transition, WO3 exhibits low absorption coefficients close to the band edge. Consequently, in order to harvest substantial portion of the visible spectrum, relatively thick WO3 film photoanodes must be used. In this presentation we will compare the photoelectrochemical activity for water splitting of nanostructured WO3 films deposited by the sol-gel method onto conductive glass FTO substrates with that of the films grown by thermal oxidation of preformed nanoporous tungsten metal samples.

(ICACC-S7-P106-2013) Preparation and characterization of hydroxyapatite covered biocompatible TiC nanocomposite thin films

K. Balazsi*, I. Lukacs, Hungarian Academy of Sciences, Hungary; M. Vandrovcova, L. Bacakova, Institute of Physiology, Czech Republic; C. Balazsi, Hungarian Academy of Sciences, Hungary

Hydroxyapatite (HAp) and titanium alloys are found to be the most suitable biomaterials. The major inorganic constituent of bones and teeth is calcium phosphate, whose composition is similar to that of synthetic hydroxyapatite (HAp; Ca10(PO4)6OH)2. This similarity provides HAp based materials excellent bioactivities like bone bonding capability, osteoconductivity, and biocompatibility. In the other hand, the relatively high stiffness of titanium, as compared to surrounding bone, can lead to problems of stress-shielding and subsequent implant loosening. In this work, this problem is aimed to corigated by bioactive Hap coating on Ti-based nanocomposite thin film surface. The TiC nanocomposite thin films were prepared by dc magnetron sputtering on on silicon (001) substrates with 300 nm thick oxidized silicon sublayer. The HAp thin film on TiC surface was prepared by spin coating. The structure of films were studied by transmission electron microscopy (TEM), scanning electron microscopy (SEM) and atomic force microscopy (AFM). The in-vitro tests of biocompatibility and bioactivity of TiC coat-ings on the adhesion, growth, maturation, viability, stress adaptation and potential immune activation of osteogenic MG-63 cells in cultures on these materials were studied.

(ICACC-S7-P109-2013) Graphene-semiconductor hybrid materials: electronic and photophysical properties

K. Ojha*, M. Makkar, P. K. Chowdhury, A. K. Ganguli, Indian Institute of Technology, Delhi, India

Graphene based hybrid materials are important for their very high electronic mobility which can be utilized for photovoltaic propertiesand is significant forthe future energy industry. In a hybrid graphene-semiconductor material the 2D planar π-conjugated graphene sheets inhibit the recombination of electron-hole pairs generated from the conjugated semiconductor. There are reports of ultrafast energy transfer from CdS QDs to graphene as shown by life time measurements of the charge carriers generated in the CdS QDs. However, this energy transfer process taking place at the interface between graphene and CdS is yet to be studied in detail. In addition to photovoltaic properties the photocatalytic efficiency of semiconductors like TiO2, has been enhanced in hybrid TiO2 - graphene nanostructures. Here we discuss our efforts to synthesize graphene-CdS hybrid materials where CdS particles are uniformly embedded in between the graphene layers. We have studied the detailed properties (photocatalytic and photocurrent generation) of these CdS – graphene conjugates.

(ICACC-S7-P110-2013) Deposition and Modification of Semiconducting Metaloxides with Enhanced Photoelectrochemical Properties via PE-CVD

A. Mettenboerger*, A. P. Singh, P. Golus, S. Mathur, University of Cologne, Germany

The plasma enhanced chemical vapor deposition (PE-CVD) is a powerful tool for the deposition of metaloxide thin films. It allows the deposition of semiconducting structures at slightly increased temperatures at a large scale. The properties, like the film thickness, the cristallinity and the morphology, of the resulting films can be tuned by changing the deposition parameters. In this work we present the deposition of semiconducting metaloxide (TiO_2, Fe_2O_3) films deposited via PE-CVD using titanium isopropoxide and iron pentacarbonyl as precursors. The photoelectrochemical properties like the photocurrent density and the donor density were investigated and optimized by varying the used plasma power. Furthermore the optimized films were post treated and modified using hydrogen plasma, which leads to a partial reduction of the metaloxide. This films showed modified optical, electrical and photoelectrochemical properties. The hydrogen treated semiconducting films exhibited a substantially improved photocurrent density and solar-to-hydrogen efficiency due to a reduced bandgap and increased donor density.

S11: Next Generation Technologies for Innovative Surface Coatings

S11 Poster Session

Room: Ocean Center

(ICACC-S11-P135-2013) Formation of S-phase layer on AISI 304 stainless steel by low pressure gas nitriding

J. Kim, Hanbat National Univesity, Republic of Korea; K. Moon, Korea Institute of Industrial Technology, Republic of Korea; Y. Kim*, Hanbat National Univesity, Republic of Korea

Formation of nitrogen-rich modified layer, S-phase, on stainless steels is a good solution to improve surface hardness and wear resistance without a corrosion resistance loss. Most of the S-phase was formed by plasma nitriding treatment at low temperature, below 773 K because of a dense passive layer on the surface of a stainless steel. However, plasma nitriding compared with gas nitriding needs to expansive equipment and production process cost is also high. In this work we try to form the S-phase on AISI 304 stainless steel using low pressure gas nitriding. The dense passive layer on the stainless steel was removed by pretreatment, several times of oxidation and reduction using N2O and NH3 gas. Low pressure gas nitriding was carried out in NH3 at 420oC and 500oC at 220torr. Nitride surfaces were characterized by x-ray diffraction, scanning electron microscopy and Vickers microhardness. We will discuss the properties of S-phase compared with it formed by plasma nitride at the same temperature.

(ICACC-S11-P136-2013) Fabrication of Highly Ordered Freestanding ZnO-based Nanostructure Arrays and its Application

W. Kwack, H. Choi, S. Kwon*, Pusan National University, Republic of Korea

One dimensional nanostructured materials such as nanowires, nonotubes, nonorods, and nonobelts, have been of great interest because they can have unique properties that are not seen in bulk or three-dimensional materials. As the interest in these materials grows higher, various approaches have been developed for the fabrication of nanomaterials. Among them, the template-assisted approach combined with atomic layer deposition (ALD) has been distinguished from the others as a simple and well-controlled method. ALD is considered to be a promising and competitive approach for the fabrication of nanostructured materials due to its self-limiting growth nature which offers advantages such as precise thickness control, superior thickness uniformitiy, and conformal growth properties, good step coverage. Also, ALD can be carried out at low temperatures, even at room temperature. In this study, we prepared highly ordered freestanding ZnO-based nanostructure arrays by depositing ALD-ZnO based thin films on BCP template with high aspect ratios. Also, we applied these ZnO-based nanotstructures to naodevices. The device performances will be reported.

(ICACC-S11-P137-2013) PECVD of Ti-Ru-N nancomposite films on stainless steel as bipolar plates for PEMFC

W. Kwack, H. Choi, S. Kwon*, Pusan National University, Republic of Korea

Polymer electrolyte membrane fuel cell (PEMFC) are generally considered as an adequate power sources in home cogeneration system and electric automobiles because they allow short-time warm-up and low operation temperature. As a major part of the PEMFC stack, the bipolar plate acted as separators and current collectors, distributing reactants uniformly, and mechanically supporting the cell stack. The bipolar plate material should have excellent corrosion resistance in PEMFC operation environments, low interfacial contact resistance, low gas permeability, light weight, and good mechanical strength. Although the stainless steel is considered as an optimal bipolar plate material for PEMFC due to its anti-corrosion and good electrical properties, it requires an additional coating layer because bare stainless steel suffers corrosion attack in the harsh acidic and humid environments. In this study, we prepared the Ti-Ru-N nanocomposite coatings by plasma-enhanced chemical vapor deposition (PECVD) to improve corrosion resistance and conductivity of stainless steel bipolar plates. PECVD technique was used to prepare Ti-Ru-N nanocomposite coatings because the excellent step coverage of PECVD is very attractive for the complex shapes of bipolar plate. In the presentation, the electrical properties and corrosion behavior of the Ti-Ru-N coated stainless steel bipolar plate will be also discussed in detail.

(ICACC-S11-P138-2013) Influence of oxidation-reduction process on the low-pressure gas nitriding of stainless steel

K. MooN*, H. Park, C. Byun, KITECH, Republic of Korea

Generally, it is considered that the plasma nitriding process is the best option for nitriding of stainless steel, because the etching process in plasma atmosphere could remove dense oxide film existing on the surface of stainless steels. Also, the plasma nitriding could be carried out in lower temperature where the formation of CrN could be limited. This induces the increase of hardness without reduction of corrosion properties in stainless steel. But during the plasma nitriding the glow discharge is directly engaged on the specimens, it is not easy to nitride large quantity of specimens and complex shape specimens. In this study, to solve such problems in the plasma nitriding, a low-pressure gas nitriding (around 200 torr) has been tried to form a nitride layer on the surface of austenitic stainless steel at low temperature. According to the previous research, the surface activation by oxidation-reduction process by N2O and NH3 gases was very effective to nitride of steels. It was revealed that the surface energy was higher in the steels pretreated by the oxidation-reduction process compared with that by plasma etching process. So, the usefulness of the oxidation-reduction process as a pretreatment before nitriding of stainless steel has been investigated in this study.

(ICACC-S11-P139-2013) The effects of the elements (Ti, Cr, Mo, N, F) on the properties of DLC films prepared by PECVD process

K. Moon*, J. Kim, D. Jung, kitech, Republic of Korea; J. Park, Hanyang university, Republic of Korea

DLC films have been applied to diverse industrial fields because of good tribological properties like high hardness, low friction coefficient and chemical stability etc. They have found applications in tribology, mechanics, electronics, and biomedicine. However DLC has the weakness of high temperature instability and low electrical conductivity. This restricts the wide applications of DLC. So in this study, the elements such as Ti, Cr, Mo, F, and N were added to investigate there effect on the structure and the properties of DLC. In this study, DLC films were deposited by PECVD process with C2H2 and Ar gases after the deposition of interlayer with one of the elements such as Si, Ti, Cr, Mo at room temperature. To incorporate metal elements such as Ti, Cr, Mo, a subsidiary sputter target source was used. The elements such was N, F was add as gaseous source as N2 and CF4. The structure of DLC films was confirmed by Raman and the hydrogen contents in the DLC films were measured by RBS analysis. In additions, the mechanical properties of DLC films were analyzed by scratch tester for adhesion, nano-indenter for hardness and Tribometer for wear properties including friction coefficient. Also, the electrical resistivity was measured by four point probe system. The electrochemical property was measured by potentiodynamic polarization test in 3.5% NaCl solution.

(ICACC-S11-P140-2013) Characteristic studies on the Zr-based metallic glass thin films by magnetron sputtering process

C. Lee, S. Shin, J. Sun*, K. Moon, Korea Institute of industrial technology, Republic of Korea

Zr based metallic glass alloys with high glass forming ability have attracted a great interest to fabricate amorphous thin film. However, it is quite difficult to lead to a congruent transfer of the target elements into the film. In this study, Zr-Al-Cu and Zr-Al-M-Cu amorphous thin films are deposited by DC magnetron sputtering process with an alloyed target. The operating conditions for the sputtering system were set a working pressure of 5mTorr, target to substrate distance of 5 cm, respectively. Sputtering rates of the films were in the range of 0.08~0.12 μm/min with increasing the sputtering power from 3.3 W/cm2 to 6.6 W/cm2 and there was no resolvable crystalline peak in the XRD and TEM analysis. In addition, the films had morphology of uniform amorphous phase in the TEM observation and vein pattern which is typical fracture surface of the amorphous alloy were observed in the cross sectional fractographs. As a result of EPMA analysis, it appears unary amorphous target composed of more than 3 elements can lead to a quasi-congruent transfer of the target stoichiometry to the film by sputtering process. When the sputtering time was lengthened for 120 min with sputtering power of 4.4 W/cm2 and 5.5 W/cm2 respectively, we can get amorphous films with more than 10 μm thickness by the ternary and quaternary amorphous single targets.

(ICACC-S11-P141-2013) Residual stress and elastic properties of CrMoN films deposited by hybrid PVD

Y. Oh*, Y. Yang, KICET, Republic of Korea; I. Lyo, Hyundai & Kia, Republic of Korea; S. Park, Hyundai Hysco, Republic of Korea; D. Lim, Korea University, Republic of Korea

Chromium Moly Nitrde (CrMoN) is one of the promising materials in the machining field and precision component as a protective hard coating for its lower frictional compared to conventional single phase films such as CrN, TiN and so on. This material has been studied to apply as coating parts through the hybrid PVD consisting of arc ion plating and UBM sputter. High residual stress is commonly found in the hard coating for high hardness, therefore the coating may have problems of crack formation that residual stress causes from the thermal expansion mismatch between the substrate and the coating. These have been considered as one of the greatest obstacle to commercial applications. In this study, we tried to develop a multi-composition coating with superlattice nanostructure having high adhesion strength. Hybrid PVD technique was used to get columnar nano/micro complex structure of the Chromium Moly Nitride films. Also the nano-indentation technique is used to analyze the adhesion strength of the coating and measured the elastic properties. Based on the results, we tried to discuss the origin of the sound coating regardless of the thermal expansion mismatch between the coating and the substrate.

(ICACC-S11-P143-2013) PEO on Eco-Al as a tool for lightweight metal protection against corrosion and surface decoration

J. Park*, T. Hwang, KITECH, Republic of Korea

There has always been a strong demand for lightweight metals from industries like automobile and mobile electronic devices makers. The most commonly discussed lightweight metals are Al, Ti and Mg, which are accepted as an alternative to high strength steel and plastics reducing the total weight of products due to the high specific strength. Recently we see very active tries of making various automobile parts using Al, however, the substitution is hindered by the poor machinability of Al far behind the industrial standards. In the mean time, the patented Eco-Al was developed by KITECH with enhanced mechanical properties such as improved ductility and yield strength, and it also exhibited slightly improved corrosion resistance shedding a hopeful light for successful application. In this study, we tried PEO on Eco-Al for a surface protection against corrosion. Microstructure of deposited oxide layer on Eco-Al was investigated using SEM and TEM. Addition to the PEO on Eco-Al, a potential application of PEO in surface decoration of lightweight metals was also demonstrated.

(ICACC-S11-P144-2013) Study on the Probability of Gas selectivity on single device of Sol-gel prepared porous TiO2 thin film by a concurrent AC/DC electrical investigation

J. Park*, T. Hwang, KITECH, Republic of Korea

Highly sensitive gas sensors are always of great interest for both scientists and engineers, and oxide semiconductor gas sensors have been in the center of great attention due to their high sensitivity and high thermal reliability. Because of the great endeavor of researchers from all over the world, the sensitivity of the gas sensors reached a certain level of satisfaction. However, the selectivity is still an unsolved problem. Selectivity, in this case, definitely means an ability to separately detect a specific gas from the mixture of gases with a precision of concentration of the gas concerned. For this purpose, array of multiple sensors of different kind could be used with a pattern recognition technique. However, the pattern recognition technique, a pure mathematics, is a very tricky art that frequently fails to give precise information when a complex mixture of gases is encountered. The purpose of this work is to shed a light for a novel method to achieve the gas selectivity from a single sensor device. Porous TiO2 thin films were prepared by a simple sol-gel preparation method, where dispersed nano-particulate TiO2 was used for the skeleton and Titanium isopropoxide was used for a precursor of network former.

(ICACC-S11-P145-2013) Multi-phase nano composite coating for high power engine component

I. Lyo*, W. Hong, K. Choi, H. Kang, D. Han, KITECH, Republic of Korea

Engine development trend is down-sizing for higher efficiency. Plasma coating techniques for automobile have focused on low friction, wear resistance and heat resistance with the trend. A DLC coating is a type of low-friction coating that has been mainly used to coat conventional vehicle components. While DLC coatings are advantageously already mass-produced and have been broadly used, it has insufficient friction and wear resistance at high temperature. CrN and TiN coating materials have excellent heat resistant and wear resistant properties. However, due to insufficient low-friction properties, its application to various drive components is limited. Accordingly, to obtain the necessary low-friction property at high temperature, we have developed nano composite coating materials.

(ICACC-S11-P146-2013) Tribological behaviors of ternary amorphous B-C-N coatings

D. Kim*, D. Jeong, Pusan National University, Republic of Korea; J. Park, Korea Institute of Science and Technology, Republic of Korea; K. Kim, Pusan National University, Republic of Korea

The amorphous boron carbon nitride (BCN) coatings were synthesized using radio-frequency magnetron sputtering technique by a boron carbide (B4C) target with mixture of N2, CH4 and Ar gases. Effects of the partial pressure of Ar and N2 and CH4 on morphology, chemical composition and tribological property of films were studied. Various surface analysis techniques such as scanning electron microscopy, Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy revealed that the partial pressure of N2 and CH4 gases highly influences chemical composition of BCN films. In addition, tribological properties evaluation showed that the best friction and wear characteristics can be achieved at the optimum composition of BC1.9N2.3 among the studied coatings. The particular BC1.9N2.3 showed lowest friction coefficient with subtle wear among the deposited BCN coatings. FTIR and XPS analysis on the worn surface suggested that the transferred C-C and h-BN bonds on counterpart surface contribute low friction and wear.

(ICACC-S11-P147-2013) The characterization of MoN-Cu-Cr nano-composite coatings deposited by magnetron sputtering process with single alloying target

D. Jung*, K. Moon, H. Lee, S. C. Lee, Korea Institute of Industrial Technology, Republic of Korea

In this study, we tried to deposit MoN-Cu-Cr thin coatings showing high hardness and low friction at low and high temperatures to reduce energy consumption and wear problem in engine parts. This kind of nano-composite coating is generally made by various processes using multiple targets such as Mo, Cu and Cr. However, during the deposition with multiple targets, it is not easy to control the exact composition, and homogeneous deposition of large scale specimens. To overcome this problem, it had been tried to make the alloying target with the composition in which the MoN-Cu-Cr nanocomposite coatings had the best properties. The MoN-Cu-Cr nanocomposite coating were deposited by unbalanced magnetron sputtering method with the single alloying target. With the addition of ternary element such as Cr resulted in further decrease of microstructure and this induced the higher hardness and lower young's modulus of the coatings. Accordingly, this resulted in the better mechanical properties of the MoN-Cu coatings. According to the wear tests by ball on disc method, the MoNCu-Cr coating by single alloying target had 20% lower friction coefficient compared with that of MoN-Cu coating. And the wear resistance of the former coating was the better because they showed a narrow track after wear test than the latter coating.

(ICACC-S11-P148-2013) Enhancement of electrochemical properties of thin films containing composite nanoparticles synthesized from microemulsion medium

M. Pyeon*, T. Hwang, KITECH, Republic of Korea

Recently, thin films with composite nanoparticles dispersed through out the film network are of growing interest in achieving novel or enhanced features of films, where inorganic-organic hybrid structures are frequently employed. For the synthesis and size control of the composite nanoparticles, microemulsion system that provides nano-sized reactors could be used. Addition to the synthesis of nanoparticles, a subsequent dispersion of the composite nanoparticle into a desired solution either organic or aqueous is also an important engineering skill. The physical and electrochemical properties enhancement of the deposited thin films containing the composite nanoparticles could be easily expected. However, control of the whole engineering process is not that easily attainable than it is postulated. In this study, we tried thin films with a dispersion of composite nanoparticles containing some useful active components on various kinds of substrates. A microemulsion processing method for the synthesis of composite nanoparticles comprising active polymer and inactive silica skeleton is described. Properties enhancement of the active components by the composite structure is demonstrated on the sol-gel deposited thin films.

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

S12 Poster Session

Room: Ocean Center

(ICACC-S12-P149-2013) Improved processing of carbon nanotube/magnesium alloy composites

A. Goodarzi*, H. Taylor, Harvard University, USA

Carbon nanotubes (CNTs) are promising reinforcements for light weight and high strength composites due to their exceptional properties. However, until now, the main obstacle is to obtain a homogenous dispersion of the CNTs in the desired material matrix. Quite a few methods have been studied to help improving the dispersion of CNTs in a polymer matrix. But not much research has been conducted on how to disperse CNTs in metal matrices. In this study, a two-step process was applied. In the first stage, a block copolymer was used as a dispersion agent to pre-disperse multi-wall carbon nanotubes (MWNTs) on Mg alloy chips. Then the chips with the well dispersed MWNTs on their surface were melted and at the same time vigorously stirred. The molten MWNT Mg alloy composites were poured into a cylindrical mould to solidify quickly. For the pre-dispersion step, the microstructures of the Mg alloy chips were studied under SEM. MWNTs were quite successfully dispersed on the surfaces of the Mg alloy chips. The mechanical properties of the MWNT/Mg composites were measured by compression testing. The compression at failure, the compressive yield strength and ultimate compressive strength have all been improved significantly up to 36% by only adding 0.1 wt% MWNTs to the Mg alloy.

(ICACC-S12-P150-2013) ZrC-based composites for high temperature applications

I. Hussainova*, D. Yung, L. Kollo, N. Voltsihhin, R. Traksmaa, Tallinn University of Technology, Estonia

The study is aimed at development, fabrication and preliminary mechanical characterization of ZrC-based composites for high temperature applications. The improvement in densification was achieved through introduction of second phase (molybdenum, zirconia, and titanium carbide). ZrC powder was produced by cost-effective in situ reactive sintering of nano-sized zirconium dioxide and graphite. The powder mixtures were pressureless sintered in vacuum at temperatures lower than 2000 0C. The final densities of the composites varied between 96 – 98%. Materials obtained were quite hard (HV10 > 17 GPa) while relatively tough (IFT > 6.6 MPa m1/2).

(ICACC-S12-P152-2013) Processing and Characterization of Porous Ti2AlC with Controlled Porosity and Pore Size

L. Hu*, R. Benitez, S. Basu, I. Karaman, M. Radovic, Texas A&M University, USA

: In this work, we demonstrate a simple and inexpensive way to fabricate porous Ti2AlC, one of the best studied materials from the MAX phase family, with controlled porosity and pore size. This was achieved by using NaCl as the pore former which was dissolved after cold pressing but before pressureless sintering at 1400 oC. Porous Ti2AlC with volume fraction of porosity ranging from ~10 to ~71 vol.% and different pore size ranges, i.e 42-83 um, 77-276 um and 167-545 um, were successfully fabricated. Fabricated samples were systematically characterized to determine their phase composition, morphology and porosity. Room temperature elastic moduli, compressive strength and thermal conductivity were determined as a function of porosity and/or pore size. For comparison, several samples pressureless sintered without NaCl pore former, or fabricated by spark plasma sintering (SPS) were also characterized. The effects of porosity and/or pore size on the room temperature elastic moduli, compressive strength and thermal conductivity of porous Ti2AlC are reported are discussed in this work. It follows that porosity can be a useful microstructural parameter to tune mechanical and thermal properties of Ti2AlC.

(ICACC-S12-P153-2013) High temperature oxyacetylene torch testing and oxidation behavior of graphite, ZrB2, and ZrB2-SiC at temperatures greater than 1500°C

P. Neff*, University of Arizona, USA; A. Powell, Missouri University of Science & Technology, USA; L. S. Walker, E. L. Corral, 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 an oxidizing environment. Thus, choosing a suitable TPS requires extensive testing of fundamental material properties at these extreme conditions however it is not possible to recreate these exact flight environments on land. Therefore, oxyacetylene torch testing is one method that has the potential to be used as an extensive screening tool for land based testing. Thermodynamic calculations show the adiabatic flame temperature during torch testing can reach 3048°C.and the oxygen content of the flame may be controlled to make it an oxygen rich environment. Our torch facility has been developed to be able to control flame temperature, oxygen content, and heat flux for reliable and reproducibly testing up to 2200 °C. Ultra-high temperature ceramics ZrB2 and ZrB2-SiC are tested for oxidation behavior above 1500°C where heat flux and ablation rates were recorded. Results from oxidation studies performed on the oxyacetylene torch show that ZrB2-SiC demonstrates enhanced oxidation resistance over ZrB2 and oxidation rate increases with increasing temperature.

(ICACC-S12-P154-2013) A Testing Facility for Root Cause Analysis of Failure Under Extreme Temperatures

J. Chatterjee, H. Chen, M. Mooty, J. Reali, J. R. Brenner*, Florida Tech, USA

A tensile test chamber with feedthroughs for gas phase flow and liquid nitrogen cooling has been constructed to simulate cryogenic embrittlement along with with one or more of the following failure mechanisms: cyclic fatigue, interstitial embrittlement, and corrosion. Multiple hermetically-sealed fiber optic sensors at different wavelengths are used to measure strain, temperature, and gas phase concentration simultaneously. An inverse fiber optic sensor in which the fibers approach each other when strains are greater than one percent is under development. Partners are being sought for development of a similar chamber using laser-based localized sample heating for creep testing. These systems are expected to assist root cause analysis when multiple failure mechanisms are present.

(ICACC-S12-P155-2013) Spark Plasma Sintered ZrB2–SiC Composites

R. Stadelmann*, University of Central Florida, USA; V. M. Sglavo, University of Trento, Italy; N. Orlovskaya, University of Central Florida, USA

Ultra High Temperature Ceramic (UHTC) ZrB2- 10, 20, 30wt%SiC composites are of high interest for hypersonic air-breathing vehicles. In this work ZrB2- 10, 20, 30wt%SiC UHTC composites were produced by Spark Plasma Sintering (SPS) technique. After sintering, almost dense ceramics with ~ 5-8% porosity were produced. Their mechanical properties, such as Young's modulus, 4-point bending strength, and SEVNB fracture toughness were measured. The thermal residual stresses in ZrB2-20wt%SiC and ZrB2-30wt%SiC were measured by micro-Raman spectroscopy. To study the oxidation behavior of ZrB2-30wt%SiC the heating experiments were performed using high temperature heating stage coupled to micro-Raman spectrometer.

(ICACC-S12-P172-2013) Mechanistic investigations in carbothermal reduction of 3 mol% yttria stabilized zirconia

A. Sondhi*, C. Morandi, University of North Texas, USA; S. Chattopadhyay, Argonne National Laboratory, USA; R. E. Reidy, T. W. Scharf, University of North Texas, USA

Zirconium carbide (ZrC) is an important ultra-high temperature ceramic due to its refractory properties. It is commonly synthesized via carbothermal reduction of zirconia above 1657° C according to following reaction, ZrO2(s) + 3C(s) $\rightarrow$ ZrC(s) + 2CO(g) Prior research indicates that carbon monoxide (CO) was the responsible species for carburizing ZrO2 to form ZrC. To explore this reaction pathway, investigations were performed by making two mixed phase pellets with 3 mol% yttria-stabilized zirconia (YSZ) and graphite. Each pellet is composed of an upper half of YSZ and the lower half of one sample consists of pure graphite and the other of finely mixed YSZ and graphite powder. Similar experiments were conducted with sintered YSZ upper halves. After reacting at 1800 ° C, x-ray diffraction analysis revealed higher ZrC conversion for the YSZ pellet face in direct contact with pure graphite suggesting that zirconia more efficiently reacts with solid carbon than CO to form ZrC. These findings differ from previous work that suggested CO was the main reactive species in the carbothermal reduction of YSZ. Diffusion experiments showed ZrC conversion occurred to a depth of ~25μm. This concurs with diffusion lengths calculated using a diffusion coefficient of 3×10^{-14} m^2/sec at 1800 ° C for solid state carbon diffusion in YSZ.

S13: Advanced Ceramics and Composites for Sustainable Nuclear Energy and Fusion Energy

S13 Poster Session

Room: Ocean Center

(ICACC-S13-P156-2013) Ab initio molecular dynamics simulations of recoil events in thoria

B. Liu*, Oak Ridge National Laboratory, USA; H. Xiao, The University of Tennessee, USA; Y. Zhang, Oak Ridge National Laboratory, USA; W. J. Weber, The University of Tennessee, USA

Thorium dioxide (ThO_2), or thoria, is of great interest in nuclear energy research because of the great abundance of natural thorium and the proliferation resistance of thoria-based fuel cycle, which also reduces the production of minor actinides as nuclear waste. However, knowledge of the structural evolution of thoria under irradiation is more limited compared to other nuclear fuels. Radiation-induced defects drive microstructure evolution in nuclear fuels and ultimately lead to degradation of thermal and mechanical properties. However, due to the short time and small length scale of the radiation-damage events, a fundamental understanding of defect production is difficult to achieve. In this study, ab initio molecular dynamics simulations are used to investigate recoil events in ThO_2. The aims are to gain a fundamental insight into defect production mechanisms and to explore the role of charge transfer during the recoil events.

(ICACC-S13-P157-2013) Effects of Size and Geometry on the Equibiaxial Flexural Test of Fine Grained Nuclear Graphite

C. Shih*, Y. Katoh, Oak Ridge National Laboratory, USA; T. Takagi, Ibiden, Japan

Reduction of specimen size is an essential requirement for neutron irradiation effect studies of materials since space in nuclear reactors for those studies are often very limited and costly. Reducing the specimen size can dramatically reduce the cost of these studies, the irradiation exposure to personals involved in post irradiation examination and the volume of radioactive waste. In this study, 4 specimen sizes were systematically varied to examine the size effect on the equibiaxial flexure test of fine grain nuclear graphite in non-irradiated conditions at room temperature. A statistically significant sample population of 30 was used for each specimen geometry or dimension. The results showed that the round shaped samples followed weibull distribution with Weibull modulus of 25 to 35. The average strength followed the trend of the weakest link theory. The 2 sizes of square shaped samples had Weibull modulus of 29 and 40. Data from round and square samples agree with others reasonably and collectively follow the Weibull scaling theory. It is concluded that the equibiaxial flexural test using adequate population of small specimens provides useful and reliable information on the statistical strength properties for fine-grained nuclear graphite materials.

(ICACC-S13-P158-2013) Effect of Neutron Irradiation on Bonded Fiber Silicon Carbide Composite

Y. Katoh*, K. Ozawa, S. Kondo, Oak Ridge National Laboratory, USA; Y. Kawaharada, S. Higuchi, Toshiba, Japan

Silicon carbide-based ceramic composites are promising structural materials for use in high radiation environments including commercial nuclear reactor core. Bonded fiber silicon carbide composite made to near-stoichiometric compositions is particularly attractive for fuel cladding application because of its ability to withstand high mechanical loading and to make into thin walled tubular components with structural homogeneity and tightness against gaseous fission products. This paper will report the physical, mechanical, and thermal properties of near-stoichiometric bonded fiber silicon carbide composite after neutron irradiation to more than 5 displacement per atom at 593K in High Flux Isotope Reactor, Oak Ridge National Laboratory.

FS4: Advanced Ceramic Materials and Processing for Photonics and Energy

FS4 Poster Session

Room: Ocean Center

(ICACC-FS4-P163-2013) Nano Cr-doped crystalline composite in silicate glass host induced by CO2 laser and thermal heat treatment for broadband applications

J. Wang*, Y. Chen, National Sun Yat-Sen University, Taiwan

Chromium has very broadband emissions in both Vis and NIR regions upon its existence in trivalent or tetravalent states in host, respectively. The broadband emissions are attractive to many photonics applications, such as tunable laser source, low coherence source for Optical coherence tomography (OCT), ultra short pulse laser, etc. In this study, glasses were selected as hosts for the chromium doping since their great tunalbility in compositions and properties, which may enable the further optimization for many specific applications, i.e. nano Cr-incorporated crystalline silicate optical fiber. As known it is rarely to demonstrate lasing from Cr-doped glasses because of the high non-radiative rate in glass hosts. In contrast, it has been successfully demonstrated that Cr-doped crystals have better lasing properties. However, their crystal sizes have to be well controlled below submicron in order to avoid significant scattering loss in optical waveguides. In this study, the composition effect on trivalent and tetravalent concentrations, crystallization behaviors, and crystalline sizes upon CO2 laser and thermal heat treatments will be discussed. Their potential applications in broadband devices will be particularly addressed.

(ICACC-FS4-P164-2013) Design of Multi-Layered Ceramic Devices for Energy Harvesting

J. Song*, S. Kim, J. Jo, I. Kim, S. Jeong, M. Kim, Korea Electrotechnology Research Institute, Republic of Korea

An energy harvesting technique for a mechanical switch device with electromechanical coupling was investigated. Piezoelectric ceramics of $0.4Pb(Mg_{1/3}Nb_{2/3})O_3$- $0.25PbZrO_3$-$0.35PbTiO_3$ were prepared by a conventional solid state reaction method. Li_2O, Bi_2O_3 and CuO additions were used as sintering aids to develop piezoelectric ceramics for low-temperature sintering of piezoelectric device applications. When the Samples were sintered at 950°C, for 4h in air, the electromechanical properties were found to reach the values for d_{33} of 410 pC/N, kp of 0.62, ε_r of 1995, respectively. Multilayer piezoelectric ceramics with 10x10x3 mm^3 size were manufactured by conventional tape casting method using the powder prepared and Ag-Pd inner electrode. The output power of the samples showed a maximum value of 0.45 mW at 100kg force. Switch devices were designed by considering simple concepts of direct mechanical impact to piezoelectric multilayer ceramics. The prototype model of the piezoelectric battery-less switch device was developed and the performance of the device was excellent enough to be practically used. These results show that the new concepts of battery-less switch device and the possibility of using piezoelectric energy harvesting applications.

(ICACC-FS4-P165-2013) Fabrication of Nanostructured ZnO films for Plastic Dye-sensitized Solar Cells

H. Utsunomiya*, S. Ueno, S. Fujihara, Keio University, Japan

Typical photoanodes of dye-sensitized solar cells (DSSCs) consist of conducting glass substrates and metal oxide semiconductor layers adsorbed with sensitizing dyes. To fabricate flexible and lightweight DSSCs, it has been explored to utilize plastic substrates for electrodes instead of glass substrates. In this case, nanoporous semiconductor layers should be fabricated on substrates below heatproof temperature of plastic substrates. We propose a pyrolysis method which is to convert preformed layered hydroxide zinc acetate (LHZA) films into ZnO films at temperatures below 120 °C. We fabricated the flower-like LHZA films on ITO-coated polyethylene naphthalate (ITO-PEN) substrate at 60 °C by a chemical bath deposition (CBD) method, and then these films were pyrolyzed at 90-120 °C. The resultant ZnO films maintained the flower-like morphology. The ZnO formation reaction rate depends strongly on the pyrolysis temperature and the ZnO crystalline size could be controlled by the pyrolysis conditions. During pyrolysis the acetate-related compounds were formed inside the films and these impurities can disturb the adsorption of dyes and the electron transport. We found these impurities could be dissolved by immersing in water at 90 °C. The energy conversion efficiency of DSSCs using the ZnO/ITO-PEN electrodes actually increased from 3.0% to 3.3% by removing these impurities.

(ICACC-FS4-P166-2013) Design and Fabrication of Smart-skin Structures with a Spiral Antenna

D. Kim, J. Kim, W. Hwang*, Pohang University of Science and Technology, Republic of Korea

Communication areas will in the future be expanded by the use of satellite communication and satellite Internet availability in vehicles. To implement these satellite services, especially in vehicles, antenna technology will be central. Antennas located on the surface of a structure take up much space, and suffer from large path-loss and junction-loss. In view of these problems, the Structures Division of the US Air Force's Wright Laboratory is sponsoring the development and demonstration of CLAS. This program is called "Smart-Skin Structure Technology Demonstration (S3TD)". The program opted for a multi-arm spiral antenna embedded in a CLAS fuselage panel. The final demonstration article was a structurally effective 36 x 36 inch curved multifunction antenna component panel. It successfully withstood running loads of 4,000 pounds per inch and principal strain levels of 4,700 micro-strain, and featured a broadband (150 MHz to 2.0 GHz), multifunction communication, navigation and identification, and electric warfare (CNI/EW) antenna. The present study aims to design, fabricate and investigate the structural and electrical performances of microstrip antennas of composite sandwich construction as part of the next generation of structural surface technology.

(ICACC-FS4-P167-2013) Evaluation of Compression Characteristics for Composite-Antenna-Structures

J. Kim, D. Kim, D. Shin, W. Park, W. Hwang*, Pohang University of Science and Technology, Republic of Korea

Nowadays, there are a number of wireless communication systems and broadcasting services which must be integrated into vehicles. Through the innovative integration of antenna elements, amplifiers and ground plane, the reception quality and manufacturability of vehicles is expected to be significantly improved. Even though the articles published to date indicate that the technology has had some spectacular success in its initial stages, little has been published about the problems that remain to be overcome for use in an operational vehicle. The most important outstanding problem that is structurally effective materials cannot be used without reducing antenna efficiency. The present study aims to suggest electrically and structurally effective antenna structures which are termed composite-antenna-structures(CAS), and study mechanical and electrical behavior characteristics of CAS after compression test. The CAS is composed of two composite laminates(GFRP, CFRP), nomex honeycomb, and antenna element. And that is the dual-mode annular ring antenna and the microstrip patch antenna for the global positioning system(GPS), satellite digital multimedia broadcasting(DMB) and direct broadcast satellite(DBS), and consists of a coupling feed line and four slots on the annular ring patch.

Engineering Ceramics Summit of the Americas

ECSA Poster Session

Room: Ocean Center

(ICACC-ECSA-P168-2013) Sol-Gel Synthesis of Mullite Starting from Different Inorganic Precursors

L. Tellez-Jurado, R. M. Arévalo-Hernández, Universidad Politécnica de Victoria, Mexico, Universidad Politécnica de Victoria, MexicoESIQIE-IPN, Mexico; E. Rocha*, Universidad Politécnica de Victoria, Mexico

Using silicon tetraetilortosilicate (TEOS) mixed with aluminum trisecbutoxide (TSBAI) or aluminum clorure they were fabricated mullite ceramics by the sol-gel method. The used amounts of each substance were those that let to obtain stoichiometric mullite (3Al2O3.2SiO2). The followed experimental methodology for obtaining mullite consisted in: sol-gel synthesis of precursor materials, isothermal treatment of those materials and characterization of resulting materials. In order to determine the reactions advanced during mullite formation, they were carry out isothermal treatments between 300 and 1600°C, remaining the samples at each temperature during 4h. From XRD results, it has that precursor powders amorphous originally, start to crystallize in Al2O3 and SiO2 at 1200°C, whereas at 1200°C starts the mullite formation, completing it at 1600°C. The use of TSBAI favors the formation of mullite crystals at lower temperature. From SEM observations it has a microstructure that presents primary mullite with random oriented grains of secondary mullite with acicular shapes and sizes than ranges between 0.25 and 0.50 microns.

(ICACC-ECSA-P169-2013) Alumina Ceramics Reinforced with Silver Particles

E. Refugio-García, M. Gaeta-Conchas, Universidad Autónoma Metropolitana, Mexico; J. G. Miranda-Hernández, Universidad Autónoma del Estado de Mexico, Mexico; E. Rocha*, Universidad Politécnica de Victoria, Mexico

Al2O3/Ag composite ceramics were fabricated by the use of mechanical milling and pressureless sintering. Al2O3 + 10 wt.% Ag were mixed and milled during 12 h at 300 rpm in a horizontal mill, then with the powder mixture it was conformed cylindrical samples by uniaxial pressing using 300 MPa. The pressed samples were sintered during 1 h in an electrical furnace at 1300, 1350 and 1400 °C respectively. During sinter it was used an argon atmosphere inside the furnace in order to inhibit silver oxidation. From XRD results it has that silver retains its crystalline structure. On the other hand density of samples is better with increments in temperature. However, the final relative density is small and about of 85%. Optical microscopy observations show a microstructure of alumina with a fine and homogeneous distributions of silver particles.

(ICACC-ECSA-P170-2013) Physical Properties of the Sr4Al6O12SO4 Ceramic Compound

J. A. Rodríguez-García, E. Rocha*, J. López-Hernández, E. Martínez-Peña, Universidad Politécnica de Victoria, Mexico; J. M. Almanza-Robles, J. Torres-Torres, CINVESTAV, Mexico

The Sr4Al6O12SO4 ceramic compound was synthesized by a solid state reaction starting from stoichiometric mixtures of 3:3:1 molar ratio of SrCO3, Al2O3 and SrSO4 respectively. Cylindrical samples were conformed by uniaxial pressing at 100MPa, and then were heat treated at 1400°C during 4 hours. Subsequently, the samples were ground and re-conformed in cylindrical shape samples by uniaxial pressing at 300Mpa. The new samples were heat treated at 1400°C during 24 hours; all this was in order to increase the density of the samples. The Sr4Al6O12SO4 ceramic compound was characterized by the study of its physical properties such as: density, mechanical properties (micro hardness tester), thermal expansion and stability, enthalpy of formation, magnetic properties and electrical conductivity. Experimental results show that the maximum density obtained for the Sr4Al6O12SO4 ceramic was 2.913grcm-3, with a coefficient of thermal expansion of 10.12E-06(°C-1), also it presents an enthalpy of 2.3KJmol-1 and an excellent thermal stability at elevated temperatures in different atmospheres. The Sr4Al6O12SO4 compound is not electrically conductive, is not magnetic and does not present good mechanical properties.

(ICACC-ECSA-P171-2013) Mechanism of the carbothermal synthesis of MgAl2O4-SiC refractory composite powders

H. Zhu*, H. Duan, W. Yuan, C. Deng, Wuhan University of Science and Technology, China

MgAl2O4 and SiC play an important role in the carbon-containing refractory. In this paper, MgAl2O4-SiC refractory composite powders were prepared by using forsterite, alumina and carbon black via carbothermal reaction. The effects of the calcined temperature and the proportion of carbon black on phase composition and microstructure of MgAl2O4-SiC-C powders were investigated. The mechanism of synthesis processing was discussed. The result shows that the crystallization of MgAl2O4 from the liquid phase at 1573 K according to phase diagram and experimental result. SiC generated at 1873 K.

Thursday, January 31, 2013

S1: Mechanical Behavior and Performance of Ceramics & Composites

Tribological Performance and Impact Testing of Ceramics and Composites

Room: Coquina Salon D
Session Chairs: Jiangang Sun, Argonne National Laboratory; Oyelayo Ajayi, Argonne National Lab

8:00 AM

(ICACC-S1-054-2013) Tribological Performance of Carbon-Ceramics Composite Materials

A. Oyelayo*, C. Lorenzo-Martin, S. Torrel, D. Singh, Argonne National Lab, USA; L. Manocha, G. Prasad, Sardar Patel University, India

Carbon-based materials such as carbon-carbon (C/C) composite are currently used in a variety of challenging engineering applications such as rocket nozzles and high temperatures in space and aeronautical systems as well brake discs, biomedical and sport equipment. In recent years, efforts are being devoted to further enhance the properties of carbon based materials by adding ceramic materials to form carbon-ceramic composite. The carbon ceramic composites materials have a potential for use in tribological applications, especially under severe service conditions. This paper presents the results of friction and wear performance evaluations of three carbon-ceramic composite materials under unidirectional and reciprocating sliding contacts using a ball-on-flat contact configuration. Significant differences were observed in the friction, wear and mechanisms of the three materials when sliding against two balls materials under dry conditions. These differences are attributed to differences in the materials microstructures. Transitions in the wear rate with increasing loads are also connected with each material microstructure.

8:20 AM

(ICACC-S1-055-2013) Tribological Properties of Alumina/Zirconia Composites With and Without h-BN Phases

L. Xue*, Timken, USA; G. L. Doll, University of Akron, USA

The tribological performance of alumina/zirconia composites (alumina with 10 vol% zirconia) with and without h-BN added to the material has been examined. Whereas the baseline composite (without h-BN) was conventionally sintered, h-BN containing composites were sintered by Spark Plasma Sintering. Friction and wear tests were conducted in unlubricated, reciprocating sliding. Testing of self-mated pairs revealed that only composites with low concentrations of h-BN exhibited low friction coefficients. When mated against steel, all compositions had relatively high friction coefficients and had noticeable wear, especially with higher concentrations of h-BN. The tribological behavior of the composites with higher amounts of h-BN appeared to be greatly influenced by residual porosity and h-BN particle pull-out.

8:40 AM

(ICACC-S1-056-2013) The Sliding Wear Behaviour of TiC-316L Stainless Steel Composites

C. C. Onuoha, Z. N. Farhat, G. J. Kipouros, K. P. Plucknett*, Dalhousie University, Canada

Ceramic-metal composites, or cermets, have a wide range of applications in the chemical, aerospace, automotive and oil and gas sectors, due to their unique combination of high hardness and wear resistance, good strength characteristics, and resistance to aqueous corrosion. In the present study, a family of novel titanium carbide (TiC)/stainless steel cermets has been produced for potential application in demanding wear and corrosion environments. Processing of the TiC/steel cermets involved vacuum melt infiltration, between 1475 and 1550°C, with the steel binder contents varied from 5 to 30 vol. %. For the present study, the microstructure and tribological response of TiC-316L steel cermets is presented. The reciprocating wear behaviour is assessed for loads between 20 and 80 N, with the cermet material sliding unlubricated against a 6.35 mm diameter tungsten carbide/cobalt sphere in a conventional ball-on-flat geometry. Characterisation of the wear response has been performed using a combination of optical and scanning electron microscopy, optical profilometry and focused ion beam microscopy. In terms of the wear behaviour, the specific wear rate was observed to increase with both the applied load and the steel binder content. It was demonstrated that the wear resistance is improved for TiC-316L cermets processed with a finer grain size. The operating wear mechanism(s) wear will be discussed.

9:00 AM

(ICACC-S1-057-2013) Tribological profile of binderless niobium carbide

M. Stuart, CBMM Companhia Brasileira de Metalurgia e Mineração, Brazil; K. Mohrbacher, Niobelcon BV, Belgium; M. Woydt*, BAM Federal Institute for Materials Research and Testing, Germany

The unlubricated (dry) friction and wear behavior of alumina (99,7%) mated against binderless niobium carbide (NbC) rotating disks under the type of motions of unidirectional sliding (0,03 m/s to 7 m/s; 22°C and 400°C) and oscillation (f= 20 Hz, Δx= 200 mm, 2/50/98% rel. humidity, n= 105/106 cycles) will be shown. The microstructure and mechanical properties are also presented. Thanks to the tribological database TRIBOCOLLECT of BAM; the obtained tribological data will be benchmarked with different ceramics, cermets and thermally sprayed coatings. The established tribological profile revealed a strong position of NbC under tribological considerations and for closed tribosystems against traditional references, like WC, Cr3C2, (Ti,Mo)(C,N), etc..

9:20 AM

(ICACC-S1-058-2013) Comprehensive ablation characteristics of ceramic fibers impregnated rubber composites

N. Iqbal*, National University of Sciences and Technology (NUST), Pakistan; M. Khan, National University of Sciences and Technology (NUST), Pakistan, National University of Sciences and Technology (NUST), PakistanNational university of Sciences and Technology, Pakistan; S. Sagar, A. Maqsood, National University of Sciences and Technology (NUST), Pakistan

Four diverse concentrations of aluminum silicate fibers were incorporated into ethylene propylene diene monomer rubber to fabricate ablative composites for high temperature applications. Ceramic fibers (CFs) were impregnated in the rubber matrix using two roller mixing mill. Ablation testing of the composite specimens was carried out according to ASTM E285-08, in which oxy – acetylene torch was used as a high temperature source. Backface temperature evolution, insulation index, linear/mass ablation rates and % char yield of the ablative composites were evaluated in the ablation study. Anti-ablation performance of the polymer composites was augmented with increasing fibers concentration in the polymer matrix. Thermal degradation of the fabricated composites was diminished with the progressive incorporation of CFs in the host matrix. Ultimate tensile strength, elongation at break, and modulus of elasticity of the composite specimens were reduced due to weak fill to matrix interaction while Shore A rubber hardness was augmented with increasing fiber to matrix ratio. Voids formation & polymer pyrolysis of the ablated specimens, char reinforcement interaction, CFs dispersion in the polymer matrix, elemental analysis & diameter measurement of the CF, and the compositional analysis of ablative composite were analyzed using scanning electron microscopy coupled with energy dispersive spectroscopy.

10:00 AM

(ICACC-S1-059-2013) Use of NDE and Health Monitoring Techniques to Assess High-Velocity Impact Performance of Various SiC/SiC Composites

C. R. Baker*, G. N. Morscher, University of Akron, USA; A. L. Gyekenyesi, Ohio Aerospace Institute, USA; C. Faucett, S. R. Choi, Naval Air Systems Command, USA

Implementation of ceramic matrix composites (CMCs) in jet engine applications necessitates the understanding of high velocity impact behavior. To this end, various melt-infiltrated SiC/SiC composites were impacted at room temperature at ~350 m/s with different support systems and tensile tested to failure. Examination of pre and post impact electrical resistance (ER) shows that ER is sensitive to impact damage. Similarly, flash thermography was used to examine the impact damage extent in the composites, which is a function of support system, constituent content and impact velocity. Finally, modal acoustic emission and ER was used to understand and characterize the post-impact tensile damage propagation.

10:20 AM

(ICACC-S1-060-2013) Multilayer Ceramic Composite Armor Design and Impact Tests

F. Elaldi*, University of Baskent, Turkey

Alumina (Al2O3) ceramic with the properties of good hardness, thermal shock resistance, and chemical corrosion resistant features as aluminum based ceramic plate is sandwiched by two layers of Kevlar composite plates. The multilayer composite plates manufactured were tested by low velocity impact testing machine and damage analysis was made. Minimum impact energy level and its fragment-velocity equivalent were studied to be determined. The data obtained through impact testing were finally verified by Ansys /Autodyne FE analysis.

S3: 10th International Symposium on Solid Oxide Fuel Cells (SOFC): Materials, Science and Technology

Processing/Performance

Room: Coquina Salon H
Session Chairs: Jeff Stevenson, Pacific Northwest National Laboratory; Jong Shik Chung, POSTECH

8:00 AM

(ICACC-S3-035-2013) Recent developments on direct ethanol solid oxide fuel cells (Invited)

F. C. Fonseca*, S. D. Nobrega, IPEN, Brazil; F. B. Noronha, INT, Brazil; P. Gelin, IRCELYON, France; S. Georges, M. C. Steil, LEPMI, France

Direct use of hydrocarbon or alcohol fuels is considered as a major advancement towards solid oxide fuel cell (SOFC) commercialization. Among potential primary fuels, a great deal of attention has recently been given to ethanol as an efficient and cost competitive renewable source of hydrogen. Ethanol is a widely available fuel that has been blended with gasoline for vehicular propulsion in some countries and in Brazil the ethanol derived from sugar cane represents ~40% of the road transportation fuel. However, the direct use of carbon-containing fuels in SOFCs has a number of practical issues that need further development, such as the stability of the standard Ni-based cermet anodes and the optimization of both the exothermic electrochemical and the endothermic reforming reactions. Most of the reported studies on ethanol fueled SOFCs use a mixture of alcohol and water as fuel to suppress carbon formation, decreasing efficiency and adding complexity to the fuel cell system. More recent developments have shown that an adequate catalyst layer can promote the gradual internal reforming of ethanol in which the water released from the electrochemical oxidation of hydrogen is used to the alcohol reforming reaction. By using a ceria-based catalytic layer, standard SOFCs were shown to operate with good stability for more than 100 hours without water addition.

8:30 AM

(ICACC-S3-036-2013) Solid oxide fuel cell activities at POSTECH (Invited)

J. Chung*, N. M. Sammes, POSTECH, Republic of Korea

Research activities on SOFC, started as early as 2003, has been rather small in scale due to the lack of budget. National budget is now alocated to more fundamental research. Meanwhile, big dompanies such as POSCO, LG, SK and Samsung are in consideration to enter the business by importing technologies. Recently, LG group purchased the Ohio-based Rolls-Royce research institute and will speed up the development toward more product-oriented direction. During the past 5 years, Pohang city in Gyungbuk province has evolved as a hub of high temperature fuel cells. With a business success of MCFC by POSCO after installing 46 MW throughout Korea, it is under development of 10-25 KW SOFCs by 2014. Small scales are also under development by several companies. POSTECH plays roles in leading research with its own model of MEGA cell. MEGA cell is flat tube and stacking type with a high current density. Flat tube has air channels incorporated so that a stacking unit is made of all ceramic material. After stacking, it becomes a ceramic monolith having hydrogen channels inside the flat tube and air channels between tubes. So far, we have a performance of 350 mW/cm2 for stacks of 50~500 W scale. POSTECH is also in operation of HFCTB organization with funds coming from central and local governments to test, evaluate and standardize parts, modules and systems with 63 companies involved at present.

9:00 AM

(ICACC-S3-037-2013) Planar metal supported solid oxide fuel cells fabricated with ultra-thin YSZ membranes

C. O. Belda*, E. Dietzen, M. Kusnezoff, N. Trofimenko, A. Michaelis, Fraunhofer Institute for Ceramic Technologies and Systems IKTS, Germany

Metal-supported cells (MSC) for solid oxide fuel cells (SOFC) have increasingly attracted attention over the last decade, especially for portable and mobile applications. Currently different MSC concepts are being developed and evaluated regarding cost-efficiency, reliability and electrochemical performance worldwide. A main challenge is the reliable manufacturing of gas tight electrolyte layer in combination with porous metal supports. Recently a new fabrication concept for planar metal-supported cells has been developed at the Fraunhofer IKTS, simplifying the requirements for the utilization of wet-chemical technologies and reducing sintering temperatures to ≤ 1250 °C by laminating pre-fired thin electrolyte sheets (≤ 40 μm). Despite the simple manufacturing route, problems with nickel agglomeration in the anode and adhesion between all functional layers have been observed. First results of optimizing the multilayer structure and analysis of the polarization losses in cells, depending on the nickel content in the anode, are presented in the paper. The impact of low temperature fired cathode materials ($T < 950$ °C) will be discussed on basis of impedance spectra obtained on symmetrical cells.

9:20 AM

(ICACC-S3-038-2013) Metal supported SOFCs by Freeze Tape Casting

P. Wei, M. Ren, McMaster University, Canada; S. W. Sofie, Montana University, USA; A. Petric*, McMaster University, Canada

Our group has recently developed a new method for fabrication of metal-supported cells: freeze tape casting is used to fabricate the porous metal support with aligned pore structure and screen printing is used to deposit electrode layers onto the metal tapes. A co-firing process was developed to sinter the complete cell in a reducing atmosphere. The key issue for co-firing single cells is to match the shrinkage rate of metal support with that of the ceramic layers. In this paper, some preliminary results on shrinkage rate measurements of porous metal tapes are discussed. It has been found that the shrinkage rates of the metal support depend on many factors including steel powder size, sintering temperature and time, solid loading, green metal tape thickness and sintering atmosphere. Based on the investigation, the optimized parameters for co-firing have been determined, and metal-supported single cells have been successfully fabricated.

10:00 AM

(ICACC-S3-039-2013) Solid Oxide Fuel Cell Materials Development at PNNL (Invited)

J. Stevenson*, Y. Chou, J. Hardy, O. Marina, D. Reed, J. Choi, E. Stephens, C. Coyle, J. Templeton, R. Scott, 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. Materials R&D funded by the SECA Core Technology Program is focused on 1) development, optimization, and validation of advanced interconnect and cell component materials, and 2) development of improved understanding and mitigation of cell/stack degradation mechanisms. The goal of this work is to assist SECA industry teams in meeting SECA's electrical performance, performance stability, and cost targets. Specific areas of emphasis include interconnect alloys, protective coatings and surface treatments, glass-based seals, and electrode materials and interactions.

10:30 AM

(ICACC-S3-041-2013) Anode-Supported Solid Oxide Fuel Cells with LaGaO3-based Electrolyte Film Fabricated by a Simple One-step Co-firing Process

Y. Chen*, Y. Gong, Z. Yang, University of South Carolina, USA; Z. Yang, China University of Mining & Technology, China; J. Bunch, F. Chen, University of South Carolina, USA; M. Han, China University of Mining & Technology, China

Application of LaGaO3 based electrolyte for anode-supported solid oxide fuel cell has often been limited by the cost of thin film preparation. In this paper, anode-supported solid oxide fuel cells with La0.4Ce0.6O2/La0.8Sr0.2Ga0.83Mg0.17O3 (LDC/LSGM) bi-layer as electrolyte have been prepared successfully by a simple and cost-effective screen-printing and co-firing method. The half cell with bi-layer electrolyte and anode substrate prepared via freeze-drying-tape-casting shows shrinkage of about 19 % after co-firing at 1450 oC for 12 h. Microstructures of half cell and single cell have been investigated by scanning microstructure microscope (SEM). The NiO-Gd0.1Ce0.9O2 (NiO-GDC) supported cells with LDC/LSGM bi-layer as the electrolyte, La0.6Sr0.4Co0.2Fe0.8O3-GDC as the cathode show maximum cell power density of 1.17 Wcm-2 at 800 oC using hydrogen (3vol % H2O) as fuel and ambient air as oxidant. This work has demonstrated a promising simple and cost-effective method to fabricate high performance electrochemical devices for various applications.

10:50 AM

(ICACC-S3-042-2013) Electrochemical Performance and Redox Cycling Tolerance of an Infiltrated Tubular Fuel Cell

A. R. Hanifi, A. Torabi*, T. H. Etsell, University of Alberta, Canada; P. Sarkar, Alberta Innovates - Technology Futures, Canada

The electrochemical performance and redox cycling tolerance of a fully infiltrated tubular cell was studied in this research. Ni-SDC (Sm0.2Ce0.8O1.9) was infiltrated into the porous YSZ support to form the anode of the infiltrated cell and LSM (La0.80Sr0.20MnO2.9) was infiltrated into a thin porous YSZ layer to form the cathode. The infiltrated cell delivers a reasonable power density especially at low temperatures (600-700 degree centigrade). The microstructure of the infiltrated fuel cell shows a suitable distribution of fine LSM and Ni-SDC particles (50-100 nm) at the electrodes/electrolyte interface and within the electrodes. Result of stability tests indicate that the power degradation is governed by both poor current collection and Ni sintering. The cell showed excellent redox cycling resistance with only a small drop in power density. Co-precipitated Ni and ceria based electrocatalysts into a porous YSZ structure are suggested as potential SOFC anodes.

11:10 AM

(ICACC-S3-043-2013) The development of plasma sprayed metal-supported solid oxide fuel cells at Institute of Nuclear Energy Research

C. Chang*, C. Hwang, C. Tsai, S. Nien, C. Chuang, S. Cheng, S. Wu, Institute of Nuclear Energy Research, Taiwan

Due to the advantages such as high thermal shock resistance and mechanical robustness to compare with anode-supported cells (ASCs), the metal-supported cells (MSCs) attract more and more interest in the stationary and mobile applications. The planar MSCs composed of a well-prepared porous Ni-Fe plate as a supporting substrate, double layers of $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-\delta}$ (LSCM) and nanostructured $La_{0.45}Ce_{0.55}O_{2-\delta}$/Ni (LDC-Ni) as an anode, a LDC layer as a diffusion barrier, a $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (LSGM) layer as an electrolyte, double layers of different contents of $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$-LDC (SSC-LDC) composite layers as a cathode were successfully fabricated by atmospheric plasma spraying (APS) technique at Institute of Nuclear Energy Research (INER). A post heat-treatment with a pressure of 0.8 kg/cm^2 at 850°C for 4 hrs was applied to the sprayed cells to improve its performances. The measured power densities of the MSC-MEA (Membrane Electrode Assembly) in cell test are 650, 568 and 443 mW/cm^2 at 750, 700 and 650°C, respectively. The durability tests of the MSC stack had performed for 1600 hrs at the test condition of 400 mA/cm^2 and 700°C. The measured degradation rate is less than 1 %/kh, which indicates that the MSC-MEA made by INER reveals an inspired performance.

11:30 AM

(ICACC-S3-040-2013) Extrusion and optimization of tubular IT-SOFCs

A. Azzolini*, V. M. Sglavo, G. Fantini, E. Vitorbi, University of Trento, Italy

Extrusion is a fast and reliable way to shape moldable pastes into long tubes with constant cross section. This technique can be applied to the fabrication of one or more functional layers of small tubular Solid Oxide Fuel Cells (SOFC). In this work the composition and preparation of pastes for the co-extrusion and co-sintering of anodic and electrolytic layers in anode supported SOFCs were optimized. Considering that the cell is to be operated at intermediate temperatures (around 700°C) and to be fed with methane or light hydrocarbons, 10 mol% gadolinia doped ceria powder (CGO10) was employed as ionic conductive phase in both layers. To avoid carbon deposition, copper was chosen as the electronic conductive phase within the anode. To match the firing treatments for the co-extruded half-cell, and to avoid the phase separation of copper oxide, cobalt oxide was added to the electrolyte composition as sintering aid. The two pastes were individually extruded in tubular shape through a ram extruder connected to a mechanical testing machine to optimize paste properties and then subjected to the same sintering treatment at 1100°C for 2 h. Tubes with external diameter of 4 mm and constant wall thickness of 300 um were obtained. The anode showed tailored porosity and well connected and extended triple phase boundary. The electrolyte reached full density when doped with 2 mol% of CoO.

S5: Next Generation Bioceramics and Biocomposites

Medical Ceramics

Room: Coquina Salon C
Session Chairs: Kurosch Rezwan, Advanced Ceramics, University of Bremen; Christian Bonhomme, UPMC

8:00 AM

(ICACC-S5-001-2013) Fluorescently labeled metal oxide colloidal particles for nanotoxicological in vitro screening (Invited)

K. Rezwan*, Advanced Ceramics, University of Bremen, Germany

In the light of nanotoxicological in vitro studies fluorescence labeling has become a prerequisite for particle localization within the cell environment. However, fluorescence labeling is also known to significantly alter the particle surface chemistry and therefore potentially affect the outcome of cell studies. Hence fluorescence labeling is ideally carried out without changing e.g. the isoelectric point. A simple and straight-forward method for obtaining fluorescently labeled spherical metal-oxide particles with well-defined isoelectric points and narrow size distribution is presented in this talk. The coating quality was confirmed by high-resolution transmission electron microscopy (HR-TEM), energy filtered-TEM and electrochemical characterization. The coating was proven to be stable for at least 240 h at different pH conditions. The synthesized and well-defined fluorescent particles can be directly used for biomedical investigations, e. g. elucidation of particle-cell interactions in vitro.

8:20 AM

(ICACC-S5-002-2013) Theranostics Based on Hybrid Nanoparticles for Early Cancer Detection and Treatment (Invited)

M. Wang*, S. Li, The University of Hong Kong, Hong Kong; L. Ren, Xiamen University, China

Early cancer detection and treatment are vitally important for millions of people around the world. Nanomedicine emerged a decade ago and uses nanotechnologies to detect and treat diseases. Combining diagnosis with therapy can provide enormous benefits to patients and national healthcare systems. The research on "theranostics", nanodevices that have the dual role of diagnosis and therapy, has thus attracted great attention. Suitably developed theranostics can have multiple functions. There are different inorganic nanoparticles (NPs) that can provide the basic unit for theranostics, and gold NPs are particularly appealing due to their biocompatibility and unique optical properties. For AuNPs, the ability to control their size and shape during synthesis for achieving the desired plasmonic property and their surface conjugation with macromolecules (e.g., antibody) allow for both selective, early detection and killing of cancer cells. This paper gives an overview of our research on multifunctional theranostics based on AuNPs, Ag NPs or bimetallic Au-Ag NPs. These systems include polymer-metal hybrids and ceramic-metal core-shell structured nanodevices and possess functions of cell targeting, anticancer drug delivery, photothermal therapy, etc. The synthesis of nanodevices, their structural features and designed functions are discussed. The biological performance of some nanodevices is presented.

8:40 AM

(ICACC-S5-003-2013) Bioactive Glass and Ceramic Scaffolds for Bone Regeneration (Invited)

M. N. Rahaman*, Missouri University of Science & Technology, USA

This presentation will review our recent studies on the development of bioactive glass and ceramic scaffolds for the regeneration of loaded and non-loaded bone. Autologous bone grafts are the gold standard for the regeneration of large bone defects and bone allografts are alternatives. However, limitations of these treatments have increased the need for synthetic bone graft substitutes. Scaffolds under development include hollow hydroxyapatite (HA) microspheres with a mesoporous shell wall and bioactive glass scaffolds with a controlled three-dimensional architecture prepared by robotic deposition. When loaded with a growth factor, hollow HA microspheres are showing a large capacity to regenerate bone in rat calvarial critical sized defects. Strong porous scaffolds of silicate (13-93) bioactive glass with a grid-like microstructure (porosity = 50%; pore width = 300 microns) show compressive strengths comparable to those of human cortical bone as well as a large capacity to regenerate bone in rat calvarial defects. Potential applications of these scaffolds to the regeneration of loaded and non-loaded bone will be discussed.

9:00 AM

(ICACC-S5-004-2013) Nature-inspired Materials Design and Manufacturing (Invited)

X. Li*, University Of South Carolina, USA

Nacre is a natural nanocomposite with superior mechanical strength and eminent toughness. What is the secret recipe that Mother Nature uses to fabricate nacre? What roles do the nanoscale structures play in the strengthening and toughening of nacre? Can we learn from this to produce nacre-inspired nanocomposites? The recent discovery of nanoparticles in nacre is summarized, and the roles these nanoparticles play in nacre's strength and toughness are elucidated. It was found that rotation and deformation of aragonite nanoparticles are the two prominent mechanisms contributing to energy dissipation in nacre. The biopolymer spacing between nanoparticles facilitates the particle rotation process. Individual aragonite nanoparticles are deformable. Dislocation formation and deformation twinning were found to play important roles in the plastic deformation of individual nanoparticles, contributing remarkably to the strength and toughness of nacre upon dynamic loading. Inspired by nature's design, a commercial cotton T-shirt was used as both the template and carbon source to synthesize large quantities of radially aligned B4C nanowires on carbon microfibers. The B4C nanowire - carbon microfiber hybrid structures can block 99.8% UV irradiation and achieve superior reinforcing effect in their epoxy composites.

9:20 AM

(ICACC-S5-005-2013) Revisiting electro-spinning procedure for preparation of biologically active fiber mats (Invited)

H. Yoshihara, Y. Shirosaki, Okayama University, Japan; S. Chen, N. Hanagata, National Institute of Materials Science, Japan; S. Hayakawa, Okayama University, Japan; A. Stambourlis, University of Birmingham, United Kingdom; Y. Nakamura, A. Osaka*, Okayama University, Japan

Electro-spinning procedure has been applied in order to form nano- and micro-fibers of synthetic polymers, ceramics, and polymer/ceramic composites. The fibres are aligned to some extent to the lateral direction and therefore the spaces among the polymer/oligomer fibers (including oligomers of ceramic fiber precursors) can accommodate small molecular species but not larger molecules when post-spinning modification is conducted. The present study revisits the electrospinning process of polymers, like poly(vinyl alcohol) or chitosan, in order to make possible to control the inter-fiber spaces. These e-spun fibers were compared with those obtained from simple freeze-drying procedure in terms of yielding solid ceramic fiber mats or hollow ceramic micro-tube mats; e.g., silica solid and hollow fiber mats. In addition, surface modification of the fibers was conducted using silane coupling agents or other biologically active molecules and a study in order to examine whether the active molecules were directed attached to the fibers was conducted.

10:00 AM

(ICACC-S5-006-2013) New synthetic biomineralization media for the in vitro testing of synthetic biomaterials

A. Tas*, University of Illinois at Urbana-Champaign, USA; N. Temizel, G. Girisken, Yeditepe University, Turkey

This study investigated the role of the biomineralization medium used in testing the phase transformations to be observed during the immersion tests, usually conducted at 36.5 C, of synthetic biomaterials. Such tests claim to examine the changes to occur in the synthetic materials once they come into contact with blood and researchers typically used SBF (synthetic/simulated body fluid) solutions for this purpose. Brushite (dicalcium phosphate dihydrate, DCPD, CaHPO4x2H2O) was selected as the synthetic biomaterial to be tested in this study. Brushite was transformed into octacalcium phosphate (OCP, Ca8(HPO4)2(PO4)4x5H2O), but not hydroxyapatite, in seven different newly developed biomineralization media, all inspired from the commercial DMEM solutions, over the temperature range of 36. to 90 C with ageing times varying between 1 h and 6 days. DCPD used in this study was synthesized in our laboratory by using a wet-chemical technique. DCPD was found to transform into OCP in the Ca2+, Mg2+, Na+, K+, HCO3-, Cl- and H2PO4- containing aqueous biomineralization media in less than 72 hours at 36.5 C, even without stirring. The same media were able to convert DCPD into OCP in about 2 hours at 75-80 C, again without a need for stirring. Samples were characterized by using powder X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM).

10:20 AM

(ICACC-S5-007-2013) Spectroscopy and simulations: towards a better understanding of complex biomaterials (Invited)

C. Bonhomme*, UPMC, France

In this lecture, the latest developments in spectroscopy (including NMR and DNP) and first principles calculations will be applied to the detailed description of complex biomaterials. Several examples related to bioactive glasses will be described.

10:40 AM

(ICACC-S5-008-2013) X-ray imaging enhancement using nanoscience (Invited)

J. Johnson*, R. Leonard, UTSI, USA; C. Alvarez, Northwestern University, USA; R. Lubinsky, SUNY, USA; S. Gray, UTSI, USA; A. Petford-Long, Northwestern University, USA; S. Schweizer, Fraunhofer Institute, Germany; C. Johnson, UTSI, USA

The purpose of this work is to develop an x-ray imaging system to enhance imaging capabilities in mammography. Samples have been synthesized based on the ZBLAN (Zirconium, Barium, Lanthanum, Aluminum and Sodium Fluoride) formulation additionally doped with chlorine and one or two rare-earth halides. The glasses are prepared in an inert atmosphere and later heat-treated in order to develop $BaCl_2$ nanocrystals within the glass matrix. Characterization methods include differential scanning calorimetry, photoluminescence, photostimulated luminescence (PSL), x-ray diffraction, Mössbauer spectroscopy and *in situ* TEM. The results show an enhanced PSL effect by co-doping with europium and holmium. *In situ* TEM shows that BaF_2 nanocrystals develop before the $BaCl_2$ nanocrystals. All crystal structures of the nanoparticles have been identified by a diffractogram. The work is not yet complete but the team is well on the way to elucidating the structure-property relationships of these materials and taking them forward as image plates. In addition to the image plate a new readout system has been developed tailored to enhance the performance of this particular material.

11:00 AM

(ICACC-S5-009-2013) Biomimetic apatites : surface state and potential interfacial issues (Invited)

C. Drouet*, N. Vandecandelaere, C. Rey, CIRIMAT Carnot Institute, France

Biomimetic nanocrystalline apatites occupy a major position in bone tissue engineering due to their high analogy to bone mineral, in terms of chemical composition, nonstoichiometry, (micro)structure, surface state and reactivity. Provided that a biomimetic-like process is set up for elaborating such compounds, through adapted synthesis conditions, the bioceramics obtained via powder or gel processing can be seen a priori as extremely well adapted for the production of bioactive scaffolds. The impact of synthesis/postsynthesis parameters should however not be underestimated as they could lead to noticeable modifications of apatite physicochemical features. An "equilibration" of the surface of such bioceramics (containing labile ionic surface species) is also bound to occur during the first moments following in vivo implantation, or at the occasion of in vitro assays, which may also be a source for modifications of the bioceramic characteristics. An adequate pre-equilibration step may then be considered during the bioceramic production so as to limit for instance acidification effects after immersion in biological fluids. In this contribution, these aspects will be discussed in regard with a potential use in the field of bone regeneration. Our results may prove helpful for the understanding of transient cytotoxicity effects that may be noticed on apatite-based systems when contacted with biological fluids.

11:20 AM

(ICACC-S5-010-2013) Evaluation of Bioactive Borate Glass Fibers In-vitro and In-vivo for Wound Care Applications

S. Jung*, Mo-Sci Corporation, USA

Bioactive borate glass was evaluated for safety and efficacy using in-vivo animal models and in-vitro cell culture using standard ISO-10993 testing for a Class II topical medical device. In addition, the bioactive borate glass fibers were tested in a subcutaneous diabetic mouse model to study wound healing rates, wound collagen (hydroxyproline) content, in-vivo antimicrobial effectiveness, analysis of myeloperoxidase (MPO), macrophage content in-vivo, wound vascularity as a function of time, wound breaking strength after healing, and collagen ultrastructure. The results of this work along with a 58 patient preclinical trial will be reviewed. The goal for the present work is to answer questions about safety and efficacy for the bioactive borate fibers and prepare for and an eventual regulatory filings and approvals for a novel wound care product.

S7: 7th International Symposium on Nanostructured Materials and Nanocomposites

Innovative Processing of Functional Materials

Room: Coquina Salon B

Session Chairs: Oliver Diwald, University of Erlangen Nürnberg; Gunnar Westin, Uppsala University

8:00 AM

(ICACC-S7-049-2013) Nanoparticle Surface Design for Controlling their Dispersion Stability and Processing Functional Composite Materials (Invited)

M. Iijima*, H. Kamiya, Tokyo University of Agriculture and Technology, Japan

The control of dispersion and aggregation behavior of nano-scaled materials is one of the essential processes to improve/tune the final properties of composite materials. Since there are various species of solvents which are used during processing composite materials, understanding the strategy to control the dispersion/aggregation phenomena of nanoparticles in the desired media will be a powerful tool. A surface structure control of nanoparticles by using mixed silane coupling agents or by using multi-purpose anionic surfactant which can maintain the stability of nanoparticles in various organic solvents will be focused as well as the usage of surface modification process such as bead milling operation. A controlled surface modification can lead to the success-able preparation of dry nano-powder which can be easily re-dispersed into various organic solvents near the size of their primary particle size. These surface modified nanoparticles were useful to process nanocomposite materials, and several examples of their applications toward the fabrication of transparent polymer nanocomposite materials with high nanoparticle concentrations will be introduced.

8:30 AM

(ICACC-S7-050-2013) Structure-Property Relations in Designing Functional Nanomaterials and Nanocomposites

E. V. Timofeeva*, Argonne National Laboratory, USA; M. R. Moravek, Argonne National Laboratory, USA; D. Singh, Argonne National Laboratory, USA; W. Yu, Argonne National Laboratory, USA; D. France, Argonne National Laboratory, USA

Variety and unique characteristics of nanomaterials allow for engineering the multifunctional composites with new desired characteristics. The strategies to utilization of the specific to nanoscale mechanisms often are not always straightforward. Nanocomposites are multivariable system, where properties of the system as a whole could be different from the properties of the system individual components. Nanomaterial concentration, particle shape, size and size distribution, interactions between the nanomaterials and the matrix all can be critical for the system performance. Nanomaterial suspensions in fluids (nanofluids) are essentially composites and represent the new expanding area in nanotechnology, with applications in biomedical, lubrication, thermal management, energy generation, conversion and storage. This talk will focus on approaches that we use in designing the nanofluids with advanced heat transfer properties. Morphology and composition of hybrid nanomaterials were designed to engage plasmonic and percolation heat transfer mechanisms. Experimental synthesis of these hybrid nanomaterials demonstrated the ability to dramatically boost the cooling efficiency of the heat transfer fluid at very low concentrations. A simple, low cost, and up-scalable wet chemical synthesis method was developed for hybrid nanomaterials and investigation of thermo-physical properties of their dispersions.

8:50 AM

(ICACC-S7-051-2013) Boron Nitride Nanotube Reinforcement for High Temperature Composite Applications

J. Hurst*, D. Santiago, C. Hung, NASA Glenn Research Center, USA

Research focused on Boron Nitride Nanotubes (BNNT) has generated significant interest due to their potential for high temperature applications. Whether as a high modulus, thermooxidatively stable reinforcement within composites or as high temperature nanodevices, boron nitride nanotubes offer significant promise. This effort focused on incorporating BNNT within SiC composites as a high temperature reinforcement phase. BNNT was successfully grown on various SiC fiber surfaces as well as within SiC composites. This BNNT material was evaluated by a variety of techniques including field emission scanning electron microscopy (FeSEM), electron microprobe (EM) and Fourier transform infrared spectroscopy (FTIR). The effect of BNNT growth on mechanical strength of both SiC fiber tows and SiC composites was examined.

9:10 AM

(ICACC-S7-052-2013) Nanocomposite Films With Low-Field Magnetoresistance or Magnetoelectric Properties (Invited)

M. Jain*, University of Connecticut, USA

Solution methods, such as co-precipitation, sol-gel, and hybrid methods, have been used to grow nanoparticles and nanocomposite films of functional oxides. In nanocomposites, concentration and distribution (connectivity) of the two phases play an important role in defining their physical properties. In this talk, the results of two nanocomposite systems: (i) colossal magnetoresistive materials with low-field magnetoresistive effect and (ii) magnetoelectric composite with strain coupling will be presented. Magnetoresistive materials with high magnetic field sensitivity are of great interest for various applications including magnetic field sensors and spintronic devices. In the manganite:insulator ($La_{1-x}Sr_xMnO_3$:MgO and $La_{1-x}Sr_xMnO_3$:ZnO) nanocomposite films grown in our group, enhanced low-field magnetoresistance have been achieved. Also, indirect magnetoelectric (ME) coupling in nanocomposites can be achieved by combining piezoelectric and magnetostrictive materials. In such ME multiferroic nanocomposites, ME coupling arises via strain between the two order parameters. In case of composites, the concentration of the magnetostrictive phase ($CoFe_2O_4$) in piezoelectric phase (lead zirconium titanate) has been shown to affect its ME performance.

Surfaces and Controlled Interface Properties

Room: Coquina Salon B

Session Chairs: Menka Jain, University of Connecticut; Motoyuki Iijima, Tokyo University of Agriculture and Technology

10:00 AM

(ICACC-S7-053-2013) Chemical and Thermal Effects on Phase Evolution and Cation Gradients in Solution-Derived Thin Film Ferroelectrics (Invited)

G. Brennecka*, J. Ihlefeld, Sandia National Laboratories, USA; K. Nittala, University of Florida, USA; K. Meyer, New Mexico Institute of Mining and Technology, USA; R. Wilkerson, Missouri University of Science and Technology, USA; S. Mhin, J. Jones, University of Florida, USA

Thin film ferroelectrics are important for a variety of integrated electrical applications ranging from decoupling capacitors to electrooptic modulators. While solution deposition offers several advantages for the fabrication of these types of devices, it is accompanied by many challenges as well, including precise control of film stoichiometry, chemical homogeneity, and microstructure development during crystallization, all of which are critical to obtaining the desired performance from the film. This talk describes recent advances in characterizing and controlling the evolution from liquid solution to ceramic perovskite film with a focus on PZT-based and BaTiO3-based thin film ferroelectrics. Solution chemistry and substrate interactions play critical and coupled roles in the phase, interface, and microstructure development during thermal processing. Only by understanding and controlling these effects can we obtain nanoscale ferroelectric thin films with bulk-like electrical properties. This work was funded by the Laboratory Directed Research and Development program at Sandia National Laboratories. Sandia 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.

10:30 AM

(ICACC-S7-054-2013) Interface Controlled Property Changes of Titanate Nanostructures (Invited)

M. J. Elser, A. K. Sternig, B. Schuerer, W. Peukert, O. Diwald*, University of Erlangen Nürnberg, Germany

Mechanistic insights into shape and structure transformation of metal oxide nanostructures are critical to our understanding of how synthesis parameters and chemical environment affect their properties. Na2Ti3O7 nanowires, which are composed of titanate nanosheets and which contain sodium ions in the interlayer region, are thermodynamically unstable in acid solutions. [1] At room temperature nanosheet delamination along the nanowire length axis leads to coiled-up nanoscrolls. At 373 K a dissolution and TiO2 recrystallization process gives rise to colloidal anatase nanoparticles. We comprehensively investigated these reactions with X-ray diffraction and electron microscopy and for the first time tracked processes at the solid-liquid interface such as nanosheet delamination by time-resolved second harmonic generation (SHG) measurements. Moreover, we explored the stability of the solution grown titanate nanostructures under high vacuum and in oxygen atmosphere. Annealing induces changes in structure and morphology. In addition to the characterization of resulting transformations of nanowires and nanoscrolls, the effect of oxygen vacancy formation and stoichiometry changes on the photoelectronic ensemble properties will be discussed.[2] [1] B. Schürer et al. J. Phys. Chem. C 2011, 115, 12381-1237. [2] A. Vittadini et al. Langmuir 2012, 28, 7851-7858.

11:00 AM

(ICACC-S7-055-2013) Solution based processing of doped zinc oxide and titanium dioxide as transparent conducting materials

K. Elen*, H. Damm, A. Kelchtermans, K. Schellens, A. Hardy, M. K. Van Bael, Hasselt University - imomec, Belgium

A current challenge in the production of transparent conducting oxides (TCOs) is that reliable synthesis routes have to be developed that allow mass production at reasonable cost. In this respect solution based processing and deposition is an appealing alternative to standard physical deposition methods that require a high vacuum. Secondly, there exists a strong demand for inexpensive, and efficient alternative materials to indium tin oxide. (Doped) zinc oxide (ZnO) and titanium dioxide (TiO2) are such a promising TCO compounds. The approach for the wet-chemical processing of TCO coatings, as presented here, can be divided into two general routes. The first route is a solution based route in which first molecular precursor solutions are prepared these precursors deposited on substrates and transformed to the oxide through an adjusted thermal treatment. We show that chemical solution deposition (CSD) of aluminium-doped zinc oxide (AZO) from a 2-butoxyethanol precursor yields TCO coatings with a promising resistivity upon high temperature annealing in a reducing atmosphere. We also present a method for aqueous CSD of group 5 doped TiO2. This method produces an anatase-based TCO, having the lowest reported for solution deposited TiO2 so far.

11:20 AM

(ICACC-S7-057-2013) All Inkjet-printed Field Effect Transistors with p-type CuO Nanoparticles Ink

M. Vaseem*, A. Hong, Y. Hahn, Chonbuk National University, Republic of Korea

Based on various ink-formulations, until now polymer based photovoltaic, light emitting device, thin film transistors and organic semiconductor based thin film transistors, have been extensively studied. However, ink formulation and inkjet printed inorganic semiconductors have been seldom reported. In this regards, we have synthesized CuO nanoparticles (NPs) by a simple solution process. As-synthesized nanoparticles were investigated in detail in terms of structural and optical characterization, and further formulated as inks using mixed solvents of water, ethanol, isopropanol and diethylene glycol. Ink-jetting behavior of the as-formulated inks samples were examined with printing lines on Si/SiO2 substrates as a function of CuO NPs concentration at room-temperature printing condition. It was observed that the CuO concentration and the number of over-printing are important factors for optimizing the uniformity and thickness of printed lines with smooth edge definition. In this report, we present the first results of inkjet printed CuO (channel) and Cu (source/drain) based field effect transistors (FET) on Si/SiO2 (gate material) substrate. As-printed devices show p-type conductivity with high carrier mobility, which can be applied further for various applications.

11:40 AM

(ICACC-S7-056-2013) Structural and magnetic properties of Zn1-xNixO diluted magnetic semiconductors synthesized by a polymer precursor method

J. Jadhav, M. Patange, S. Biswas*, The LNM Institute of Information Technology, India

Zinc oxide (ZnO) is an attractive wide band gap semiconductor for potential applications in several fields including UV light emitters, optical transducers, transparent solar cells, electrochemical coupled sensors and other optoelectronic devices. Ferromagnetic functionality induced in transition metal ion doped ZnO further extends its potentiality for novel spintronics applications. Here, we report a simple low temperature chemical synthesis method of doped Zn1-xNixO nanoparticles via a polymer precursor. The process involves a novel chemical method of forming a Zn2+-Ni2+-PVA precursor by reaction of dispersed metal cations (Zn2+ and Ni2+) with PVA-sucrose in aqueous solution at 50-60 C. After reaction, a controlled drying followed by heating the obtained precursor powder at 400-600 C in air forms refined Ni-doped ZnO nanoparticles. The structural, morphological and magnetic properties of the derived Zn1-xNixO samples were studied by X-ray diffraction (XRD), high resolution transmission electron microscopy (HRTEM), and vibrating sample magnetometer (VSM).

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

Novel Characterization Methods and Lifetime Assessment I

Room: Coquina Salon F
Session Chair: Guo-Jun Zhang, Shanghai Institute of Ceramics

8:00 AM

(ICACC-S12-030-2013) High Temperature Oxidation Induced Crack Healing of MAX phases (Invited)

W. Sloof*, L. Shen, Delft University of Technology, Netherlands; S. Li, Beijing Jiaotong University, China; G. Song, C. Kwakernaak, S. van der Zwaag, Delft University of Technology, Netherlands

MAX phase materials such as Ti3AlC2, Ti2AlC and Cr2AlC are very attractive materials in their own right as they combine desirable metallic and ceramic properties at the same time due to their atomically layered and hexagonal crystal structure. In our earlier studies we demonstrated that these materials possess interesting crack-healing properties when exposed to high temperatures in an oxidizing environment. The recovery of mechanical strength is due to the formation of a residue of mainly α-Al2O3 . In case of the Ti3AlC2 and Ti2AlC also some TiO2 is formed in the crack gap. This is avoided when Cr2AlC is used. To determine the crack healing efficiency of the MAX phases considered here, their high temperature oxidation kinetics is studied. The increase of oxide grain size upon high temperature exposure leads to abnormal oxidation kinetics, which turned out to be beneficial for crack healing. On the basis of microscopic observations and measured oxide growth kinetics, a quantitative model was devised to describe the growth of oxides on the MAX phase surfaces. In the work to be presented, we demonstrate quantitatively the strength recovery after healing of the crack damage. Also the prospect of multiple healing, i.e. several consecutive sequences of fracture and healing, will be presented. To this end, the decay of fracture toughness was determined as a function of the fracture and healing cycles.

8:30 AM

(ICACC-S12-031-2013) Synthesis and characterization of Ti2Al(C(1-x)Nx)y MAX phase solid solutions

W. Yu, V. Gauthier-Brunet, C. Tromas, T. Cabioc'h, S. Dubois*, Institut PPRIME, France

Using different initial reactant powder mixtures, 2Ti:1.05Al:0.85C, 2Ti:1.05Al:0.66C:0.22N, 2Ti:1.05Al:0.46C:0.46N, 2Ti:1.05Al:0.24C:0.72N, 2Ti:1.05Al:N, Ti2AlC, Ti2AlN and sub-stoichiometric Ti2Al(C(1-x)Nx)y (y<1) MAX phase solid solutions have been successfully synthesized. Powders were thoroughly mixed in a turbula@ and uniaxially cold-pressed. The compacts were sealed in glass containers and heat treated at 1400oC for 4h and 80MPa for 3h by using a Hot Isostatic Press (HIP). Rietveld refinement is used to carefully characterize the lattice parameters, the cell volume and the octahedron and trigonal prisms distortion parameters as a function of the Ti2Al(C(1-x)Nx)y solid solutions stoichiometry. Microstructures of the HIPed samples are observed by Scanning Electron Microscopy. Wavelength Dispersive X-ray Spectroscopy analyses are performed to determine the C and N contents of the solid solutions. Nanoindentation has been used to measure the intrinsic hardness and the Young's modulus of the different Ti2Al(C(1-x)Nx)y solid solutions. Hardness values of some Ti2Al(C(1-x)Nx)y solid solutions are finally discussed and compared to the ones of the Ti2AlC and Ti2AlN end-members.

8:50 AM

(ICACC-S12-032-2013) Critical analysis of effects from geometry and size on oxidation behavior of ultra-high temperature ceramics in tube and thermogravimetric furnace

M. Miller-Oana*, L. Walker, E. Corral, University of Arizona, USA

We investigate the influence of specimen size and geometry on oxidation behavior in the tube furnace for ultra-high temperature ceramics.We are interested in the effect of size and geometry to compare results from multiple studies that investigate oxidation behavior on a wide range of sizes and geometries. We introduce a parameter that accounts for edge length and surface area of the specimen being oxidized. This parameter is the ratio of total edge length to total surface area. We prefer this parameter because we are interested in how the edges/corners influence the oxidation behavior. We investigate the in situ mass measurements as a function of time up to 1600°C in the thermogravimetric furnace. We examine the oxidation behavior of rectangular prisms with constant edge length to surface area ratios at 1500°C for 60 min to compare mass gain and oxide scale thickness in the tube furnace. We examine the mass gain and oxide scale thickness for cylindrical prisms with smaller ratios. We also study the oxidation behavior as a function of the ratio parameter to determine the effect of total edge length and surface area on mass gain and oxide scale formation. We determine the effect of geometry and size on oxidation and the effect of time on oxidation kinetics to reliably measure oxidation results including oxide scale and mass gain.

9:10 AM

(ICACC-S12-033-2013) Effects of hyperthermal and thermal oxygen beam exposures on oxidation behavior of ultra-high temperature ceramics

M. Miller-Oana*, L. Walker, University of Arizona, USA; V. Murray, T. Minton, Montana State University, USA; E. Corral, University of Arizona, USA

We investigate the influence of high energy and low energy oxygen beams on oxidation behavior of ultra-high temperature ceramics. The high energy (>5 eV) beam is a hyperthermal oxygen beam composed of ~80% O atoms as compared to the low energy (~0.04 eV) plasma beam that is composed of ~30% O atoms. The ultra-high temperature ceramics (ZrB2 or ZrB2-SiC) are exposed for 14 hours under high vacuum (>10-6 torr) at room temperature or 300°C. Before exposure some specimens are heat treated at 300°C or sputtered with Ar. The surfaces of exposed and as processed specimens are examined after exposure using scanning electron microscopy (SEM), X-Ray photoelectron spectroscopy (XPS), and Raman spectroscopy. From the oxygen beam exposures, we are able to investigate the initial stages of oxidation of ZrB2 and SiC grains, and we confirm presence of oxidation by detecting oxide products on the polycrystalline material due to the oxygen beams using SEM, XPS and Raman spectroscopy. Specimens exposed to the thermal plasma beam also exhibit early stages of oxidation confirmed with SEM, XPS, and Raman. Ongoing investigations will also be presented for higher temperature exposures (≥500°C) under ambient conditions to simulate the early stages of oxidation seen using the oxygen beams. We determine the initial stages and mechanisms of oxidation for ultra-high temperature ceramics.

9:30 AM

(ICACC-S12-034-2013) XRD and TG-DSC Analysis of the Silicon Carbide-Palladium Reaction

M. Gentile*, P. Xiao, The University of Manchester, United Kingdom

The attack of palladium on silicon carbide was investigated using high purity powders of α-SiC and palladium blended to produce a mixture with composition of 95 at.% SiC and 5 at.% Pd and cold pressed to pellets. The palladium-silicon carbide reaction was studied by thermogravimetry (TG) and differential scanning calorimentry (DSC), the phase composition of the specimens was analysed using X-ray diffraction (XRD) before and after thermoscans. Thermoscans of α-SiC-5at.%Pd pellets present three exothermic peaks at 773K, 1144K and 1615K that indicate the presence of three reaction stages. XRD patterns of α-SiC-5at.%Pd pellets show the presence of PdxSi phase that developed after the thermal treatment. This work provides a better understanding of the palladium-silicon carbide reaction mechanism, in particular this study analyses the interaction between palladium and α-SiC.

Novel Characterization Methods and Lifetime Assessment II

Room: Coquina Salon F
Session Chair: Wim G. Sloof, Delft University of Technology

10:00 AM

(ICACC-S12-035-2013) High-Temperature Strength Measurements and Arc-Jet Testing of Cf-HfB2 UHTC Composites

A. Paul, J. Binner*, B. Vaidhyanathan, Loughborough University, United Kingdom; A. Heaton, P. Brown, Dstl, United Kingdom

Ultra-high temperature ceramic (UHTC) materials are required for future hypersonic applications. It is widely accepted in the UHTC community that the major disadvantages with monolithic UHTCs are their poor defect tolerance and thermal shock resistance. In order to overcome this and to meet the oxidation resistance requirements at extreme temperatures, UHTC composites were prepared using carbon fibre (Cf) preforms and a variety of UHTC powder combinations via a slurry impregnation route. An ultra-high temperature oxyacetylene flame was used to compare the relative performance of these composites above 2500°C, with Cf-HfB2 displaying the best results. Room and high temperature (1400°C) strength of Cf-HfB2 composites were determined using 140 x 25 x 10 mm specimens at 80 mm span in a 4-point bend testing configuration and the results were compared with those of benchmark carbon-carbon composites. CTE and thermal diffusivity of the composites have also been measured and reported. We are also hoping to present the results from the arc-jet testing and characterisation of Cf-HfB2 composites, planned for September 2012 at DLR Germany.

10:30 AM

(ICACC-S12-037-2013) Repeatability of Measurements and Initial Stage Oxidation in ZrB_2-30vol%SiC

K. N. Shugart*, E. J. Opila, University of Virginia, USA

This work focuses on the repeatability of oxidation tests of ZrB_2-30vol%SiC and the initial stages of oxidation. A box furnace is used to oxidize test bars for 30 seconds to 100 minutes at temperatures of 1300°-1550°C. The samples are characterized using mass change, x-ray diffraction, scanning electron microscopy and energy dispersive spectroscopy to quantify the oxidation behavior. Weight gain measurements after 100 minutes of exposure have shown differences of up to $2mg/cm^2$ for the same testing conditions. Extreme variation in the thickness of each layer of the oxide is also seen. Results of oxidation tests at very short times may explain some of the non-repeatability. The start of oxidation has been shown to be very rapid. Even at times as short as 30 seconds when oxidized at 1500°C, SiO_2 and ZrO_2 have formed over the entire surface, and variation in surface features is seen on a scale larger than the initial grain size. This work has shown inhomogeneity of initial oxide formation likely affects long term oxidation kinetics.

10:50 AM

(ICACC-S12-038-2013) Studies on Oxidation of C-ZrB_2-SiC at 1800^{o}C Using a Novel Ultra-high Temperature Oxidation Testing Apparatus

Z. Gao*, J. Xu, M. Li, Institute of Metal Research, Chinese Academy of Sciences, China

Wind tunnel and oxyacetylene torch are two commonly-used techniques for the testing and evaluation of materials in extreme environments (above 1600^{o}C in oxidizing atmospheres). However, the oxidation environments obtained by these methods are not well controllable, especially the temperature and the oxygen partial pressure. To specifically characterize the oxidation behavior of materials at ultra-high temperatures, an oxygen partial pressure controllable induction heating oxidation testing apparatus was established. The isothermal oxidation behaviors of a C-ZrB_2-SiC composite at 1800^{o}C in air and/or pure oxygen with different oxygen partial pressures were studied. The results show that, in all cases, the specific weight loss of this material followed linear characteristics. The oxidation rate increased with increasing the oxygen partial pressure, while decreased with increasing the total gas pressure. The oxidation mechanism of C-ZrB_2-SiC was discussed.

11:10 AM

(ICACC-S12-039-2013) In-situ observation of the growth kinetics of SiO2 during passive oxidation of SiC under various Ar/O2, Ar/CO2, Ar/CO2/O2 gas mixtures at very high temperatures

F. Teyssandier*, M. Brisebourg, F. Rebillat, CNRS-LCTS, France

Oxidation behavior of silicon carbide under various oxidative gases is investigated at very high temperatures (1550-1850°C) in order to further understand the passive oxidation kinetics of SiC. Experiments are conducted on TEXTRON SCS-6 fiber samples Joule heated inside an airtight vessel under different Ar/O2, Ar/CO2, Ar/CO2/O2 gas mixtures at atmospheric pressure. Silica scale thickness is in situ observed by means of an interferometry method using a two-color pyrometer. Passive oxidation rate is found to follow a linear/parabolic law according to the Deal & Grove model. Kinetics constants are independent of gas phase composition at high temperature and increase with partial pressure of O2 at low temperature. The partial pressure of CO2 does not seem to influence the growth kinetics, neither in Ar/CO2 nor Ar/CO2/O2 gas mixtures. These observations are in accordance with the results of Zheng et al.1 in the parabolic regime, suggesting a transition towards vacancy mechanism at high temperature. We furthermore, confirm this behavior in the linear regime. 1) Z. Zheng, R. E. Tressler, and K. E. Spear, J. Electrochem. Soc., Vol. 137, No.3, March 1990

11:30 AM

(ICACC-S12-036-2013) Effect of air exposure temperature and time on room temperature strength of ZrB2 and ZrB2-SiC composite

M. Patel*, J. J. Reddy, V. V. Bhanu Prasad, Defence Metallurgical Research Laboratory, India; V. Jayaram, Indian Institute of Science, India; A. A. Ghokhale, Defence Metallurgical Research Laboratory, India

ZrB2 based composites are promising candidate materials for the applications involving very high temperature in oxidative environment.

For application involving thermal cycling, residual strength (room temperature strength after exposure in air at high temperatures) of these materials becomes important. Residual strength of hot pressed ZrB2 (with different amount of B4C) and ZrB2 -SiC composites (with different amount of SiC) were evaluated over different exposure temperatures (1000-1700°C) for different time duration (0-600 min). Exposure of hot pressed ZrB2 and ZrB2 -SiC composites to high temperatures in air resulted in formation of multilayer oxide scale structures. The composition and thickness of these multilayered oxide scale structure were dependent on exposure temperature, time and composition of bare material. The flexural strength of hot pressed ZrB2-10 vol% SiC was found to be 393 ± 114MPa, which increased to 520 ± 90 MPa after exposure to 1500°C for 150 min. Further increase in exposure time to 300 min and 600 min at 1500°C resulted in the flexural strength of 515 ± 29 MPa and 419 ± 15 MPa, respectively. An attempt was made to correlate the residual strength with the microstructural changes in the oxide scales with respect to composition, temperature and time of exposure.

S13: Advanced Ceramics and Composites for Sustainable Nuclear Energy and Fusion Energy

Ceramic Technology for Light Water Reactor Fuels

Room: Ponce DeLeon
Session Chairs: Lance Snead, ornl; Shannon Bragg-Sitton, Idaho National Laboratory

8:00 AM

(ICACC-S13-010-2013) Advanced LWR Nuclear Fuel Cladding Development Status (Invited)

S. Bragg-Sitton*, Idaho National Laboratory, USA

The Light Water Reactor Sustainability (LWRS) Program Advanced LWR Nuclear Fuel Development Pathway encompasses strategic research focused on improving reactor core economics and safety margins through the development of an advanced fuel cladding system. Significant steps beyond incremental improvements in the current generation of nuclear fuel are required to achieve significant operating improvements, such as improved fuel economy via power uprates and increased fuel burn-up allowance, while potentially improving safety margin through the adoption of an "accident tolerant" fuel system that would offer improved coping time under accident scenarios. Top-ranked materials and fabrication concepts will undergo a rigorous series of mechanical, thermal and chemical characterization tests to assess operating potential in a relatively low-cost, nonnuclear test series. A reduced number of options will advance to test rodlet fabrication for in-pile nuclear testing. Recent investigations point to the potential benefits of silicon carbide (SiC) for nuclear fuel cladding. The LWRS development program is currently investigating SiC fiber ceramic matrix composite (CMC) cladding, fully ceramic cladding that incorporates SiC CMC and monolithic SiC layers, and SiC CMC – metal hybrid cladding (SiC CMC over an inner metallic liner tube). The current status of work on SiC-based cladding designs will be presented.

8:30 AM

(ICACC-S13-011-2013) Probabilistic Failure Analysis for Wound Composite Ceramic Cladding Assembly

J. Hemrick*, E. Lara-Curzio, Oak Ridge National Laboratory, USA

Advanced ceramic matrix composites based on silicon carbide (SiC) are being considered as candidate material systems for nuclear fuel cladding in light water reactors. The SiC composite structure is considered due to its assumed exceptional performance under accident scenarios, where its excellent high-temperature strength and slow reaction kinetics with steam and associated mitigated hydrogen production are desirable. The specific structures of interest consist of a monolithic SiC cylinder surrounded by interphase-coated SiC woven fibers in a tubular form and infiltrated with SiC. Additional SiC coatings on the outermost surface of the assembly are also being considered to prevent hydrothermal corrosion of the fibrous structure. The inner monolithic cylinder is expected to provide a hermetic seal to contain fission products under normal conditions. While this approach offers the promise of higher burn-up rates and safer behavior in the case of LOCA events, the reliability of such structures must be demonstrated in advance. Therefore, a probability failure analysis study will be performed of such monolithic-composite hybrid structures to determine the feasibility of these design concepts. This analysis will be used to predict the performance of candidate systems in an effort to determine the feasibility of these design concepts and to make future recommendations regarding materials selection.

8:50 AM

(ICACC-S13-012-2013) Spark Plasma Sintering of high Thermal Conductivity UO2 and UO2-SiC Composites

G. Subhash*, L. Ge, J. Tulenko, S. Yeo, R. Baney, University of Florida, USA

UO2 powder (2.4 microns) has been sintered at a range of temperatures using spark plasma sintering (SPS) technique. The starting powder stoichiometry (metal to oxygen ratio) and the processing parameters in SPS have been systematically varied to sinter UO2 powder to various densities. It was found that UO2 can be sintered to 96% density with a hold time of less than 1 min at 1050 oC. The sintering temperature was varied between 850-1500 C with ramp rates varying between 200c/min and 50C/min. The resulting pellet theoretical density varied between 85-97%. The mean grain size varied from 3.8 microns for a hold time of 1 min to 6.6 microns for 10 min hold time. The Vickers hardness remained the same for all three grain sizes at a value of around 6.3 GPa. Thermal conductivity measurements revealed that the SPS sintered UO2 pellets have the same thermal conductivity value as the reported values in the literature at temperatures of 100, 500 and 900 C. The UO2-SiC composite pellets are being processed using SPS. The preliminary results reveal extreme promise in SPS ability to process these composites to desired theoretical density (96%). The measured thermal conductivity values for these composites are 30-60% greater than the UO2 pellets. These measurements and their relationship to the evolved microstructure will be discussed in detail during the presentation.

9:10 AM

(ICACC-S13-013-2013) Enhanced Thermal Conductivity of Uranium Dioxide-Silicon Carbide Composite Fuel

S. Yeo*, E. Mckenna, R. Baney, G. Subhash, J. Tulenko, University of Florida, USA

The most common nuclear fuel Uranium dioxide (UO2), has poor thermal conductivity resulting in high center-line temperature which can increase cladding temperature in a loss of coolant accident leading to reactions with water and production of hydrogen gases that may cause an explosion. The purpose of this study is to increase thermal conductivity of nuclear fuel by incorporating Silicon carbide (SiC) into the UO2 matrix. One μm diameter beta SiC powders with different vol% was mixed with UO2 powder. Spark plasma sintering (SPS) was employed to fabricate high density SiC-UO2 pellets. The Archimedean Immersion Method and Laser Flash Method were utilized to investigate density and thermal conductivity. SEM was used to examine the grain size, SiC particle dispersion, and Interfacial contact between UO2 and SiC of fabricated pellets. In contrast to conventional sintering, the SPS technique enabled sintering UO2-SiC composites with over 95% relative density. Good interfacial contact between two materials and homogeneous dispersion of SiC were observed by SEM. Thermal conductivity measurement at 100oC, 500oC, and 900oC revealed maximum 62% higher thermal conductivity with 10vol% SiC, when compared to the theoretical value of UO2 pellet. The result of this research provides valuable insight for preparing accident tolerant UO2-SiC composites fuel that performs high level of thermal conductivity.

9:50 AM

(ICACC-S13-015-2013) Accident Tolerance of SiC-matrix based Fuels (Invited)

L. Snead*, K. Terrani, T. Cheng, K. L. More, ORNL, USA

The performance current nuclear reactors and fuels under normal conditions are remarkable owing to decades of materials and systems optimization. However, the performance of reactor systems under either design-basis and non-design basis accidents lead to significant release of fission products to the system and potentially the public. The purpose of this paper is to present experiment analysis of an accident tolerant fuel designed to withstand steam attack expected in both standard loss-of-coolant (LOCA) and beyond design basis accident conditions. Specifically, the fuel consists of TRISO fuel, for which the SiC shell provides the primary fission product barrier. These TRISO fuel spheres are then compacted into a nano-powder SiC-based LPS matrix of high-density, forming a secondary barrier to fission product release. A series of steam attack experiments have been carried out on both the SiC-based matrix and the chemically vapor deposited shell of the TRISO, yielding attack kinetics for each constituent. It is seen that, while SiC is inherently self-protective forming either or both amorphous or crystalline SiO2, as it is slowly attacked by steam, the rate, kinetic description, microstructure, and controlling mechanisms of protection are somewhat different for the TRISO shell and fuel matrix. These will be discussed in detail with the overall implications to fission product release under the accident conditions.

10:20 AM

(ICACC-S13-016-2013) Silicon Carbide Recession Kinetics in High-Pressure Steam at Elevated Temperature

T. Cheng*, P. F. Tortorelli, K. L. More, Oak Ridge National Lab, USA

During certain severe accidents in fission power reactors, the high temperature and high pressure steam environments can cause rapid oxidation of the zirconium alloy cladding. Silicon carbide is one of the fuel cladding candidate materials which provide better accident tolerance than zirconium alloys. Chemical-vapor deposited silicon carbide specimens were exposed in 0.34 MPa steam, low gas velocity, at elevated temperature from 800 °C to 1350 °C in order to study the SiC recession kinetics in high temperature and high pressure steam. A two-layer SiO2 scale which comprised of a porous cristobalite layer above a dense amorphous SiO2 layer grew on SiC due to exposure in various steam conditions. A general kinetics model was derived to describe the SiO2 scale growth in which a dense protective layer formed by a diffusion process and was linearly consumed by an amorphous to crystalline or dense to porous phase transition process which is controlled by nucleation, granulation and grain growth. The two-layer SiO2 scale was found to largely depend on temperature and steam pressure.

10:50 AM

(ICACC-S13-018-2013) High Temperature Steam Corrosion of Cladding for Nuclear Applications: II. Experimental

K. M. McHugh, J. E. Garnier, S. Rashkeev, M. V. Glazoff, G. W. Griffith, S. M. Bragg-Sitton*, Idaho National Laboroatory, USA

Stability of cladding materials under off-normal conditions is an important issue for safety of nuclear reactors. Metals and alloys with coatings, ceramics such as silicon carbide and hybrid combinations of ceramics and metals are being investigated for water-cooled reactors that may substitute or modify traditional Zircaloy based cladding. For these initial out-of-reactor experiments, we constructed an enclosed steam-clad test apparatus using RF induction heating to achieve very high temperatures (2000+C) under controlled environmental conditions of temperature, time, water (pH)/steam, flowing steam and select covering gases. Heating of tubular cladding was achieved for metal, ceramic or hybrid ceramic metal cladding samples using an inserted molybdenum rod enabling specimen RF heating from the inside-out. Some test rodlets were also helium pressurized to simulate radial tension with temperature. Video recording of surface appearance and emissivity changes are also being evaluated as a means to monitor the initiation and formation of zirconium oxide or silicate oxides. As the surface oxide is formed, overall clad electrical resistivity changes were monitored and correlated with post test cross-section microstructures. Results will be discussed in relationship to models for complex silicate formation based on first-principles predictions described in a Part I presentation.

11:10 AM

(ICACC-S13-019-2013) NITE SiC Processing for Nuclear Applications

K. Terrani*, J. Kiggans, Y. Katoh, L. Snead, Oak Ridge National Laboratory, USA

Nano-Infiltration Transient-Eutectic forming (NITE) SiC is a special type of liquid-phase-sintered (LPS) silicon carbide that utilizes nanopowder as feedstock. The feedstock is a mixture of SiC nanopowder mixed thoroughly with a limited quantity of oxide additives. The oxide additives are alumina-rare earth oxide mixtures where yttria has been commonly used in the past. The NITE processing route is currently being used to produce the matrix for SiC/SiC composites and advanced fuel concepts such as the fully ceramic microencapsulated (FCM) fuel form where a spherical ceramic coated fuel particle is embedded in SiC. The NITE process is of interest for nuclear applications because, given the current set of experience, it yields SiC materials with irradiation behavior approaching that of CVD SiC. In addition, neutron poisons (burnable absorbers) that are necessary for nuclear fuel applications can be easily accommodated during processing by substituting high neutron capture cross section rare earth elements for yttrium. In this study a discussion on the current processing knowledge pertinent to the NITE methodology is offered. Thermogravimetric techniques have been utilized to characterize the evolution in the feedstock during thermal processing. Results from microstructural characterization and thermal properties of a wide set of specimens with various additives are also reported.

FS1: Geopolymers and Chemically Bonded Ceramics

Microstructure, Synthesis and Processing

Room: Coquina Salon A
Session Chair: Hubert Rahier, Vrije Universiteit Brussel

8:00 AM

(ICACC-FS1-001-2013) Influence of the Interaction between Various Metakaolins and Alkaline Solutions on Geopolymer Formation (Invited)

S. Rossignol*, CEC GEMH ENSCI, France

Geopolymer materials are extensively studied through the world due to their low environmental impact and their possible use as building materials. This class aluminosilicate binder displays an amorphous three-dimensional network and may be synthesized at room temperature by alkaline activation of aluminosilicates raw materials. Previous study has already shown the possibility to obtain a material with a controlled porosity by using various raw materials. This study aims to put in evidence the geopolymerisation phenomenon by the use of various metakaolins and silicate alkaline solutions using in situ infrared spectroscopy, porosimetry, NMR measurements and compressive tests. Geopolymer formulations were synthetized from three metakolins and two alkaline solutions (commercial and laboratory) at moderated temperature. The various formulations reported in the Si-Al-K/O ternary permit to evidence a range of existence for these types of compounds. The main results demonstrated polycondensation reactions to geopolymers, gels and stratified materials. The kinetics of the reaction is governed by the silicate solution. The type of materials and their potential applications is governed by the Si / Al and Si / K ratios issue from metakaolin source.

8:30 AM

(ICACC-FS1-002-2013) The Effects of Water Content and Chemical Composition on the Structure and Compressive Strength of K- and Na- Activated Geopolymers (Invited)

M. J. Westwick, Texas A&M University, USA; M. Lizcano, NASA Glenn Research Center, USA; M. Radovic*, Texas A&M University, USA

The effects of water content, i.e. H2O/(SiO2 + Al2O3), SiO2/Al2O3 and K/Al or Na/Al molar ratios on the density, open porosity, microstructure and the thermal and mechanical properties in K and Na activated geopolymers (GPs) were systematically investigated. All GPs samples were prepared from high purity metakaolin using the same mixing and curing conditions. XRD, NMR as well as alcohol immersion technique were used to characterize the structure of processed GPs. It was found that the amount of water used to process GPs is the governing factor affecting their porosity, while SiO2/Al2O3 and K/Al or Na/Al molar ratios play a secondary role. The K- and Na-activated samples have similar amounts of residual water after aging for 21 days at ambient conditions, regardless of the initial water content and SiO2/Al2O3 ratios. Compressive strengths were found to be strongly affected by H2O/(SiO2 + Al2O3) only at higher water ratios. At low H2O/(SiO2 + Al2O3) ratios, SiO2/Al2O3 molar ratios also play an important role: i.e. GPs compressive strength increases significantly with increasing Si content. Practical implications of these results on tailoring GPs thermal and mechanical properties are discussed in more detail.

9:00 AM

(ICACC-FS1-003-2013) Mechanical strength development of geopolymer binder: the effect of quartz content

C. H. Rüscher*, Leibniz University Hannover, Germany; M. H. Gougazeh, Tafila Technical University, Jordan; A. Ritzmann, GNF e.V., Germany; A. Schulz, Leibniz University Hannover, Germany

It has been shown that alkali activated metakaolin in an water glass to metakaolin ratio optimized for about 100% reaction gains high mechanical strength during ageing related to the cross linking of preformed poly-siloxo chains (Si-O-Si) via sialate bonds (Si-O-Al). However, such a composition invariably also leads to a weakening of strength if a destruction of the long poly-siloxo chains could not be prohibited during further ageing. A protection of preformed poly-siloxo chains could be achieved in the presence of higher amounts of unreacted metakaolin and Ca-ions in the binder due to a significant influence on the reaction kinetics and Ca2+ as a structure directing agent, respectively. Another interesting fact is that a change in reaction kinetics – and therefore – strength developments occurs with the addition of significant amounts of quartz "sand" to the binder. This reveals higher strength and no obvious weakening during ageing. Similar effects could be observed in the presence of significant amounts of quartz in the kaolinite raw material used for producing metakaolin.

9:20 AM

(ICACC-FS1-004-2013) What is the Role of Calcium in Geopolymers?

G. M. Canfield*, J. Eichler, K. Griffith, J. Hearn, Universal Technology Corporation, USA

Geopolymers (GP) with varying calcium content were analyzed to determine the role of calcium in GP synthesis and in the final structure. Samples were synthesized using blends of a Class F and a Class C/F fly ash where each successive reaction mixture incorporated a higher weight percent of the Class C/F ash and therefore higher calcium content. Previous research suggests that increased calcium content in GP synthesis would lead to formation of calcium silicate phases or calcium silicate/calcium GP phases. Initially this was verified by observations of faster gel set times and increased compressive strengths. However, calcination of these higher-calcium GPs revealed a successive increase in the amount of leucite crystallization with only small contributions from calcium silicate phases. This indicates that for samples with increased calcium content, the initial amorphous phases consist predominantly of GP framework. Preliminary evidence suggests that this GP framework may be calcium substituted; confirmation with ion exchange experiments is forthcoming. In addition, a red shift in the T–O stretching vibration for samples with higher calcium content indicates an increase in the aluminum content of the GP framework. Measured fly ash dissolution rates also show that calcium may play a role in the release of aluminum. Therefore, we propose that increased calcium content promotes formation of calcium-substituted GP phases.

10:00 AM

(ICACC-FS1-005-2013) The role of SiO2 & Al2O3 on the properties of geopolymers with and without Calcium (Invited)

P. De Silva*, Australian Catholic University, Australia

The rapid setting properties high calcium fly ash based geopolymers (HCFG) has restricted potential application of these binders compared to those derived from bituminous coal or metakaolin. In calcium-free systems, initial SiO2 and Al2O3 contents known to play a key role in controlling setting and final properties of these binders. This study investigates the effect of SiO2 and Al2O3 contents on setting and hardening of HCFG and the outcomes are compared with calcium free metakaolin-based systems (MG). A series of HCFG mixes were formulated with varying amounts of SiO2 and Al2O3 to achieve SiO2/Al2O3 in the range 2.7 –4.8. It has shown that the effect of varying SiO2 and Al2O3 in HCFG on setting and hardening is markedly different from that observed for MG systems. Increases in either SiO2 or Al2O3 content appear to shorten the setting time of calcium-based systems unlike MG where increasing Al2O3 accelerates setting. When calcium is present, the setting process was associated primarily with CSH or CASH formation and there appears to be a prevailing SiO2/Al2O3 ratio that prolongs setting. Furthermore, in HCFG, SiO2/Al2O3 ratios in the range of 3.20–3.70 resulted in products with highest strengths and longest setting times. The results suggest that the initial predominance of Ca2+ and its reactions effectively help maintaining a SiO2/Al2O3 ratio at which amorphous geopolymer phase is stable.

10:30 AM

(ICACC-FS1-006-2013) Synthesis of Thermostable Geopolymer from Waste Glass (Invited)

J. Zhai, Z. Sun*, D. Tao, H. Cui, Q. Li, Nanjing University, China

Waste glass is a by-product from human daily activities, its reuse always inevitably induces high energy consumption and secondary pollution, and the reutilization of cullet in mix colors is especially challenging. To solve this problem, waste glass was introduced into geopolymer for the first time as a source material, activated by a series of alkalis hydroxides and/or sodium/potassium silicate solutions. The synthesized products were characterized by mechanical testing, SEM, XRD, as well as FTIR analyses, and thermal stability was determined in terms of compressive strength evolution via exposure to 800 °C. Compressive strength measurements show a maximum strength of 119 MPa after 28 days. Thermal treatment at 100, 200, 400, 600 and 800 °C is necessary but sufficient to obtain strength of more than 79 MPa. All results show that waste glass could serve as a satisfying source material for thermostable geopolymer, with promising potential in applications of mechanical strength requiring and fire hazards concerning areas.

Porosity I

Room: Coquina Salon A
Session Chair: Sylvie Rossignol, CEC GEMH ENSCI

11:00 AM

(ICACC-FS1-007-2013) Geopolymer Mesoporosity Control Using Alkoxysilane Additives (Invited)

B. E. Glad*, W. M. Kriven, University of Illinois at Urbana-Champaign, USA

Geopolymer (GP) microstructure is dominated by porosity at various length scales, which tend to have a detrimental effect on bulk mechanical properties. Here, gas adsorption porosimetry and mercury intrusion porosimetry are used to demonstrate mesoporosity prevention through small amounts (≈0.1 mol/mol GP) of certain organic additives. Methacryloxypropyltrimethoxysilane (MEMO) additive to Na-GP caused a fivefold decrease in mesoporosity volume compared to unmodified Na-GP. The choice of organic silane functional group was found to be instrumental in mesoporosity control. The additives were not found to inhibit the equilibrium degree of reactivity, but did slow the reaction. Resulting samples were characterized through a variety of methods, including x-ray diffraction, electron microscopy and Fourier transform infrared spectroscopy. Bulk mechanical properties were compared to literature values and controls using standard compression and flexure tests. The mechanisms of the mesoporosity control are elucidated in detail.

11:30 AM

(ICACC-FS1-008-2013) Effective thermal conductivity of porous inorganic polymer cements: effects of the bulk composition and the microstructure (Invited)

E. Kamseu*, University of Modena, Italy; B. Nait-Ali, Centre Europeen de la Céramique, France; M. C. Bignozzi, University of Bologna, Italy; C. Leonelli, University of Modena, Italy; S. Rossignol, D. Smith, Centre Europeen de la Céramique, France

Experimental results and theoretical models are used to assess the effective thermal conductivity of porous inorganic polymer cements, often indicated as geopolymers, with porosity between 30 and 70 vol.%. It is shown that the bulk chemical composition affects the microstructure (grains size, pores size, spatial arrangement of pores, homogeneity, micro cracks, bleeding channels) with consequently the heat flow behaviour through the porous matrix. In particular, introduction of controlled fine pores in a homogeneous matrix of inorganic polymer cements results in an increase of pore volume and improvement of the thermal insulation. The variation of the effective thermal conductivity with the total porosity was found to be consistent with analytical models described by Maxwell–Eucken and Landauer.

FS4: Advanced Ceramic Materials and Processing for Photonics and Energy

Advanced and Nanostructured Materials for Photonics

Room: Oceanview

Session Chairs: Giovanni Fanchini, University of Western Ontario; Fiorenzo Vetrone, Université du Québec

8:00 AM

(ICACC-FS4-002-2013) Surface ablation of dielectrics with forefront laser technology (Invited)

F. Legare*, INRS, Canada; B. Chimier, O. Uteza, N. Sanner, M. Sentis, Université de la Méditerranée, France; P. Lassonde, F. Vidal, J. Kieffer, INRS, Canada

Material processing with ultrafast laser technology is of key importance for biomedical and industrial applications, such as for ophthalmic surgery and the fabrication of optical devices by the photonics industry. One important aspect of material processing is the requirement to perform highly precise features that are free of defects. To fulfill this requirement, intense femtosecond (fs) laser pulses are ideal as the interaction with the material becomes non-thermal leading to the processing of very clean features. Within the last decade, laser development as lead to the generation of pulses with duration near the fundamental limit of the optical cycle, i.e. 3 fs for Titanium-Sapphire laser. At the Advanced Laser Light Source located at INRS-EMT, we have access to such unique technology and we have studied surface ablation of fused silica by varying the pulse duration from 7 fs to 300 fs. From this study, we have confirmed that 7 fs pulses provide the cleanest ablation features, which are free of defects, and we have measured that the ablation threshold becomes highly deterministic when pulse duration approaches the single optical cycle limit. Those observations have been attributed to the increasing importance of tunnel ionization as the only mechanism for the generation of free carriers in the conduction band when the pulses are composed of only few optical cycles.

8:20 AM

(ICACC-FS4-003-2013) Two photon polymerization of organically modified ceramic materials for biomedical applications (Invited)

R. Narayan*, UNC/NCSU Joint Department of Biomedical Engineering, USA

In two photon polymerization, femtosecond laser energy is tightly focused in a near infrared light-transparent photosensitive resin (e.g., an organically-modified ceramic material). Nearly simultaneous absorption of two near infrared photons in a small volume within the photosensitive resin results in selective polymerization. The energy associated with absorption of two near infrared photons is equivalent to the energy associated with absorption of a single ultraviolet photon. Femtosecond titanium:sapphire lasers are commonly used in two photon polymerization because these lasers exhibit short pulse width and high peak power values. The minimum size of material processed by means of two photon polymerization is related to the numerical aperture of the objective lens, exposure time, laser power, resin photosensitivity, and voxel-voxel distance. Two photon polymerization does not require clean room facilities of other specialized processing environments. Indirect rapid prototyping involving micromolding has been used to create replicas of two photon polymerization-fabricated structures. We have used two photon polymerization to create a variety of medically-relevant structures out of organically-modified ceramic materials.

8:40 AM

(ICACC-FS4-004-2013) Towards ZnO large scale controlable nanostructuring : UV photonics (Invited)

G. Lerondel*, K. Nomenyo, R. Aad, H. Kadiri, R. Salas Montiel, S. Kostcheev, C. Couteau, A. Gokarna, University of Technology of Troyes, France

If photon confinement finds an echo in numerous applications such as sensing, photovoltaïcs, lighting, it remains an issue in the UV. The main raison lies in the structuration size typically between 40 and 50 nm. After introducing the motivations for UV photonics, we will address the problematic of large scale controllable nanostructing emphasizing on easy to implement and low cost techniques. ZnO is a material of choice for UV photonics. The presented different approaches include electron beam lithography combined with lift-off and dry etching processes, interferential lithography combined with chemical dissolution and finally localize growth using nanosphere lithography. Preliminary results about direct interferential writing will also be presented. While large scale controllable ZnO structuring at a scale of less than 50 nm is an issue for UV photonics, it is also of interest for numerous other emerging applications based on phonon or electron confinements due to the multifunctional character of the material.

9:00 AM

(ICACC-FS4-005-2013) Calcium-barium-niobate thin-film synthesis and etching for the development of electro-optical waveguide modulators (Invited)

M. Chaker*, S. Vigne, E. Mortazy, INRS, Canada

Considering the lack of convenient materials for modulator application, we explored the fabrication of a new exciting electro-optical material in the form of thin films, namely calcium-barium-niobate (CBN). These films exhibit a high Curie temperature (> 250°C) ensuring thermal stability. Epitaxial CBN thin films were successfully grown on both MgO and NSTO substrates using Pulsed Laser Deposition at 800°C. Low oxygen pressure (1 mTorr) enables to synthesize high-quality CBN thin films with both low surface roughness and out-off plane lattice parameter comparable to that of CBN bulk material. The optical characterization of the CBN thin films reveals a high optical transmission (> 85 %), a refractive index of 2.22 at 1.55 μm and a very high electro-optic coefficient of 130 pm/V. Recently, patterning of CBN thin films was investigated from a thorough etching study. A process involving both highly resistant nickel hard mask and chlorine plasma was developed and implemented to enable the fabrication of low loss waveguides with vertical sidewalls. This work represents a significant step towards the integration and the potential use of CBN films for high performance electro-optical waveguide modulators. Finally, promising results were obtained for the deposition of CBN thin films on nanopatterned silicon substrate for integrating CBN on common Si substrates.

9:20 AM

(ICACC-FS4-006-2013) Multiphoton Excited Nanoparticles for Luminescence Nanothermometry in Living Cells (Invited)

F. Vetrone*, Université du Québec, Canada

Multiphoton excited luminescent nanomaterials such as semiconductor quantum dots and lanthanide-doped upconverting nanoparticles are emerging as useful tools in diagnostic medicine and therapeutics. These nanomaterials are excited with near-infrared (NIR) light mitigating some of the drawbacks associated with the use of UV light as the excitation source. NIR light is silent to tissues thus minimizing autofluorescence, possesses greater tissue penetration capabilities and does not incur damage to the sample. The multiphoton excited luminescence properties of these types of nanoparticles are sensitive to temperature and thus can be used to glean knowledge of nanostructured systems whose dynamics and performance are strongly determined by temperature. This is particularly true in biology where temperature is known to play a crucial role in determining dynamics and properties, for example, determining cell division rates and hence, determining the rate of tissue growth. This thermal sensing platform is quickly becoming a reality with the recent development of nanothermometers, which due to their reduced size can be incorporated into tumors and cancer cells and subsequently provide the requisite thermal information. Here, we will discuss the various types of multiphoton excited luminescence nanothermometers and show how they can be used to non-invasively monitor the temperature of living cells.

10:00 AM

(ICACC-FS4-030-2013) THz Faraday rotation in magnetic nanosospensions: towards broadband isolators in the THz regime (Invited)

M. Shalaby, INRS-EMT, Canada; M. Peccianti, Institute for Complex Systems-CNR, Italy; Y. Ozturk, Ege University, Turkey; M. Clerici, I. Al-Naib, INRS-EMT, Canada; L. Razzari, Italian Institute of Technology, Italy; T. Ozaki, INRS-EMT, Canada; A. Mazhorova, M. Skorobogatiy, École Polytechnique de Montréal, Canada; R. Morandotti*, INRS-EMT, Canada

Ferrofluids, colloidal suspensions of ferrimagnetic nanoparticles in a carrier liquid, underwent extensive investigation since their first development in early 1960s. While based on a ferromagnetic material, they behave as paramagnets and show net magnetization only under the application of external magnetic fields. The flexibility of the liquid form and the low magnetic field requirements to observe the desired effects give them a significant advantage over their solid counterparts for a wide range of applications. For example, they can be used as an infiltrated core of dielectric waveguiding structures. In isotropic ferrofluid, an external magnetic field parallel or orthogonal to the polarization plane of a propagating EM wave can induce linear (Voigt) or circular (Faraday) birefringence, respectively. Faraday rotation (FR), for example, has been demonstrated in the visible, NIR , and MIR regimes. Here we investigate FR in the terahertz (THz) regime. Specifically we demonstrate that in ferrofluids THz waves undergo strong FR with remarkably low net absorption at room temperature, paving the way to a new generation of non-reciprocal devices.

10:20 AM

(ICACC-FS4-007-2013) Hierarchically structured ZnO photoanodes for highly efficient dye sensitized solar cells

I. Concina*, CNR-IDASC SENSOR Laboratory & Brescia University, Italy; N. Memarian, S. M. Rozati, University of Guilan, Islamic Republic of Iran; G. Sberveglieri, A. Vomiero, CNR-IDASC SENSOR Laboratory & Brescia University, Italy

We report hierarchically structured ZnO films as photoanodes in dye sensitized solar cells for the enhancement of photoconversion efficiency, based on three main concepts: (i) high optical density of the sensitized layer, allowing complete light absorption in the spectral range of the dye; (ii) high light scattering of the absorbing layer, enhancing the residence time of light inside the sensitized film and improve light absorption; (iii) inhibition of back reaction, which causes electron recombination between the conducting layer at the anode and the electrolyte. The films are prepared by the simple, cheap and large area scalable spray pyrolysis method. The films are composed of polydispersed ZnO aggregates consisting of nanosized crystallites. The aggregates are submicrometer-sized and, thus, can act as efficient light scattering centers, while the nanoparticles deliver the mesoporous structure and the high specific surface area needed for high dye loading. A ZnO compact buffer layer is formed between the conducting substrate and the layer composed of polydispersed aggregates, which efficiently acts as a blocking layer for the back reaction. Optimized structure led to high light absorption, efficient electron transport and collection, inhibition of back reaction electron recombination, and resulted in unprecedented overall photoconversion efficiency up to 7.5%.

10:40 AM

(ICACC-FS4-009-2013) Low-index waveguides and their applications

A. Horth, N. Quitoriano*, McGill University, Canada

Generally, light is guided through high-index waveguides using total-internal reflection to keep the light within the waveguide. Slot waveguides, however, use the electric field discontinuity between low- and high-optical index materials to help guide the light. These slot waveguides typically have low optical confinement (~45%), however, and can have issues with dispersion. Recently, we have developed a novel, low-index waveguide which is a hybrid between a high-index and slot waveguides. In these waveguides, we have modeled a confinement factor of ~70%, nearly as high as a high-index waveguide. We discuss the modeling of this device and its implementation as well as applications towards coupled nanowire-based lasers.

Engineering Ceramics Summit of the Americas

Ceramic Education, Training, and Collaboration

Room: Coquina Salon G
Session Chairs: Richard Sisson, Worcester Polytechnic Institute; Enrique Rocha, Universidad Politécnica de Victoria

8:00 AM

(ICACC-ECSA-007-2013) New Imperatives in Materials Processing Education (Invited)

R. D. Sisson*, Worcester Polytechnic Institute, USA

Traditionally education in materials processing focused on the technical aspects of a variety of processes. The mechanics and science of the processes were emphasized. Recently many courses have added the concepts of quality and cost analysis. Now it has become important to incorporate sustainability and environmental impact into the materials processing syllabus. In this presentation the experiences at

WPI with course design and delivery to integrate green engineering concepts into our courses will be presented and discussed. The effectiveness of team teaching with environmental and materials engineers will also be discussed. The importance of open ended design and analysis team assignments to effective learning will be emphasized.

8:30 AM

(ICACC-ECSA-008-2013) Integrating Ceramic Education and Research in an Undergraduate Applied Manufacturing Engineering Program (Invited)

R. Asthana*, University of Wisconsin-Stout, USA

As a special mission institution within the University of Wisconsin System, UW-Stout is a comprehensive, career-focused polytechnic university with historic strengths in applied learning. The university's manufacturing engineering B.S. degree program is the largest ABET-accredited program in the nation. While program curriculum does not require independent coursework on ceramics, students are introduced to ceramics in three separate courses in freshmen through junior years. Students are also offered opportunity to learn about special topics in ceramics via independent study projects, summer internships with the NASA Glenn Research Center, and materials science and nanoscience concentrations in the university's B.S. in applied science program. Student engagement with direct, purposeful learning experiences with ceramics leads to increased knowledge, comprehension, retention and depth of learning and influences student career choices and their professional and technical accomplishments and perceptions. A broad vision of applied research and enquiry on ceramic materials consistent with the goals of the university's manufacturing engineering program will be articulated to provide an example of how knowledge about ceramics can be integrated in engineering programs that are not ceramic-intensive.

8:50 AM

(ICACC-ECSA-009-2013) Shaping the Ceramics Researchers of Tomorrow Through a Continuum of STEM Experiences (Invited)

A. Heyward*, Ohio Aerospace Insittute, USA

There is widespread national recognition of the importance of bringing students into Science, Technology, Engineering and Mathematics educational experiences to shape their career interests and scholastic experiences for future success in STEM careers. This presentation will discuss some of the experiences of the Ohio Aerospace Institute in engaging students in a variety of STEM related learning experiences at all ages and what seem to be some best practices to attract and retain students in STEM majors and careers, with a special focus on ceramics research.

9:20 AM

(ICACC-ECSA-010-2013) Overview of Scientific Issues and Applications of Ceramics-Glasses in the Silica-Alumina Phase System (Invited)

S. Risbud*, UC Davis, USA

While the silica-alumina phase system is acknowledged to be the single most important binary diagram in ceramics and glass technology several scientific issues such as metastability, immiscibility, and precipitation of crystalline phases solid solutions still remain unresolved. With the success of new ceramic processing technologies in the last 10 to 20 years it has become possible to make materials by rapid melt-quenching, sol-gel techniques, or other non-equilibrium methods. In this overview, I will outline and revisit previous work in the ceramics literature on mapping metastable phase boundaries of different phase systems (e.g. silica-alumina without mullite, or silica-mullite without alumina) and immiscibility domes applicable to glass-ceramic technologies. Recent efforts to model these boundaries by computer aided theromodyamic calculations and the future possibilities of high resolution imaging and characterization of these metastable materials will be discussed. Finally, specific applications in the refractory industry will be given to show how knowledge of metastable silica-alumina phases diagrams have proved helpful to engineer products for high temperature service.

10:10 AM

(ICACC-ECSA-011-2013) The Rare Earth Elements among the Critical Elements (Invited)

G. Meyer*, University of Cologne, Germany

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 lighthing 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.

10:40 AM

(ICACC-ECSA-012-2013) Commercialising University Research: Thoughts on the Challenges Based on Experience Gained in the Field of Ceramic Processing in the UK (Invited)

J. Binner*, Loughborough University, United Kingdom

Transferring technology from University to industry is rarely a simple matter and there are many challenges that need to be overcome. This talk will outline some of the lessons learnt, both positive and negative, during a UK-based career spanning 3 decades in the field of ceramic processing that has seen several different technologies transferred into industry, via both spin out and licensing routes – and a number of other technologies fail to be transferred. The talk will also outline how properly designed Government funding schemes can be of tremendous assistance in the process of crossing the so-called 'Valley of Death'.

11:10 AM

(ICACC-ECSA-013-2013) Iron Phosphate Glasses and Melts- A US-Brazil Research Collaboration on Novel Materials for Nuclear Waste Remediation (Invited)

R. K. Brow*, M. E. Schlesinger, Missouri S&T, USA; E. D. Zanotto, Federal University of Sao Carlos, Brazil

Iron phosphate (FeP) glasses can be processed at relatively low temperatures with a wide variety of other oxides while retaining an outstanding chemical durability, and so these materials are of interest as alternatives to borosilicate glasses for nuclear waste vitrification applications. The baseline FeP composition (mole% 40Fe2O3-60P2O5) is unusual because the glass does not possess a continuous network structure of glass-forming polyhedral. A recent collaboration of faculty and students in the US and in Brazil produced new information about the glass-forming tendency, structures and properties of FeP glasses and melts, and this research will be reviewed and its implications for the use of FeP glasses for waste vitrification will be discussed. In addition, some observations about organizing a successful North America-South America collaboration will be made.

11:40 AM

(ICACC-ECSA-014-2013) Production of Al2O3/Ti/TiO2 Ceramics by Means of Oxidant in Air of Al2O3/Ti Ceramics

S. J. Esparza, E. Rocha*, J. A. Rodríguez-García, Universidad Politécnica de Victoria, Mexico; J. G. Miranda-Hernández, Universidad Autónoma del Estado de Mexico, Mexico; E. Refugio-García, M. Gaeta-Conchas, Universidad Autónoma Metropolitana, Mexico

The production of Al2O3/Ti/TiO2 composite materials through the oxidant in air of previously Al2O3/Ti fabricated composites was done. The matrix for the preparation of the composite materials is create of an Al2O3-based composite that presents a fine and homogeneous dispersions of very fine metallic particles of Ti. After oxidant practice, microstructural observations were carry out on the transversal zone of the materials' surface, showing the presence of a very thin film of about 50 μm of a constituent that was identified with the help of EDS as TiO2. In addition, micro-hardness measurements performed on the surface and in the core of the transversal section of the composite materials indicate major hardness on the surface than in the core, reflecting in this way the presence of a ceramic as TiO2 in this zone of the composite, in contrast with the presence of Ti in the core of the same material.

S1: Mechanical Behavior and Performance of Ceramics & Composites

Environmental Effects on Mechanical Performance of CMCs

Room: Coquina Salon D
Session Chairs: Marina Ruggles-Wrenn, Air Force Institute of Technology; Greg Morscher, University of Akron

1:30 PM

(ICACC-S1-061-2013) Modeling of Oxidation Effects on Mechanical and Thermal Behavior of ZrB2-20vol%SiC Ceramic at High Temperature

L. R. Dharani, J. Wei, K. Chandrashekhara, G. Hilmas, W. G. Fahrenholtz*, Missouri University of Science and Technology, USA

The addition of silicon carbide (SiC) to zirconium diboride (ZrB2) improves its oxidation resistance. Oxidation of ZrB2-20vol%SiC in air at high temperatures (1400 - 2240 K) results in the formation of an oxide scale containing solid ZrO2, liquid B2O3, amorphous SiO2, and residual porosity. This study relates to a micromechanics based finite element model of oxidation effects on heat transfer and mechanical behavior of ZrB2-SiC ceramics at high temperature. A cylindrical representative volume unit consisting of the underlying matrix, the oxide scale, and an equivalent pore diameter is treated as a 2D axisymmetric model (pseudo-3D). Steady-state heat transfer analysis followed by a 30 minute cool-down transient heat transfer analysis is first carried out. The resulting temperature distributions are then applied to the subsequent thermal stress analysis. An adaptive remeshing technique is employed, followed by a "global-local modeling" technique that combines the finite elements with infinite elements for thermal stress analysis. All thermal and mechanical properties of the materials involved are temperature dependent and are incorporated into the model. Temperature, as well as thermal and residual stress distributions in the material will be presented.

1:50 PM

(ICACC-S1-062-2013) Fatigue of Hi Nicalon filaments at elevated temperature: size and stress effects on rupture times

J. L. Lamon*, CNRS, France; M. R'Mili, University of Lyon, France

The structural performance of CMCs is controlled by fiber strengths, which define the maximum strength attainable by CMC. Fiber strengths depend not only on the filament that is considered (intrinsic variability resulting from the presence of flaws) but also on temperature, environment and loading history. Thus, the sensitivity of fiber strength to these factors is an important issue for the development of composites with durable load carrying capability. Recently, the phenomenon of slow crack growth in SiC-based fibers has been evidenced in air at temperatures ≤ 1200°C on multifilament bundles. The present paper investigates the resistance to fatigue of Hi Nicalon SiC-based filaments in the intermediate temperature range where creep is ineffective. Single filaments were tested in static fatigue at 500°C and 800°C. Closed form equations of the statistical distribution of rupture times as a function of applied stress and specimen size were developed on the basis of model of slow crack growth. Which allowed the intrinsic slow crack growth constants to be estimated from the experimental distributions of rupture times. Trends in the effects of applied stress and filament size on lifetime were anticipated. Implications for the lifetime of SiC/SiC composites are discussed.

2:10 PM

(ICACC-S1-063-2013) Creep Behavior of Hi-Nicalon S Fiber Tows at Elevated Temperatures in Air and in Steam

M. Ruggles-Wrenn*, B. Steffens, T. Shillig, Air Force Institute of Technology, USA; G. Fair, R. Hay, Air Force Research Laboratory, USA

Creep of Hi-Nicalon™-S SiC fibers was investigated at temperatures in the 800-1100°C range in air and in steam. Tensile creep behavior was examined for creep stresses ranging from 80 to 1250 MPa. The fibers were tested in bundles consisting of approximately 500 filaments with an average diameter of 12 μm, as supplied by the manufacturer. Primary and secondary creep regimes were observed in all tests. The presence of steam accelerated creep rates and significantly degraded the creep performance of the fiber bundles. At a given temperature, the creep lifetimes of the Hi-Nicalon™-S SiC fiber tows were reduced by approximately an order of magnitude due to steam. In steam, better creep performance was obtained at higher temperature. Improved creep performance at 1100°C in steam is attributed to a protective SiO_2 scale, which formed at 1100°C but not at 800°C.

2:30 PM

(ICACC-S1-064-2013) Creep Behavior in Interlaminar Shear of a Hi-NiCALON/SiC Ceramic Matrix Composite at 1200° C in Air and in Steam

M. T. Pope, M. Ruggles-Wrenn*, Air Force Institute of Technology, USA

Creep behavior in interlaminar shear of a non-oxide ceramic composite with a multilayered matrix was investigated at 1200°C in laboratory air and in steam environment. The composite was produced via chemical vapor infiltration (CVI). The composite had an oxidation inhibited matrix, which consisted of alternating layers of silicon carbide and boron carbide and was reinforced with laminated Hi-Nicalon™ fibers woven in an eight-harness-satin weave (8HSW). Fiber preforms had pyrolytic carbon fiber coating with boron carbon overlay applied. The interlaminar shear properties were measured. The creep behavior was examined for shear stresses in the 16 – 22 MPa range. Primary and secondary creep regimes were observed in all tests conducted in air and in steam. In air and in steam, creep run-out defined as 100 h at creep stress was achieved at 16 MPa. Larger creep strains were accumulated in steam. However, creep strain rates and creep lifetimes were only moderately affected by the presence of steam. The retained properties of all specimens that achieved run-out were characterized. Composite microstructure, as well as damage and failure mechanisms were investigated.

2:50 PM

(ICACC-S1-065-2013) Mechanical properties degradation of the YSZ (plasma sprayed coatings) under humidity atmosphere

G. Leclercq*, S. Lambert, H. Guillaume, CEA, France; C. Jerome, O. Christian, INSA, France; T. Christophe, CEA, France

Yttria Stabilized Zirconia (YSZ) coatings, deposited by plasma sprayed process, are refractory ceramics mostly used in the Thermal Barrier Coating (TBC) applications. The low YSZ thermal conductivity associated to the good mechanical resistance ensure a high performance and efficiency of these TBC. The structure and the "complex" microstructure are responsible of the mechanical properties and must be controlled. As brittle ceramic materials, the YSZ is affected by low temperature degradation in water vapor. Material ageing results in the progressive degradation of the mechanical properties (such as fracture strength and Young modulus), which seem dwindled in time and accelerated by temperature. In this study, the mechanical properties have been evaluated through three-point bending tests at room temperature. The observations of the structure and the microstructure are respectively investigated by X-ray diffraction and SEM-imaged with material ageing. An analytical model is suggested in order to predict material behaviour's evolution in humidity atmosphere. Material ageing can be explained by a significant microstructural modification of the cracks density. To complete this study, the fracture toughness measurements will be investigated during ageing material and will be correlated to a possible threshold of bending strength.

3:30 PM

(ICACC-S1-066-2013) Influence of oxidation on the mechanical properties of oxide fibre-reinforced ceramic composites with precursor-derived mullite-SiOC matrix

K. Tushtev, E. Volkmann, L. Evangelista Lima, T. Schumacher, University of Bremen, Germany; D. Koch, German Aerospace Center, Germany; C. Wilhelmi, EADS, Germany; K. Rezwan*, University of Bremen, Germany

All-oxide ceramic matrix composites are promising candidates to fulfil the demand of thermostructural materials for use in oxidizing atmospheres. Among the potential manufacturing routes the polymer infiltration and pyrolysis (PIP) process is one of the cost-effective ones. Some of the most common preceramic polymers are polysiloxanes which will normally lead to a silicon oxycarbide (SiOC) matrix. The major drawback of this system is its oxidation when exposed to air under high temperature. In this study the influence of oxidation on the mechanical performance of mullite-SiOC-based fibre-reinforced composites manufactured by PIP process is investigated. Test samples with different infiltration cycles in as-received condition and exposed to 1000 °C and 1200 °C in air are tested. The mechanical properties are evaluated by in-plane tension, transverse tensile test and single-edge notched bending test. The results demonstrate an increase of the out-of-plane strength and a loss of in-plane strength and fracture toughness. The porosity, the mass change, and the crystallographic phases of the composites are investigated to get an impression about the influence of the oxidation on the mechanical performance. Microstructural mechanisms relevant to the mechanical behaviour and the oxidation in this class of ceramic composites are discussed.

3:50 PM

(ICACC-S1-068-2013) Hydration of ZrW_2O_8

M. Ahmad*, M. Akinc, Iowa State University, USA

Due to its isotropic negative coefficient of thermal expansion (NCTE), ZrW_2O_8 is being project as a vital component in CTE tailored nanocomposites. Stability of ZrW_2O_8 under ambient service conditions is an important factor for the reliability of such a nanocomposite. We report hydration of ZrW_2O_8 under ambient conditions, and its effect on the NCTE of ZrW_2O_8. ZrW_2O_8 powders were synthesized by hydrothermal route and stored in ambient condition for 6 months and 1 year. On storing for 6-months, about 66% of the outer annular volume was hydrated to $ZrW_2O_8{\bullet}0.35H_2O$ while 1-year stored sample was hydrated to $ZrW_2O_8{\bullet}0.72H_2O$. NCTE of the freshly prepared and hydrated samples were characterized by in-situ high temperature X-ray diffraction (XRD) measurements between 25-200 °C. It was observed that on hydration to $ZrW_2O_8{\bullet}0.72H_2O$ under ambient conditions the NCTE character was completely lost. Thermogravimetric analysis and X-ray photoelectron spectra indicated that the water molecule bonding in the hydrated samples was slightly stronger than adsorbed water molecules while weaker than of hydroxyl ions.

4:10 PM

(ICACC-S1-069-2013) Subcritical Crack Growth in Low Temperature Co-fired Ceramics: effect of humidity and temperature on the biaxial strength

R. Bermejo*, Montanuniversitaet Leoben, Austria; C. Krautgasser, Materials Center Leoben Forschung GmbH, Austria; P. Supancic, R. Danzer, Montanuniversitaet Leoben, Austria

Strength degradation in Low Temperature Co-fired Ceramics (LTCC) is strongly affected by the humidity, causing slow propagation of cracks (SCCG) under stresses below the strength of the material. In this work the combined effect of humidity and temperature on the biaxial strength of bulk LTCC has been investigated using the ball-on-three-balls test (B3B) in different environments (i.e. water, air, dry oil, and argon) at different constant stress rates (i.e. 0.01 MPa/s to 200 MPa/s). Strength results have been compared between different environments for a given temperature. Whereas high strength values can be reached during high-rate testing in argon (inert strength), as low as 50% lower strength can be measured on specimens immersed in water tested for longer time periods. Constant stress rate experiments in a relative dry environment have shown for the first time evidence of two different crack growth mechanisms in LTCC material. A model to describe the crack growth rate (i.e. v–K curves) has been implemented in this work using a double Paris-law to interpret the experimental results. The suitability of the B3B test for constant stress rate experiments is discussed and recommended for the characterisation of brittle materials and components susceptible to SCCG.

4:30 PM

(ICACC-S1-070-2013) Slow crack growth in silicon carbide

L. J. Vandeperre*, N. Al Nasiri, F. Giuliani, E. Saiz, Imperial College London, United Kingdom

It is well known that oxide ceramics suffer from sub-critical crack growth at ambient temperature in environments containing water. Based on the mechanism, one would not expect that covalently bonded materials such as silicon carbide or silicon nitride would be susceptible to slow crack growth. However, these materials are prepared using a wide range of sintering additives that affect their grain boundary chemistry. In silicon nitride slow crack growth at stress intensity values below the critical one is observed but there is very limited data in the literature for silicon carbide. Given the increased usage of silicon carbide in space projects and its potential use as a biomaterial, it was decided to investigate how microstructure and chemistry of silicon carbide influence its susceptibility to slow crack growth. Therefore a range of silicon carbide materials was produced by using non-oxide (carbon and boron) and oxide sintering additives. Hot pressing was used to produce either a fine grained ceramic or a bimodal grain distribution consisting of large grains in a small grained matrix. The susceptibility to moisture induced sub-critical crack growth was investigated using dynamic fatigue tests in water. It is found that the materials produced using oxide additives suffer from very limited slow crack growth, whereas for the materials produced using boron and carbon as additives, no slow crack growth could be detected with the present test.

4:50 PM

(ICACC-S1-071-2013) Application of SiC/SiC composite to thruster for upper stage liquid fuel engine

R. Kitazawa*, K. Goto, Japan Aerospace Exploration Agency, Japan; Y. Yoshida, Mitsubishi Heavy Industries, Japan; T. Fukunaga, Kyoto University, Japan; S. Tokudome, T. Yagishita, Japan Aerospace Exploration Agency, Japan

SiC/SiC is studied to use for thrusters for non toxic N2O/ethanol engine, however, many connected pores in SiC/SiC leaks gas, and influence on loaded equipments and performance degradation of the engine are problems. Gas leakage tests, mechanical tests and combustion tests of SiC/SiC thruster for the N2O/ethanol engine were conducted. 2D-woven SiC/SiC laminate was fabricated. Reinforcement fiber was Tirano ZMI. SiC/SiC was fabricated using CVI method and PIP method and density was increased by SPI. Fiber volume fraction is 35%. Comparing with only SiC/SiC, Si impregnation, CVD coating inhibited gas leakage. Mechanical properties of the material were obtained by tensile testing at 328, 1273, 1573, 1973K. For combustion testing, 2D-braided SiC/SiC laminate thruster was fabricated. The surface of thruster was coated by SiC by CVD method. The thruster was connected to N2O/ethanol engine of 1.5kN thrust force and combustion pressure was 2MPa. In the first test, the thruster broke immediately because of infiltration of ethanol into the pores in SiC/SiC and burst. By blowing N2O firstly, the second combustion testing for 30s finished successfully. Distributions of temperature and

stress were calculated after combustion testing. The SiC/SiC thruster was found to be able to endure combustion condition by combustion testing and FEM analysis.

S3: 10th International Symposium on Solid Oxide Fuel Cells (SOFC): Materials, Science and Technology

Interconnects/Coatings

Room: Coquina Salon H
Session Chairs: Ulrich Vogt, Empa; Yeong-Shyung Chou, Pacific Northwest National Lab

1:30 PM

(ICACC-S3-044-2013) Analysis of the corrosion behaviour of steel interconnects and coatings in solid oxide electrolysis cells (Invited)

U. F. Vogt*, J. Kim, Y. Choi, K. Couturier, A. Zuettel, Empa, Switzerland; K. Oh, Seoul National University, Republic of Korea

High temperature steam electrolysis (HTSE) offers a promising way to produce hydrogen with high efficiency. Compared with alkaline or PEM based water electrolysis, HTSE reduces the required electrical energy and thus increases the total efficiency of the process. High temperature SOEC stacks are using Cr alloys as interconnects, connecting each cell in series by conducting electricity, distribute active gas to the cells and separate the hydrogen and oxygen between the cells. One efficient way of reducing the aging processes, but also raw material and fabrication cost is to lower the operating temperature of the SOEC from 950°C to 600~700°C, thereby enabling the use of stainless steel interconnects instead of high Cr alloys. Although stainless steel interconnects can reduce the stack cost, they also introduce several challenges. Chromium oxide-forming alloys are preferred due to their high oxidation resistance associated with low electrical resistance, thus minimizing the ohmic losses within the stacks. In this study, material compatibility between the proposed coating layers and interconnects (Crofer 22APU, AISI 441) is investigated for operating temperature of 700°C with pure oxygen as anode atmosphere.

2:00 PM

(ICACC-S3-047-2013) Phase transformation and thermal-electrical properties of Lanthanum Chromite

S. Gupta*, M. K. Mahapatra, P. Singh, University of Connecticut, USA

Phase transformation, electrical and thermal properties of lanthanum chromite (LaCrO3) have been investigated. A magnetic transition (~15oC) and two structural transitions (~260 and 1300oC) have been found using high temperature XRD, differential scanning calorimetry and dilatometer. The thermal expansion co-efficient of LaCrO3 was found to be 10.8±0.2 ×10-6/oC in the temperature range of RT-1395oC. Electrical conductivity of lanthanum chromite was ~0.13Scm-1 at 960oC. Results of microstructural and elemental analysis performed using scanning electron microscopy (SEM-EDAX) and inductively coupled plasma (ICP) technique, will be presented. Experimental results will be compared with existing literature.

2:20 PM

(ICACC-S3-049-2013) Effect of additives on conductivity of copper manganese spinel for SOFC interconnects

S. Joshi*, McMaster University, Canada; R. Lawcock, Stackpole International, Canada; A. Petric, McMaster University, Canada

This study characterizes the effect of adding metal oxides such as NiO or CoO into copper manganese spinel. Spinels are used in solid oxide fuel cell interconnects as protective coatings. The narrow temperature range of copper manganese cubic spinel can be adjusted by addition of other metal oxides. Spinel solutions were prepared from metal oxide powders by solid state reaction. In-situ conductivity measurements were obtained by the four-probe DC conductivity technique. XRD was used to determine phase boundaries. Measurement of Cu1Mn2O4 and nickel doped Cu-Mn spinel showed a conductivity of ~100 S/cm at 800°C. At 600°C, Cu1Mn2O4 spinel exhibited ~30 S/cm whereas most nickel doped Cu-Mn spinel showed ~60 S/cm. Conductivity testing of Cu1.2Mn1.8O4 showed a decrease of conductivity to ~70 S/cm at 800 °C. The decrease in conductivity at lower temperature or higher Cu composition may indicate a phase transformation as is supported by XRD results. Addition of Co to the Cu-Mn-O system also exhibited similar trends. Optimized spinel compositions for different applications will be discussed.

2:40 PM

(ICACC-S3-051-2013) Advanced Conductive (MnCo)3O4 Coating on SOFC Interconnect Frames with One-Step Heat Treatment

J. Choi*, J. W. Stevenson, R. C. Scott, M. Chou, Pacific Northwest National Lab, USA

Low-cost, chromia-forming ferritic stainless steels are usually used for making interconnect plates in planar SOFCs. However, volatile Cr-containing species, which originate from the steel's oxide scale, can poison the cathode material in the cells and subsequently cause power degradation in the device. A conductive MnCo spinel coating has been developed for preventing cathode materials poisoning. However, this coating is not compatible with the formation of hermetic seals between interconnect frame components and the ceramic cell. Thus, a new aluminizing process has been developed to enable durable sealing, prevent Cr evaporation, and maintain electrical insulation between stack repeat units. However, the coating processes for the conductive and non-conductive material are very different. Therefore, it is challenging to fabricate these two coatings at the same time. The authors have previously reported success in preparing simultaneous coatings. However, to reduce cost and time, additional modifications are under development.

3:20 PM

(ICACC-S3-050-2013) Long-term evaluation of surface-treated (Mn,Co) spinel-coated AISI441 interconnect for SOFC application

Y. Chou*, J. Choi, J. Stevenson, E. Stephens, E. Mast, Pacific Northwest National Lab, USA

Ferritic stainless steel AISI441 is currently studied as a candidate metallic interconnect for solid oxide fuel cell applications. The metal; however, requires a conductive and protective coating such as (Mn, Co) spinel. To improve the coating adhesion, approach of surface treatment as sand blasting was applied and was confirmed by modeling as well as small coupons. In this work the surface-treated and spinel-coated AISI441 interconnect is being evaluated in a stack fixture using a 2"x2" commercial cell and tested at 800oC for long-term (>1000h) at a constant current mode with mixed fuel of H2:N2=1:1 versus air. After stability test, deep thermal cycling will also be conducted. Periodic impedance and I-V sweeps were conducted at every 500h. Upon completion the stack will be disassembled for post mortem analysis. The coated interconnect plates will be sectioned for detailed microstructure and interfacial characterization. The stability of surface-treated and (Mn,Co) spinel-coated AISI441 interconnect will be discussed.

3:40 PM

(ICACC-S3-052-2013) Electrodeposition of Spinel Coatings on SOFC Interconnects

X. D. Michaud*, McMaster University, Canada; R. Lawcock, Stackpole International, Canada; A. Petric, McMaster University, Canada

To prevent chromium poisoning of SOFCs by volatile Cr species, an oxide coating is applied. These coatings are most often spinels or perovskites. Spinel coatings can be deposited by electroplating from aqueous salt solutions. One candidate spinel, Mn1+xCo2-xO4, provides sufficient conductivity while exhibiting promising chromium retention. Samples of interconnect material were plated with cobalt metal using a solution of 1.3 M CoCl2. Subsequently, the samples were coated with manganese using a 1 M MnSO4 solution. This process often yielded uneven or incomplete coatings on samples of 6 cm2. It was determined that the quality of the cobalt layer plays an important role in the deposition of manganese. An investigation into the effects of solution concentration on the cobalt deposit showed that the morphology of the coating could be controlled.

4:00 PM

(ICACC-S3-053-2013) Protective Oxide Coatings for the High Temperature Protection of Metallic SOFC Components

N. J. Kidner*, M. Seabaugh, K. Chenault, S. Ibanez, K. Smith, R. Underhill, L. Thrun, NexTech Materials, USA

Cost is a key barrier to widespread commercialization of SOFCs. To reduce system costs, developers, wherever possible, have substituted lower cost stainless steel into the stack design. However, for successful implementation of these steels, protective coatings are necessary. A range of competitive coating processes has been evaluated and Aerosol Spray Deposition (ASD) identified as a commercially viable and effective method for applying protective coatings to both metallic interconnect and balance of plant (BoP) components. For the active area, conductive manganese cobaltite (MCO) oxide coatings have been widely employed. Performance testing of MCO coated ferritic stainless steel has been conducted and lifetime models based on anticipated failure modes developed. Two complementary coatings; an insulating overlay coating and an aluminide-based diffusion coating have been developed for the non-active, seal area where a different coating, with lower chemical reactivity is necessary. Processing of these coatings has been tailored to be compatible with the MCO coating to allow for co-processing. The BoP is a significant portion of the fuel cell systems weight, and cost. The aluminide coating has been identified as a promising BoP coating and has been successfully applied to a range of commercially important alloys including; austenitic stainless steels and nickel-based alloys.

4:20 PM

(ICACC-S3-054-2013) Chromium evaporation from alumina and chromia forming alloys used in Solid oxide fuel cell-Balance of Plant applications

L. Ge*, University of Connecticut, USA; P. Singh, University of Connecticut, USA; M. Brady, Oak Ridge National Laboratory, USA; E. Sun, University of Connecticut, USA

The evaporation, transport and re-deposition of chromium species from chromia forming alloys commonly used in interconnects and balance of plant (BOP) materials is one of the major cause for degradation in solid oxide fuel cell (SOFC) systems. A systematic study on the nature of scale, surface morphology and chemistry as well as chromium evaporation from select iron and nickel base alloys used in balance of plant (BOP) component materials is presented. The chromium evaporation was measured at SOFC operating temperatures using a transpiration method. The measured evaporation rates were correlated with oxide chemistry and morphology using microscopic observations of the various phase evolution in the oxide scales. In this work, we will compare Cr evaporation rates of chromia forming alloys and alumina forming alloys together with newly developed austenitic alumina forming (AFA) alloys from Oak Ridge National Laboratory. Also we will investigate the role of temperature and water vapor in Cr evaporation, scale formation.

4:40 PM

(ICACC-S3-055-2013) Processing effects on phase and microstructure of plasma sprayed Strontium doped Lanthanum Manganite

Y. Chen, S. Jung Han*, S. Sampath, Stony Brook University, USA

Strontium doped Lanthanum Manganite (LSM) oxide materials have high electrical conductivity, good electrochemical performances and stability with YSZ electrolyte and metallic interconnects at high temperature, and as such considered for applications in solid oxide fuel cells for both electrodes and protection of metallic interconnects from oxidation. Plasma spray is one of the methods for deposition of these advanced coatings. In this paper, processing effects on in-flight particle state, microstructure and phase formation of LSM oxide coatings were studied. Advanced *in-situ* particle diagnostics allows for rapid assessment of particle states (particle velocity and temperature) with respect to processing conditions (plasma energy, chemistry and dwell time). Combined with *in-situ* coating monitoring during deposition and post-spray characterization of electrical properties enables identification of optimal coating fabrication conditions as well as opportunities for coating design. The results suggest with careful control of process conditions it is feasible to suppress material degradation as well as phase destabilization allowing for synthesis of high quality coatings. Results will demonstrate the concept of advanced process maps for optimization functional ceramic coatings via thermal spray processes.

5:00 PM

(ICACC-S3-045-2013) Novel Composite Interconnect for SOFC

S. Somov*, Solid Cell Inc, USA; S. Ghosh, RocCera LLC, USA; O. A. Graeve, J. P. Kelly, M. Alberga, Alfred University, USA

Traditional SOFC materials do not completely satisfy the demands for an interconnect. Metallic alloys and conductive ceramic oxides are traditional interconnect materials, but have shortcomings. A new ceramic composite, which consists of nickel and titania doped by niobium, has a number of advantages for application as an interconnect compared to lanthanum chromates and special stainless steels. It does not contain chromium that is poisonous to cathodes. It has an adjustable CTE, dependent on the ratio of its metallic and oxide phases. It has high electrical conductivity ~103 Ohm-1cm-1 and it is made from inexpensive raw materials. Its mechanical properties are similar to metals, because nickel constitutes a significant part of the composite – mechanical stability < 950 deg C, yet flexible to resist cracking. The novel interconnect has good corrosion resistance when placed between the anode and cathode, because titania doped by niobium oxide has low protonic conductivity, allowing hydrogen penetration from the anode to the cathode side. This mechanism prevents nickel oxidation.

S4: Armor Ceramics

Synthesis and Processing II

Room: Crystal Ballroom
Session Chair: Robert Pavlacka, U.S. Army Research Laboratory

1:20 PM

(ICACC-S4-048-2013) Microstructure and mechanical property of nanocrystalline boron carbide ceramics (Invited)

Y. Shinoda*, T. Akatsu, F. Wakai, Tokyo Institute of Technology, Japan

Boron carbide (B4C) ceramics is one of the hardest materials and comes next to diamond and cubic boron nitride (c-BN) in hardness. We can relatively easily obtain such super hard B4C bulk ceramics without ultra-high pressure technique of ~10GPa as being required in diamond or c-BN. B4C ceramics has such superiority in the processing. Recently spark plasma sintering (SPS) has become one of the most popular sintering methods owing to rapid heating and cooling rate, short soaking time and relatively low sintering temperature. Therefore many studies to obtain fine-grained material by SPS have been undertaken utilizing such characteristics. The mechanical properties of polycrystalline materials such as hardness and creep behavior are influenced by grain size. In this presentation, I will report the microstructure and mechanical properties of the dense nanocrystalline B4C (n-B4C) ceramics sintered by SPS at high pressure and low temperature. These results are compared with those of the n-B4C ceramics fabricated by hot isostatic pressing (HIP) and other several kinds of B4C ceramics.

1:50 PM

(ICACC-S4-049-2013) Comparison of armor ceramics made by spark plasma sintering (SPS) and pressureless sintering

P. Karandikar*, S. Wong, M. Duke, M Cubed Technologies, Inc., USA; R. Haber, M. Vu, Rutger University, USA; J. Singh, Pennsylvania State University, USA

Armor ceramics are traditionally manufactured by processes such as hot pressing, pressureless sintering, and reaction bonding. These processes produce microstructures with grain sizes in the 1-100 micrometer range. More recently, processes such as microwave-assisted sintering and spark plasma sintering (SPS – also called field assisted sintering technology – FAST) have been introduced. Due to the nonconventional process-heat generation mechanisms, these processes achieve very high heating rates and significantly reduced process times. As a result, potential exists for achieving much finer microstructure. Armor ceramics need a good combination of hardness and toughness. This is generally hard to achieve in ceramics with micron-size grains. It is postulated that if the grain size in armor ceramics is pushed to the ultrafine grain or nano-grain regime, a better combination of hardness and fracture toughness could be achieved. This work assesses the possibility of achieving ultrafine-grained and nano-grained ceramics by SPS. Armor ceramics such as silicon carbide (SiC), boron carbide (B4C), alumina (Al2O3), and their mixtures are produced by SPS and conventional sintering. Microstructures and properties of these are compared. The parameters in both processes are systematically varied to assess their effects on microstructures and properties.

2:10 PM

(ICACC-S4-050-2013) Pressureless sintering of silicon carbide – boron carbide composites

L. J. Vandeperre*, J. Teo, Imperial College London, United Kingdom

Two desirable properties for armour ceramics are a high hardness and a low density. Not surprisingly, both silicon carbide and boron carbide are therefore lead ceramics for ballistic protection. However, removing porosity during sintering is difficult for both materials and often hot pressing is required. Hot pressing is more costly and more limiting in terms of the shapes that can be produced. Therefore, this paper will describe experiments carried out to explore the potential for pressureless sintering of composites of boron carbide and silicon carbide. Mixtures of the pure powders across the entire compositional range, as well as mixtures with a range of sintering additives were pressureless sintered at temperatures up to 2300 °C. The densification behaviour and microstructures will be reported as well as the variation of hardness with composition.

2:30 PM

(ICACC-S4-051-2013) Synthesis and Characterization of Submicron-Grained Boron Carbide

C. Haines*, D. Martin, K. Mills, R. Sadangi, D. Kapoor, US Army ARDEC, USA

Dense, nanocrystalline ceramics are of significant interest due to their unique mechanical, optical, and electrical properties, to name a few. A vast majority of the materials being reported in the open literature are oxide-based, likely due in part to the commercial availability of oxide nanopowders. Carbides and nitrides are more difficult to synthesize due to the inability to process these materials in the presence of oxygen. Efforts are currently underway to characterize the sintering behavior of boron carbide nanopowders synthesized in-house via inductively coupled plasma – inert gas condensation (ICP-IGC). Boron carbide (B4C) nanopowders were synthesized with ICP-IGC and then subsequently sintered using field-assisted sintering technology (FAST). XRD and SEM verified the submicron nature of the sintered materials. Further characterization included microhardness, fracture toughness, and oxygen analysis. For purposes of establishing a baseline, conventional micron-scale powders were sintered under identical conditions and compared with the submicron materials.

3:10 PM

(ICACC-S4-052-2013) Rapid Carbothermal Reduction Synthesis of Boron Carbide

M. F. Toksoy*, W. Rafaniello, R. A. Haber, S. L. Miller, Rutgers University, USA

Boron carbide has superior mechanical properties, such as high hardness and elastic modulus, which may not be fully realized due to limitations during the production of the materials. Powder attributes affect many of the densified boron carbide properties. Boron to carbon ratio, particle size and impurities are variables that have to be controlled during component production. Composition of boron carbide, specifically the boron-carbon ratio, can vary over wide range. The common production method for commercial boron carbide powder is carbothermic reduction in an electric arc furnace. This is a melt process characterized by slowing heating and cooling leading to inconsistent reactions which will introduce inhomogeneities to the final powder. Laboratory methods are also available, but the yield is low and process is expensive to operate. Rapid carbothermic reduction has been shown to produce a very fine, highly pure, boron carbide powder with a narrow size distribution. The average size, distribution, and morphology were shown to be controllable through changes in the carbon source and reactor temperature. The prepared powders were analyzed through x-ray diffraction and carbon analyses in order to determine their phases and stoichiometries. These analyses revealed that it was possible through careful process control to develop samples represents stoichiometric B4C.

3:30 PM

(ICACC-S4-053-2013) The Role of Interfaces on the Sintering, Microstructure Evolution, and Properties of Hot-Pressed Transparent MgAl2O4 Spinel

M. Rubat du Merac, Technical University Darmstadt, Germany; I. Reimanis*, Colorado School of Mines, USA; H. Kleebe, M. Müller, Technical University Darmstadt, Germany

Magnesium aluminate spinel has gained increasing attention for use in transparent armor, infrared-seeking missile domes, and other applications requiring transparency from the near-ultraviolet to mid-infrared. Interfaces control the sintering behavior of spinel crystallites and the microstructure evolution and many of the physical properties of spinel compacts. However, there is a lack of understanding of the fundamental atomistic mechanisms that occur at interfaces, how these are affected by stoichiometry, defect structure, and impurity content, and in turn, how properties such as grain size, fracture mode and optical transmittance are affected. In order to gain insights into interface mechanisms, experiments were conducted in which spinel compacts were fabricated using a variety of methods and interfaces examined with transmission electron microscopy, secondary ion mass spectrometry, atom probe tomography, impedance spectroscopy, and atomic force microscopy. The effect of stoichiometry, defect structure, and solute adsorption on interface migration and bulk physical properties will be discussed.

Non-Destructive Evaluation

Room: Crystal Ballroom
Session Chair: Matthew Bratcher, U.S. Army Research Laboratory

3:50 PM

(ICACC-S4-054-2013) Ultrasonic Nondestructive Characterization of Spark Plasma Sintered Silicon Carbide Microstructure

V. DeLucca*, R. A. Haber, Rutgers University, USA

Ultrasonic nondestructive evaluation has conventionally been used to measure elastic properties and locate large flaws in a number of different types of materials. Recent advances in acoustic spectroscopy have enabled ultrasound techniques that can be used to examine the microstructure of dense ceramic bodies. In this study, methodology is developed for nondestructively characterizing silicon carbide microstructure using high frequency ultrasound acoustic spectroscopy

techniques to predict the grain size and shape. The spark plasma sintering (SPS) method was used to produce several silicon carbide samples with varying microstructures. Comparison of the acoustic attenuation spectra of the silicon carbide samples with microstructural information from field emission scanning electron microscopy (FESEM) is used to determine a relationship between microstructural properties and ultrasound response.

4:10 PM

(ICACC-S4-055-2013) Nondestructive Characterization of Low Velocity Impact Damage in Protective Ceramic Components

R. Brennan*, W. Green, US Army Research Laboratory, USA

In theater, protective systems are exposed to a wide variety of ballistic and sub-ballistic threats which may compromise their ability to withstand single or multiple impacts. Low velocity impact damage can originate from a number of sources that may include vehicle collisions, extreme environmental conditions, and foreign object debris. Advanced ceramic components in these systems include materials such as aluminum oxide and silicon carbide. By subjecting these components to experimentally controlled low velocity impacts and using nondestructive bulk characterization techniques such as digital radiography, x-ray computed tomography, ultrasound, and microwave characterization to detect resulting surface and internal damage, a comparison of the baseline and damaged states can be established. Pre and post-impact evaluations can provide quantitative damage assessment to help determine critical velocity and energy threshold conditions. Establishing a relationship between processing and manufacturing defects in these different materials and the mechanisms that cause the damage can provide insight into development of improved materials and systems. By qualitatively and quantitatively characterizing these protective system components before and after impact, damage tolerance threshold levels can be identified to determine their effect on survivability.

4:30 PM

(ICACC-S4-056-2013) Evaluation of Low Velocity Strike Damage in Ceramic Tile Modules Using a Microwave Interference Scanning System

W. H. Green*, R. Brennan, U.S. Army Research Laboratory, USA

The ARL is currently performing work on the effects of low velocity impact damage on subsequent damage levels in opaque ceramics caused by higher velocity threats. Microwave frequency (interference) scanning is a relatively new NDE method that has undergone significant basic development and technical advancement over recent years. It has significant advantages in ease of use, one sided inspection, compactness, portability, applicability in varied environments, non-ionizing radiation, and no need for transferring medium between probe and specimen. A series of microwave scans were performed on a set of damaged metal backed ceramic tile modules used in the ARL research using the new technology. Microwave scans of a number of different damaged ceramic tile modules will be shown. Microwave scans of a separate module with fabricated flaws will also be shown. The characteristics and quality of the scans will be discussed as well as some comparisons to results from other NDE methods, such as ultrasonic and x-ray digital radiography/computed tomography scans or images.

4:50 PM

(ICACC-S4-057-2013) Portable Automated Microwave Interferometry Imaging in Complex Ceramics

K. Schmidt*, J. Little, Evisive, Inc., USA; W. Ellingson, ERC Company, USA; L. P. Franks, US Army Tank Automotive Research Development and Engineering Center, USA; W. H. Green, US Army Research Laboratory, USA

A portable microwave interferometry system has been automated to permit rapid examination of components with minimal operator attendance. Functionalities include multiplexed frequency-modulation, producing layered volumetric images. The technique has been used to image composite ceramic armor and ceramic matrix composite components, and other complex dielectric materials. It utilizes Evisive Scan microwave technique. Validation included artificial and in-service damage of ceramic armor, surrogates and ceramic matrix composite samples. Validation techniques include micro-focus x-ray and computed tomography imaging. The technique has demonstrated detection of cracks, interior laminar features and variations in material properties such as density. The image yields depth information through phase angle manipulation, and shows extent of feature and relative dielectric property information. It requires access to only one surface, and no coupling medium. Data are not affected by separation of layers of dielectric material, such as outer over-wrap. Test panels were provided by the US Army Research Laboratory, US Army Tank Automotive Research, Development and Engineering Center (TARDEC). This paper will describe the system and present current results. This work is supported by the US Army Tank-Automotive Research, Development and Engineering Center (TARDEC) and the US Army Research Laboratory.

S5: Next Generation Bioceramics and Biocomposites

Advanced Bioceramics

Room: Coquina Salon C
Session Chairs: Min Wang, The University of Hong Kong; Peter Ma, University of Michigan; Tomaz Kosmac, Institute Jozef Stefan

1:30 PM

(ICACC-S5-012-2013) Novel Electrospun Bicomponent Scaffolds for Nerve Tissue Repair

C. Liu, X. Zhang, M. Wang*, The University of Hong Kong, Hong Kong

Electrospinning is widely used to construct fibrous scaffolds for tissue engineering applications. With a suitable electrospinning technique, core-shell structured polymer nanofibers can also be formed as delivery vehicles for local and controlled release of biomolecules. In nerve tissue engineering, nerve growth factor (NGF) and glial cell line-derived neurotrophic factor (GDNF) can promote, separately or synergistically, peripheral nerve tissue regeneration. Our previous studies showed that NGF and GDNF could be successfully incorporated in core-shell poly(D,L-lactic acid) (PDLLA) or poly(lactic-co-glycolic acid) (PLGA) fibers through emulsion electrospinning. In this study, for the dual delivery of NGF and GDNF, bicomponent fibrous scaffolds were made via dual-source dual-power electrospinning (DSDPES). In these scaffolds, NGF and GDNF were encapsulated in PDLLA and PLGA fibers, respectively. By optimizing parameters for DSDPES, both types of fibers could be evenly distributed in bicomponent scaffolds. To maximize the synergetic effects of NGF and GDNF, in bicomponent scaffolds, the mass ratio of NGF/PDLLA fibers to GDNF/PLGA fibers (hence amounts of NGF and GDNF and their ratio) could be changed easily when conducting DSDPES. The structure and properties of novel scaffolds were characterized using various techniques. The degradation of scaffolds and in vitro release of NGF and GDNF were also studied.

1:50 PM

(ICACC-S5-017-2013) Stimuli-responsive smart hybrid capsules for on-demand delivery system (Invited)

K. Katagiri*, Hiroshima University, Japan

Capsular materials have been widely investigated over the past few decades and have attracted great interest in the areas of drug and gene delivery systems. We have developed stimuli-responsive smart hybrid microcapsules via the colloid templating technique with the layer-by-layer assembly. Inorganic materials have been hybridized by the soft solution process. UV-responsive capsules have been successfully prepared by using sol-gel derived SiO_2-TiO_2 layer on a polyelectrolyte multilayer shell. In this system, the capsular shell was ruptured by the photocatalytic reaction of TiO_2 component. These capsules have a tunable UV-triggered release function by control of composition of

SiO_2-TiO_2 layer. Magnetoresponsive smart capsules have also fabricated using polyelectrolytes, lipid bilayers and magnetic nanoparticles. Encapsulated materials were released from capsules on-demand by irradiation with an alternating magnetic field. The magnetically-induced release is attributed to the phase transition of the lipid membrane, caused by heat of Fe_3O_4 nanoparticles under magnetic stimuli, not to rupture of the capsules.

2:10 PM

(ICACC-S5-014-2013) Maturation of brushite and preparation of brushite micro-granules

A. Tas*, A. S. Madden, P. R. Larson, M. K. Jain, M. R. Kendall, M. A. Miller, University of Oklahoma, USA

Conventional flat plate (FP)-shaped brushite (DCPD, dicalcium phosphate dihydrate, CaHPO4x2H2O), produced by reacting Ca-chloride and alkali phosphate salt solutions, were found to undergo a maturation process (changing their Ca/P molar ratio from 0.8 to the theoretical value of 1) similar to those seen in biological apatites. Water lily (WL)-shaped brushite crystals were produced in non-stirred aqueous solutions at room temperature in 24 hours by using precipitated calcite and NH4H2PO4 as the starting chemicals. The hydrothermal transformation of WL-type brushite into octacalcium phosphate (OCP) or Ca-deficient hydroxyapatite (CDHA) was tested at 37 C by using four different biomineralization solutions, including Tris-buffered SBF (synthetic body fluid) and sodium lactate-buffered SBF solutions. All four solutions used in this study consumed the starting brushite in one week and caused transformation into a biphasic mixture of nanocrystalline OCP and CDHA of high surface area. WL-type brushite crystals when synthesized in the presence of small amounts of Zn2+ ions resulted in the formation of, for the first time, spherical micro-granules of brushite. Synthesis of brushite in spherical form was difficult, if not impossible, prior to this study.

2:30 PM

(ICACC-S5-015-2013) Mineralized Tissue Regeneration Using Biomimetic Scaffolds and Stem Cells (Invited)

P. X. Ma*, University of Michigan, USA

Destruction of mineralized craniofacial and dental tissues seriously affect both appearance and orofacial function of millions or patients. The shortage of replacement tissues for these patients remains a major clinical challenge. Stem cells have enormous potential for the regeneration of lost and destructed tissues. Scaffolds can provide three-dimensional tissue templates and synthetic extracellular-matrix environment to accommodate stem cells, facilitate their proliferation and guide their differentiation to regenerate the needed tissues. We take a biomimetic approach to design scaffolds emulating the structural features of extracellular matrix on the micrometer and nanometer scales. We also develop technologies to generate calcium phosphate coating on the polymer scaffolds to further mimic the extracellular matrix of mineralized tissues, such as bone and tooth. These biomimetic scaffolds are shown to advantageously facilitate stem cell growth and promote their differentiation towards bone and dental tissues. The results demonstrate the significance of the biomimetic approach for the regeneration of mineralized craniofacial and dental tissues.

2:50 PM

(ICACC-S5-016-2013) Tantalum-based Diffusion Coating for Increasing the Biocompatibility of Conventional Metal Implant Alloys

J. J. Stiglich*, B. E. Williams, Ultramet, USA

Ultramet has been developing and commercializing refractory metal and ceramic coatings and freestanding parts for corrosive and high temperature environments for more than 42 years. Tantalum has a long history as an implant material, in both bone and soft tissue, and Ultramet developed and licensed a process for fabricating open-cell tantalum metal foam orthopedic bone implants that is approved by the Food and Drug Administration. Under NASA funding, Ultramet developed a process to diffuse highly corrosion-resistant tantalum metal into the surface of conventional stainless steels and superalloys to improve the acid corrosion resistance of components used in precision space shuttle orbiter propellant transfer valves. A thin, metallurgically bonded tantalum surface layer was established that graded from pure tantalum at the surface to a mixture of tantalum and the substrate elements. A significant benefit is that the tantalum surface layer precisely replicates intricate substrate features and does not require post-process machining or polishing. Hardness and wear resistance can be increased by reacting the layer with one or more light element impurities, yielding a tantalum-based ceramic outer surface. The potential exists to use this coating to increase biocompatibility of conventional metal implant alloys. Ultramet's experience with tantalum deposition will be reviewed.

3:30 PM

(ICACC-S5-013-2013) Biological properties of ion substituted apatite coatings

H. Engqvist*, W. Xia, C. Lindahl, Engineering Sciences, Sweden; A. Ballo, Gothenburg University, Sweden; A. Hoess, S. Pujari, Engineering Sciences, Sweden; J. Lausmaa, P. Thomsen, SP Technical Research Institute of Sweden, Sweden; M. Ott, Engineering Sciences, Sweden

Incorporation of ions into apatite is a method of functionalizing apatite coatings, which could improve the bone bonding, bone in-growth, and decrease the risk of infection and implant failure. The biomimetic technique is an easy way to incorporate different ions into apatite coatings, simply via dissolving the intended ion into the soaking solution. The surface of titanium substrates is preferably activated before soaked into the above solutions. In this paper, different soaking temperatures were used to control the growth of the ion substituted apatite coatings. The cell proliferation and differentiation of the coatings were tested using osteoblasts. The bone tissue reactions to these ion substituted apatite coating were also evaluated. The amount of substitution of ions and the morphology of the coatings varied by the variation of charge and size of the intended ion. The cell studies showed the substituted ions could improve the cell proliferation and differentiation. The animal studies indicate ion substituted apatite coatings have better bone bonding and in-growth. In conclusion, ion substitution could functionalize apatite coatings and bring positive biological effects.

3:50 PM

(ICACC-S5-018-2013) 3-D printed bioactive bone replacement scaffolds of alkali substituted ortho-phosphates containing meta- and di-phosphates

F. Dombrowski, C. M. Gomes, G. Berger, BAM Federal Institute for Materials Research and Testing, Germany; P. Garcia Caso, M. Klein, M. Laschke, Saarland University Medical Center, Germany; J. Guenster*, BAM Federal Institute for Materials Research and Testing, Germany

The paper presented deals with the investigations of orthophosphates (Q0) containing none or differing amounts of meta-(Q2) and diphosphate phases (Q1) for the use as starting material for the 3D-printing process in order to create porous, bioactive, nonloadbearing bone replacement scaffolds. The main ceramic phase in all cases is Ca10[K/Na](PO4)7 hereinafter called 401545(100) consisting of 99,9% Q0 and 0,1% Q1-phase. The other phosphate ceramics i) 401545(40) consists of 75% Q0-phase, 22% Q1-phase and 4% Q2-phase ii) 401545(15) consists of 65% Q0-phase, 33% Q1-phase and 2% Q2-phase iii) 401545 consists of 56% Q0-phase, 40% Q1-phase and 4% Q2-phase. The quality and quantity determination of the crystal phases were detected via P-NMR-analysis. Cylindrical samples have been prepared via 3-D printing, followed by sintering in a temperature range between 900°C and 1300°C. Porosity, linear shrinkage, compressive strength and solubility behaviour have been determined.

4:10 PM

(ICACC-S5-019-2013) Towards a Life-Time Prediction for Yttria-stabilized Zirconia Dental Material experiencing Low-Temperature Degradation

M. Keuper*, C. Berthold, K. G. Nickel, Eberhard Karls University Tuebingen-Faculty of Science, Germany

The prediction of surficial t–m phase transformation kinetics in Yttria-stabilized Zirconia caused by exposure to moist environments typical for its medical application is a necessary precondition for any life-time modeling of dental materials. Phase transformation changes all base parameters used in life-time prediction and creates internal stresses and new defects, which can lead to slow crack growth and eventual failure. We studied behavior and proceeding of the t–m phase transformation of hydrothermally aged samples at 134°C by XRD and by examining cross sections prepared with Focused Ion Beam. The cross sections were investigated by SEM, EBSD and Raman Spectroscopy. We show that the growth of a transformed layer follows linear kinetics without any gradual decrease but a sharp boundary between layer and unaffected material. Furthermore the influence of differing alumina contents in the material and resulting consequences for its aging kinetics is shown. Merging the results of XRD from surface analyses with the direct optical insight from cross sections give first hints to translate the XRD data into real kinetics. Combining this model with data from samples aged for 4 years at 37°C, mimicking human body temperature conditions, opens the road to realistic forecasts for life-time stability and shows possible ways to extend the durability of the material.

4:30 PM

(ICACC-S5-021-2013) Solid state NMR study of the structural characteristics of apatite in bone highlighting the role of collagen (Invited)

T. Azaïs*, Université Paris 6, France, Université Paris 6, FranceUniversité Paris 6, France; Y. Wang, Université Paris 6, France; S. Von Euw, G. Laurent, Université Paris 6, France, Université Paris 6, FranceUniversité Paris 6, France; B. Florence, N. Nassif, CNRS, France

Bone is a composite material composed of an organic protein; mainly collagen and a mineral phase parented to hydroxyapatite Ca2(PO4)6(OH)2. Nevertheless, apatite in bone is not stoechiometric but highly substituted by various ions (Na+, Mg2+, HPO42-..) and by carbonates CO32- (5-8 w%). Such intimate association between the mineral and the organic counterpart confers to bone its unique mechanical properties. Solid state NMR study of three different materials, namely freshly extracted bone, bone-like material and biomimetic apatite, show that organic matrix (its hierarchical organization and density) has a strong impact on the structure of precipitated apatite crystals. 1D MAS 31P, D-based 1H→31P/13C HetCor, and triple resonance 1H→31P→13C experiments were used to demonstrate that bone apatite is CO32- substituted mainly in B and A/B sites as well as that the collagen confinement induces a local disorder in the crystal lattice due to the small crystallite size and/or carbonate substitutions. Moreover, an original approach through a 1H→31P→1H "There-and-Back" CP sequence was used to study selectively HPO42- groups demonstrating that are mainly located at the surface of apatite crystals. The modelization of the CP dynamic allows us to determine the P-H distance (2.1 Å) which is found in agreement with neutron diffraction data obtained on brushite Ca(HPO4)2H2O.

S7: 7th International Symposium on Nanostructured Materials and Nanocomposites

Patterning and Tomography I

Room: Coquina Salon B

Session Chairs: Prabir Dutta, The Ohio State University; Flavio Soldera, Saarland University; Thomas Fischer, University of Cologne

1:30 PM

(ICACC-S7-058-2013) Soft Lithographic Approaches for Patterning of Metal Oxides and Graphene on Arbitrary Substrates (Invited)

J. E. ten Elshof*, University of Twente, Netherlands

Soft lithographic methods offer low cost high throughput alternatives to pattern functional ceramics and other inorganic materials. They are receiving considerable interest due to their simplicity, scalability and mild processing conditions, which makes them compatible with many materials and substrates. This presentation highlights a number of soft lithographic fabrication tools that we developed to micropattern metal oxide films, nanoparticles, organically modified silicas and graphene on substrates such as Si and flexible plastics. Printing or molding successive layers to realize 3D stacks and patterns is also possible. All soft patterning methods use elastomeric molds and stamps with a (sub)micron-sized relief pattern. At very high resolution, the easy mechanical deformation of the protruding features of the elastomer becomes a limiting factor. It is possible to use stiffer, less deformable elastomers to pattern smaller features, but they exhibit poorer adhesion to the substrate, and tend to leave residue layers. We developed a couple of new approaches to deal with this limitation, thus allowing lateral resolutions down to 50 nm in some of our processes. The applicability of soft patterning will be illustrated, e.g. by graphene micropatterns on PET plastics, and ZnO patterns as sacrificial templates for subsequent deposition of epitaxial BiFeO3 by pulsed laser deposition.

2:00 PM

(ICACC-S7-059-2013) Tomography and 3D analysis of micro- and nanostructures (Invited)

F. Soldera*, F. Miguel, F. Mücklich, Saarland University, Germany

The three dimensional (3D) morphology of materials structures is the key to understand the relationships between the manufacturing parameters and the properties of the material. Representative characterization can be done by high resolution serial sectioning microstructure tomography. This method combines the excellent target preparation possibilities of a focused ion beam (FIB) with all types of scanning electron microscopy (SEM) contrasts. It enables serial sectioning of representative sample volumes and the imaging of chemical and structural features with a maximum resolution of about 5 nm. Once the 3D data set is available, their exploitation in 3D image analysis provides quantitative insights into the relation between processing, structure and properties. The talk will provide an overview of the potential and the limits of this technique supported by examples in nanostructures with technical relevance. In particular, FIB tomography was used to analyze the arrangement of SnO2 NWs arrays, which were grown with defined orientation, as well as nanocomposites, consisting of one-dimensional nanostructures embedded in a Ag matrix. Acquired quantitative information includes the size, spatial orientation and angles of nanostructures, the distribution of metal catalysts, which allows understanding the physical picture of growth mechanism of nanowires, as well as the local porosity distribution on composite materials.

2:30 PM

(ICACC-S7-069-2013) Shape specific synthesis of ZnO nanoparticles and applications thereof

K. Elen*, IMEC vzw, Belgium; M. Murariu, Université de Mons, Belgium; R. Peeters, XIOS Hogeschool Limburg, Belgium; H. Van den Rul, Sirris Smart Coating Application Lab, Belgium; A. Hardy, M. K. Van Bael, Hasselt University - imomec, Belgium

Because of its unique properties zinc oxide (ZnO) has captured a key role in many technological applications. Its properties can either be of an electronic, optical, thermal or chemical nature, and usually combinations of these qualities make that ZnO is such a desired material. In addition a large number of nanostructures of ZnO can be synthesized. As a result ZnO nanoparticles can be seen as an important material for current research and future applications. The topics of the research presented here are twofold. A first objective is to obtain a better understanding of the growth of ZnO nanoparticles using solution-based methods. This research demonstrates a number of uncomplicated solution-based methods that allow the synthesis of zinc oxide nanoparticles with various morphologies (spherical, rod-shaped and disc-shaped). Through optimization after a thorough study of the experimental parameters, these methods provide an inexpensive and environmentally friendly alternative to existing procedures. Secondly the application of the obtained ZnO nanoparticles in two promising technologies is demonstrated. Zinc oxide nanoparticles can successfully be used as photocatalysts for the degradation of organic contaminants and as inorganic filler for the improvement of the barrier and mechanical properties of biodegradable polymers.

2:50 PM

(ICACC-S7-062-2013) Study of Carbon Nanotubes Effect on Anti-ballistic Property of Abalone-shell-like Silicone-Epoxy Composites

H. Wang*, D. Chua, V. Tan, National University of Singapore, Singapore; Z. Sun, Z. Zhang, East China Normal University, China

CNTs stand out as a candidate of armor protection materials due to their superior mechanical and thermal properties. Their composites have been reported to have enhanced tensile strength, Young's modulus, toughness and storage modulus of composites. In this work, we report on a unique sandwich structure mimicking that of the abalone shell for armor protection. We synthesize hard-soft-hard epoxy-silicone-epoxy composites to study their anti-ballistic properties. CNTs are mixed into silicone matrix with weight ratio of 1% and 3%. A pure silicone with same dimensions is used as reference. Analytical calculation of impact results first confirms that all CNT/silicone samples have a very high energy of absorption, with Sample 1% having the highest of up to 99.15% capacity. SEM results confirm that the CNTs density of Sample 3% is much higher than that of Sample 1%, thus resulting in higher cross-linking area. All the samples are subjected to high impact test and recorded using high speed camera. In the testing, it is observed that only the back layer of the epoxy of Sample 3% remains intact. It is also found by DMA that Sample 3% has lower ability of dissipating heat during the impartment of projectile on cushion layers. The results of this work show potential of this novel composite to be applied in design and fabrication of anti-ballistic devices.

Patterning and Tomography II

Room: Coquina Salon B
Session Chairs: Prabir Dutta, The Ohio State University; Flavio Soldera, Saarland University; Thomas Fischer, University of Cologne

3:30 PM

(ICACC-S7-064-2013) Silicon nitride-graphene composites with improved strength and toughness processed from low concentrations of few layer graphene using SPS

L. S. Walker*, V. R. Marotto, The University of Arizona, USA; N. Koratkar, Rensselaer Polytechnic Institute, USA; E. L. Corral, The University of Arizona, USA

Improving the fracture toughness of ceramics is vital to expanding their use in structural applications, however their high hardness and modulus cannot be sacrificed. Silicon nitride (Si_3N_4) composites densified with additions of less than 1.5 volume % graphene were found to increase fracture toughness up to 250% while maintaining high hardness (>20 GPa) and modulus (>300 GPa) compared to pure Si_3N_4. Aqueous colloidal processing was utilized to disperse few layer reduced and exfoliated graphene within Si_3N_4 powder and ceramic composites were consolidated using SPS. During densification the graphene undergoes structural changes forming some nanodiamond phase. The unique fracture mechanisms found in these composites allow nano phase reinforcements to alter the crack propagation over a range of length scales without sacrificing other mechanical properties. Mechanical testing of flexural specimens was preformed showing consistent improvements in the mechanical properties across multiple samples with flexural strengths increasing from ~450 MPa to >650 MPa. The nano carbon phase within the composites is characterized by raman spectroscopy showing a nanodiamond spectra in addition to graphene.

3:50 PM

(ICACC-S7-065-2013) Reinforcement mechanisms in alumina toughened zirconia nanocomposites with different stabilizing agents

S. Rivera, L. Goyos, Nanomaterials and Nanotechnology Research Center, Spain; A. Fernández, Instituto Tecnológico de Materiales, Spain; L. A. Diaz*, Nanomaterials and Nanotechnology Research Center, Spain; J. Moya, Instituto de Ciencia de Materiales de Madrid, Spain; R. Torrecillas, Nanomaterials and Nanotechnology Research Center, Spain

Alumina toughened zirconia nanocomposites were fabricated with three different zirconia stabilizing agents (10 mol% Ce2O3, 12 mol% Ce2O3 and 3 mol% Y2O3) and a final Al2O3 content of 35vol% within the zirconia matrix. The materials were obtained by applying a colloidal processing route in an alcohol medium and subsequent pressureless sintering under air atmosphere. Their microstructures were observed through FESEM and TEM, both of which revealed average zirconia matrix grain sizes between 400-500 nm and a homogeneously distributed alumina second phase containing particles of 200-300 nm. Fracture toughness (KIc) values of 8-8.5 MPa$\sqrt{m}$ and flexural strength values of 600-700 MPa were obtained using the four point bending method. The threshold stress intensity factor was studied by stable propagation of indentation cracks in bending. The different stabilizing agents of the zirconia matrix did not affect the overall mechanical properties of the composites; this can only be explained by the presence of the dispersed alumina phase, similar in size and distribution for all composites, and, also, by the role of the different reinforcement mechanisms acting within the zirconia matrix: 1) plasticity induced transformation in the case of 10 mol% Ce2O3 and, 2) extrinsic toughening in the case of 12 mol% Ce2O3 and 3 mol% Y2O3.

4:10 PM

(ICACC-S7-066-2013) Fabrication and Thermal transport study of carboxylic functionalized multiwalled carbon nanotubes impregnated polydimethylsiloxane nanocomposites

S. Sagar*, N. Iqbal, A. Maqsood, School of Chemical and Materials Engineering, Pakistan

Multiwalled carbon nanotubes (MWNTs) are modified with nitric/sulfuric acid to covalently attach the carboxylic moiety with the nanotube surface. Five progressive concentrations of carboxylic functionalized multiwalled carbon nanotubes (F-MWNTs) have been uniformly dispersed in polydimethylsiloxane (PDMS). Experimental results simulate that thermal resistance of the nanocomposites is augmented with increasing filler concentration in the host matrix. FTIR analysis confirms the carboxy functionalization of the nanotubes. XRD patterns for both MWNTs and F-MWNTs illustrate that crystallinity does not alter with the surface modification of the nanotubes. Thermal conductivity and thermal impedance of the nanocomposite specimens are evaluated according to ASTM standards. Thermal stability enhancement with increasing filler incorporation into the polymer matrix is observed in TG/DTA contours. Crystallization, glass transition, and melting temperatures are examined using differential scanning calorimeter and it is observed that all these temperatures are diminished with increasing nanotubes concentration in PDMS. Scanning electron microscopy and energy dispersive x-ray spectroscopy are carried out to analyze the surface morphology/composition of the fabricated nanocomposites and uniform dispersion of F-MWNTs in the polymer matrix.

4:30 PM

(ICACC-S7-067-2013) Chemically Bonded Phosphate Ceramics Reinforced with Carbon Nanotubes

J. Wade*, H. Wu, Loughborough University, United Kingdom

As reinforcements, carbon nanotubes (CNTs) have been introduced to a range of matrices. However, problems are continually faced in regards to nanotube agglomeration, alignment and inhomogeneous dispersion in the matrix. With the development of in situ growth techniques, a plausible solution to the aforementioned issues appears to be imminent. In this study, a scalable method for the preparation of phosphate bonded ceramics reinforced by CNTs grown directly on the surface of alumina particles is presented. Alumina ceramic nanocomposites with variable CNT concentrations were comparatively characterised in both microstructure and mechanical property aspects. CNTs were grown directly on ceramic particles via an optimised chemical vapour deposition route with cobalt acting as a catalyst and methane gas as a hydrocarbon source. Phosphoric acid was impregnated into a pre-pressed ceramic matrix, followed by curing/densification at temperatures less than 200°C. Conventional mechanical testing was undertaken on each sample to determine their hardness, fracture strength, fracture toughness and Young's Modulus. Scanning electron microscopy was elected to analyse the fracture surface and cracking paths. Transmission electron microscopy was utilised to investigate the uniformity of CNT dispersion and CNT alignment. Possible micro and nano mechanisms by which the CNTs influence the mechanical properties are discussed.

4:50 PM

(ICACC-S7-063-2013) Hexagonal Boron Nitride Nanocomposite Synthesis: A Method Derived from Carbon Technology

C. Hung*, J. Hurst, NASA Glenn Research Center, USA

A layered material is "intercalated" when other chemicals are inserted into the layers. For graphite, it easily forms intercalated compounds with tens of different chemicals (intercalates), and it may be split (exfoliated) by the activities of intercalates. Also, the intercalates may exit the layers to form nanoparticles of metals or metal oxides. The end result of these reactions is a mixture of graphite and nanoparticles. It was hypothesized that the above procedure can be used to fabricate exfoliated hexagonal boron nitride (h-BN) mixed with metal or metal oxide nanoparticles. This mixture is interesting because it could be hot pressed to form an h-BN nanocomposite. Comparing to hot pressing pure h-BN, the metal/metal oxide nanoparticles could either lower the hot press temperature or improve the product's thermal or mechanical properties. A newly developed process was used to intercalate h-BN powder with metal chlorides. The intercalated compound was then exfoliated by sonication and/or high temperature heating. The metal chlorides were later converted to metal/metal oxide nanoparticles. X-ray diffraction data shows samples lost the h-BN peaks after metal chloride treatment, confirming intercalation. Scanning electron microscopic pictures show the nanoparticles mixed very well with the exfoliated (thinner than original) h-BN. Details of the composites will be presented.

S11: Next Generation Technologies for Innovative Surface Coatings

Low Friction Coating for Automobile Applications

Room: Coquina Salon E
Session Chairs: Ali Erdemir, Argonne Nat'l Lab; Taejin Hwang, Korea Institute of Industrial Technology

1:30 PM

(ICACC-S11-001-2013) Frontiers of Surface Engineering for Friction and Wear Control in Engines (Invited)

A. Erdemir*, O. Eryilmaz, Argonne Nat'l Lab, USA

With recent advances in PVD technologies, great progress have been made in the design, synthesis, and application of a variety of multifunctional nano-composite coatings and on the thermal diffusion treatment of engine parts and components. DLC coatings are still used in large quantities but increasing demands for higher efficiency and durability in future engines will require novel coatings with much lower friction and wear coefficients. In our laboratory, we have been developing a range of lubricant-friendly super-hard, nano-composite coatings that can significantly reduce friction and wear of those engine components in both the formulated and base oils. These designer coatings have an unusual ability to extract low-friction boundary films from these oils on sling engine parts and hence increase their durability and efficiency even under severe operating conditions. Tribological properties of engine components can also be enhanced by a variety of surface treatment methods. In our laboratory, a large-scale, ultra-fast boriding process has recently been developed and proven to be very effective in mitigating friction and wear related degradations. It is very quick (takes about 30 min to achieve 100 micrometer thick hard boride layers) and cost-effective, Initial laboratory studies confirm their extreme resistant to wear and ability to reduce friction substantially under lubricated test conditions.

2:00 PM

(ICACC-S11-002-2013) Hard nanocomposite coatings: Thermal stability, oxidation protection and resistance to cracking (Invited)

J. Musil*, University of West Bohemia, Czech Republic

The lecture is divided in three parts. The first part is devoted to the enhanced hardness of nanocomposite coatings and reasons of its rise. It gives a brief survey of the present state of the knowledge in the field of hard nanocomposite coatings. The second part is devoted to the thermal stability of nanocomposite coatings, thermal cycling of nanocomposite coatings and formation of amorphous coatings with thermal stability and oxidation resistance above 1000C using sputtering. As examples, (i) nc-t-ZrO2/a-SiO2 nanocomposite coatings resistant to thermal cycling in air up to 1400C and (ii) a-(Si3N4/MeNx) and a-(Si-B-C-N) amorphous coatings thermally stable and resistant to oxidation in air above 1000C are reported. The third part reports on new advanced hard nanocomposite coatings with enhanced toughness, particularly (i) NG/AM composite coatings composed of nanograins (NG) dispersed in an amorphous matrix (AM) and (ii) highly-elastic composite coatings resistant to cracking. As examples, (i) nc-TiC/a-C nanocomposite coatings with low friction and wear and (ii) Zr-Al-O, Al-Cu-O oxide composite coatings and Al-O-N nitride/oxide nanocomposite coatings with hardness H 18 GPa, low Young's modulus E satisfying condition H/E 0.1, high elastic recovery We 70% and strongly enhanced resistance to cracking are reported in detail.

2:30 PM

(ICACC-S11-003-2013) Structure and properties of nc-Zr(Al)N/Cu thin films synthesized by multi-component single target with the Zr-based bulk metallic glass alloy

K. Moon*, J. Sun, C. Lee, S. Shin, KITECH, Republic of Korea

Significant research has been devoted to the preparation of nanocomposite films to synthesize hard and super-hard thin films composed of ceramic/ceramic and ceramic/MeN nano composite. However, both hardness and elastic modulus tend to be high, and high elastic modulus of the films can cause intrinsic mismatch between substrate and thin films. It is also known that a high ratio of hardness to elastic modulus (H/E) is indicative of good wear resistance in a disparate range of materials. Therefore, new nc-MeN/metal matrix films with high H/E index which can enhance durability and get low friction properties have been suggested. This study reports on the structure and properties of nc-Zr(Al)N/Cu films synthesized by DC magnetron sputtering process with amorphous single target composed of Zr-Al-M-Cu bulk metallic glass alloys. The films were investigated with XRD, TEM and Nano indentation to confirm the structure of the films. ZrN and Cu phase were observed in XRD and TEM analysis and we confirmed that the nc-Zr(Al)N/Cu nano-composite films with 0.1 of H/E index, 26.3GPa of hardness and 279.1 GPa of elastic modulus, were synthesized. Hardness and elastic modulus were increased with increasing the sputtering power from 4.4 W/cm2 to 7.7 W/cm2, while the H/E index kept similar values of 0.1 at any sputtering conditions.

2:50 PM

(ICACC-S11-004-2013) Customized Coating Systems for Products with Added Value from Development to High Volume Production (Invited)

T. Hosenfeldt*, Schaeffler Technologies GmbH & Co. KG, Germany

Modern components and systems for automotive have to meet various requirements in multiple technical fields. Apart from properties that affect the part itself – like geometry, stiffness, weight or rigidity – the surface properties must be adjusted to the growing environmental requirements. This includes measures for corrosion and wear protection, for optimum electrical or thermal conductivity and for optical purposes. Beyond those, coatings are increasingly used to reduce the friction losses of car components, improve fuel efficiency and reduce CO2-emissions. This article describes how to use surface technology as a modern design element for components and systems to enable the increasing requirements on market leading automotive products. Therefore a coating tool box for customized surfaces has been developed and established to apply the right solutions for all that needs and requests with the corresponding coating system made by PVD-/PACVD-, spraying or electrochemical technology.

Advanced Coating for Energy Process

Room: Coquina Salon E

Session Chairs: Hosenfeldt Tim, Schaeffler Group; Do-Suck Han, Hyundai Motor Company

3:40 PM

(ICACC-S11-006-2013) Vapor-phase Synthesis of Metal Oxide Films and Nanowires for Energy Applications (Invited)

S. Mathur*, University of Cologne, Germany

Metal oxide thin films and one dimensional (1D) inorganic materials are gaining increasing attention because of their unique structural features and interesting functional properties useful for a number of technological applications. Given their structural and chemical stability, metal oxides show promising application potential in vacuum as well as in oxidizing atmospheres, which provides them a competitive edge over their polymer-based counterparts. A number of synthetic procedures have been developed and demonstrated for nanoscaled thin films; however the control over radial and axial dimensions in 1D nanostructures remains a continuing challenge. In addition, the choice of material is rather limited. We have developed a generic approach for the size-selective and site-specific growth of nanowires by combining thermal and plasma-assisted chemical vapour deposition approaches with the chemical influence of molecular precursors that allow fabrication of thin film and anisotropic structures at lower temperatures, when compared to the convention techniques This talk will address the generic feature of our approach for the synthesis of oxide thin films and nanowires of various compositions and present the results obtained on their device and application potential.

4:10 PM

(ICACC-S11-007-2013) Carbon Nanomaterials For High Efficiency Energy Applications (Invited)

W. Choi*, University of North Texas, USA

This talk will focus on engineering of carbon nanomaterials, graphene and carbon nanotubes (CNTs), and their applications in Li-ion battery and flexible solar cells. Particularly, the interfaces of graphene-substrate, CNT-CNT and graphene-CNT will be used to highlight the challenges towards high efficiency energy applications. Various organized architectures of carbon nanomaterials can be fabricated using interfacial control and direct self assembly of these structures. Our recent development of 3-dimensional carbon nanostructural anode will be highlighted. The unique 3D design of the electrode allowed much higher solid loading of active anode material, CNTs in this case and resulted in more amount of Li+ ion intake in comparison to those of conventional 2D anode. Though one such 3D anode was demonstrated to offer 50% higher capacity, compared to its 2D counterpart, its ability to deliver much higher capacity, by geometrical modification, is presented. Our recent results of bonding energy characterization in nano scale will be introduced to offer the optimum structure of carbon nanomaterials. Our efforts on the strategies of manipulation of carbon nanomaterials towards high efficiency energy applications will be reviewed and critical issues will be highlighted.

4:40 PM

(ICACC-S11-008-2013) Novel Metallic Interconnect Protective Coatings for Hermetic Sealing and Elimination of Cr Volatility in Planar SOFC Stacks (Invited)

J. Choi*, J. W. Stevenson, Y. Chou, Pacific Northwest National Lab, USA

Chromia-forming ferritic stainless steels are primary candidates for interconnects in planar solid oxide fuel cell stacks, because of their appropriate thermal expansion behavior and low cost. However, volatilization of Cr from the native oxide scale can lead to degradation of cathode performance. To prevent this volatilization, a conductive MnCo spinel coating has been developed for the active interconnect area. However, this coating is not compatible with the formation of stable, hermetic seals between the interconnect frame component and the ceramic cell. Thus, a new aluminizing process has been developed to enable durable sealing, prevent Cr evaporation, and maintain electrical insulation between stack repeat units. This paper will present recent progress regarding these novel coatings and discuss some of the compatibility issues that arise when integrating both coatings into the same component.

5:10 PM

(ICACC-S11-009-2013) Corrosion and electrical properties of the Zr-based metallic glass bipolar plate for proton exchange membrane fuel cell

J. Sun*, C. Lee, K. Moon, S. Shin, KITECH, Republic of Korea

Metallic materials for bipolar plates of proton exchange membrane (PEM) fuel cell have advantages over graphite-based ones because of their higher mechanical strength and better electrical conductivity. However, they have a significant handicap, the susceptibility to corrosion in the acid and humid environment, which may decrease metal bipolar plates' performance. The problems could be overcome or minimized by protecting metal bipolar plates by introducing coatings or developing new materials. Recently some research groups have tried to use metallic glass alloys in bipolar plates because of their unique properties such as higher mechanical strength and corrosion resistances. Furthermore, metallic glasses can show viscous flow deformation in a supercooled liquid region. The aim of this study is to investigate the corrosion and electrical properties of the Zr-based bulk metallic glass alloys to see whether they have acceptable properties for bipolar plate. In this study, Zr-Al-Cu and Zr-Al-M-Cu amorphous thin film are deposited on SUS316L substrate by DC magnetron sputtering process with an alloyed target sintered from amorphous powder, and investigated the corrosion and electrical properties. Amorphous sheets with width of 75mm and thickness of 70um produced by melt spinning process also were investigated for alternative materials of stainless steel.

5:30 PM

(ICACC-S11-010-2013) Fabrication of piezoelectric MEMS vibration energy harvester with low resonant frequency

S. Murakami*, T. Nagataki, T. Nakade, Technology Research Institute of Osaka Prefecture, Japan; H. Miyabuchi, T. Yoshimura, N. Fujimura, Osaka Prefecture University, Japan

Recently, considerable attention has been directed toward vibration energy harvesting. This arises from the fact that wasted mechanical energy from vibrations is present in various environments and can be converted into electric power for micro electronic systems. In this study, piezoelectric vibration energy harvesters using a Pb(Zr0.5,Ti0.5)O3 (PZT) ferroelectric film were fabricated by Si-micro electro mechanical systems (MEMS) processes. We used silicon on insulator (SOI) wafers as substrates and fabricated cantilevers, on which PZT ferroelectric capacitors were formed by sol-gel method. We also formed a mass in the tip of cantilever in order to improve the efficiency of energy harvesting and lower the resonant frequency to around 100 Hz. Copper plating was used as one of the effective methods to form a mass. The output of piezoelectric vibration energy harvesters was investigated in detail by using a theoretical model and vibration condition. Piezoelectric characterization of PZT films is also discussed. Acknowledgement: This study was supported by Industrial Technology Research Grant Program in 2011 from New Energy and Industrial Technology Development Organization (NEDO) of Japan.

5:50 PM

(ICACC-S11-012-2013) A self-healing scheme of biomimetic surface

T. Hwang*, H. Kim, J. Park, KITECH, Republic of Korea

Ever since the discovery of super-hydrophobicity of lotus leaf surface, the biomimetic surface technology has been one of the key issues in the competition of achieving high-performance features from artificial materials. Structure color, super hydrophobic surface, and gecko toe attachment have been the most popular subject of the nature-inspired engineering skills. The biomimetic surface coatings are not staying in the structure manipulation, but they started to pursue the novel method to mimic the bioactivity such as self-healing of the demolished or deteriorated structure. In our study, a recovery of surface structure was tried by using inorganic-organic hybrid surface structure. Inorganic honeycomb-like structure was fabricated by an anodization of sputter-deposited titanium layer and a hygroscopic polymer was incorporated into the channels. Recovery of surface structure by the adsorption of H2O molecules from the atmosphere into the hygroscopic polymer was successfully demonstrated.

6:10 PM

(ICACC-S11-011-2013) Design and Synthesis of Hybrid Functional Noble Metal based Ternary Nitride Thin Films

W. Kwack, S. Kwon*, Pusan National University, Republic of Korea

In recent years, hybrid functional or multifunctional ternary nitride thin films have received extenstive attention due to its versatility in many applications. In particular, noble metal based ternary nitride thin films showed a promising properties in the application of Cu diffusion barrier layer and heating resistor films because its good electrical properties and excellent resistance against oxidation and corrosion. In this study, we prepared hybrid functional noble metal based ternary nitride thin films by atomic layer deposition (ALD) or plasma-enhanced ALD (PEALD) method. ALD and PEALD techniques were used due to their inherent merits such as a precise composition control and large area uniformity, which is very attractive for preparing multicomponent thin films on large area substrate. Here, we will demonstrate the design concept of hybrid functional noble metal based ternary thin films. And, the relationship between microstructural evolution and electrical resistivity in noble metal based ternary thin films will be systemically presented. The useful properties of noble metal based ternary thin films including anti-corrosion and anti-oxidation will be discussed in terms of hybrid functionality.

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

Novel Methods for Joining and Machining of Components

Room: Coquina Salon F
Session Chair: Zenghua Gao, Institute of Metal Research, Chinese Academy of Sciences

1:30 PM

(ICACC-S12-040-2013) Advances in Spark Plasma Joining of Ultra-High Temperature Ceramics: An Investigation into Direct Current Assisted Joining Mechanisms & Properties (Invited)

W. Pinc, L. S. Walker, E. L. Corral*, University of Arizona, USA

Spark plasma joining (SPJ) is a direct current assisted method for rapidly joining high temperature ceramic materials at low temperatures. Our method has been developed using a spark plasma sintering furnace, ultra-high temperature ceramics, and filler materials that are based on UHTC compositions. The rapid heating and direct current assist in rapidly joining the filler material to the substrates and result in indistinguishable joint microstrostructures from the bulk that retain room and high temperature mechanical properties. We have also investigated the joining mechanisms of SPJ by comparing the joining of electrically conductive (ZrB2 and HfB2 based ceramics) and insulating materials (Si3N4) at various temperatures. Specifically the electric current and field effects are studied and have been found to play a significant role in the SPJ process. The current based joining mechanism found in the joining of conductive materials allows for low temperature joining. As a result, we are able to join by SPJ at temperature several hundred degrees below typical sintering temperatures for these materials. Lastly, an overview on joining complex shaped UHTC parts will also be presented.

2:00 PM

(ICACC-S12-041-2013) Welding of Ultra High Temperature ZrB_2 Ceramics

D. King*, G. Hilmas, W. Fahrenholtz, Missouri University of Science and Technology, USA

Plasma arc welding was used to join zirconium diboride (ZrB_2) based ceramics. ZrB_2 billets were prepared by milling ZrB_2 powder in acetone with phenolic resin as a sintering aid and hot-pressing at temperatures up to 2200°C to achieve near theoretical densities. Billets nominally 64 mm by 64 mm by 5 mm were ground and diced using an automated surface grinder. Diced pieces were welded together using an in-house plasma arc welding process. To combat oxidation and thermal shock, welding was carried out under an inert argon atmosphere in a sealed furnace designed to preheat the samples prior to welding. The effectiveness of welding parameters was examined through microstructural analysis of weld cross-sections using scanning electron microscopy. Void formation was also examined with the use of microstructural analysis and density measurements. Elastic constants for melt solidified ZrB_2 were measured using dynamic impulse excitation techniques to determine the Young's modulus for the joint. To test the strength of the joint, flexure bars were prepared so that the weld joint was under maximum load during four-point bend testing.

2:20 PM

(ICACC-S12-042-2013) High Temperature Joining Solution For Thermal Protection Systems Based On Intermetallic Alloys

J. Barcena*, C. Jimenez, M. Lagos, Tecnalia Research & Innovation, Spain; K. Mergia, N.C.S.R. "Demokritos, Greece; I. Agote, Tecnalia Research & Innovation, Spain; C. Badini, Politecnico di Torino, Italy; C. Wilhelmi, EADS Innovation Works, Germany

Future developments on thermal protection systems demands original and robust approaches able to perform under extreme mission conditions. The present research addresses a novel approach for the integration of external protective ceramic multilayers: SiC and ZrB2/SiC (UHTCs) on top of a thermostructural ceramic matrix composite core (Cf/SiC), as part of a more complex system under a reference mission (Advanced Reentry Vehicle). A filler metal based on a MAX-Phase (Ti3SiC2) produced by SHS (Self propagating High temperature Synthesis) has been employed. The integration method is based on two different techniques: hot-pressing and spark plasma sintering in order to achieve a sound joining based on diffusion/brazing bonding. The process parameters of the joining methods and their effect on the characteristics of the integrated structure are discussed. The microstructure of the assembly has been investigated by optical and scanning electron microscopy and its structure stability has been determined by in-situ X-ray diffraction measurements. An assessment is performed for both types of joining processes

2:40 PM

(ICACC-S12-043-2013) Joining of ZrB2-based ultra-high-temperature ceramic composites using Pd-based braze alloys

A. Goodarzi*, H. Taylor, Harvard University, USA

Hot-pressed ZrB2–SiC and composites with carbon (ZSC) or SCS-9a SiC fibers (ZSS) were joined using Pd-base brazes, Palco (65% Pd–35% Co) and Palni (60% Pd–40% Ni). Joint integrity was exhibited by the defect-free ZS/Palco/ZS joints with large interaction zones. The ZSS/Palco and ZSC/Palco joints revealed substantial chemical interaction and interfacial cracking due to residual stresses. The joints with Palni exhibited either poor etting/bonding or cracking. The ZS/Palco joints displayed high Knoop hardness within the ZS region and lower hardness within the Palco interlayer.

Novel Processing Methods

Room: Coquina Salon F

Session Chair: Erica Corral, University of Arizona

3:20 PM

(ICACC-S12-044-2013) Zirconium carbide ceramics for potential applications in extreme environments of ultra high temperature or strong radiation

G. Zhang*, Shanghai Institute of Ceramics, China

Refractory carbides such as ZrC, HfC and TaC demonstrate high melting point and are important ultra high temperature ceramics. They are potential candidates for the applications in the next-generation rocket engines and hypersonic spacecrafts working at 2200-3000oC. On the other hand, ZrC has low neutron absorption cross-section and a good resistance to strong radiation and corrosion of nuclear fission products. In the frame work of the Gen-IV project, ZrC is one of the inert matrix materials. In this presentation, we will report our recent results on the sintering and properties of ZrC ceramics with different additives. (1) Hot pressing of ZrC ceramics with the addition of Zr and C. The addition of Zr will improve the sintering behavior by the formation of non-stoichiometric zirconium carbide, C additive will remove oxygen and inhibit grain growth, resulting a high density and fine microstructure. (2) Hot pressing of ZrC ceramics with the addition of MC (M=V, Nb, Ta). The densification mechanisms with different carbide additives were analyzed according to the phase diagrams and the solid solution formation limitations. (3) Reactive hot pressing of ZrCx-SiC ceramics with the addition of silicon at low temperatures. The reaction mechanism and densification behavior will be discussed.

3:40 PM

(ICACC-S12-045-2013) Si-SiC-ZrB2 ceramics produced by reactive silicon infiltration

A. Ortona*, SUPSI, Switzerland; S. Biamino, Politecnico di Torino, Italy; C. D'Angelo, SUPSI, Switzerland; G. D'Amico, P. Fino, Politecnico di Torino, Italy

Si-SiC ceramics produced by silicon infiltration and reaction bonding are industrially employed in several high temperature applications because they show good thermo-mechanical properties and oxidation resistance up to1400 °C. For higher temperatures other material systems are envisaged. This paper presents a reseach study on a manufacturing methodology to produce Si-SiC-ZrB2 bulk ceramics obtained infiltrating with molten silicon a C-SiC-ZrB2 preform. Samples were then characterized focusing on their oxidation behavior in a short and long timeframe. Results were analyzed and compared with Si-SiC and SiC-ZrB2 samples oxidized in the same conditions

4:00 PM

(ICACC-S12-046-2013) Ultra-Low Temperature Sintering of Ultra-High Temperature Ceramics

H. Kimura*, Natl Defense Academy, Japan

This article reports the preliminary study on ultra-low temperature sintering of covalent bond type ceramics categorized as ultra-high temperature ceramics (UHTCs) by employing millimeter wave pressure sintering and pulsed electric current sintering of the amorphous B4C and/or B4C-SiC powder synthesized by rotating-arm reaction ball milling and planetary ball milling. With millimeter wave thermomechanical testing apparatus, the mechanically synthesized amorphous B4C powder was consolidated at a full-density at the temperature of below 250C without a need of any additive under an applied stress of 50 MPa in the case when the heating rate of 10 K min-1 was used. The heating rate is found to be a dominant variable for electric field assisted densification under millimeter wave input; at 20 K min-1, it leads to a large decrease to 150C in temperature necessary to obtain full densification of the amorphous B4C. On the other hand, pulsed electric current sintering of the amorphous B4C-SiC obtained full densification at approximately 1200 K during dc heating after rapid shrinkage by applying rectangular electric current pulses under an applied stress of 100 MPa. Thus-obtained cylindrical amorphous B4C-SiC was subjected to high-speed superplastic forging at approximately 1400K with compressibility of approximately 0.75 avoiding that a crack formation occurred.

4:20 PM

(ICACC-S12-047-2013) Synthesis and Sintering of TaC-HfC ceramics by SHS and RSPS techniques

O. Cedillos*, D. D. Jayaseelan, W. E. Lee, Imperial College London, United Kingdom; A. Chrysanthou, University of Hertfordshire, United Kingdom

Compounds in the TaC-HfC system have extremely high melting points (>3900°C), making them potential candidates for thermal protection structures in hypersonic vehicles. Self-propagating High-temperature Synthesis (SHS) and Reactive Spark Plasma Sintering (RSPS) are used in this work to fabricate TaC-HfC Ultra High Temperature

Ceramics (UHTCs). Six different compositions (TaC, HfC, TaC-80 wt%HfC, TaC-60 wt%HfC, TaC-40 wt%HfC and TaC-20 wt%HfC) were synthesised by SHS in a tube furnace at 1400°C with a heating rate of 50°C/min. The RSPS method consists of synthesising the reactant powders by SHS or carbothermic reaction followed by consolidation of them by SPS. In this case Ta, Hf and carbon black for SHS and HfO_2, Ta_2O_5 commercial powders were used along with carbon black for carbothermic reaction. Three compositions were prepared (Ta, d_{50}: 14.9 μm; Hf, d_{50}: 17.7 μm and C, ~0.04 μm) for SHS-SPS (4TaC-1HfC, 3TaC-1HfC and 5TaC-1HfC) heated at 210°C/min to 2100°C and sintered for 20 min at 20 MPa. Carbothermic reaction-SPS was conducted by preparing a 4TaC-1HfC powder mixture (HfO_2, d_{50}: 11.6 μm; Ta_2O_5, d_{50}: 11.4 μm and C, ~0.04μm) heated at 100°C/min to 1800°C for 20 min for the reaction to go to completion followed by sintering at 2100°C for 20 min and 60 MPa. XRD, SEM and TEM reveal formation of TaC, HfC and TaC-HfC solid solutions. Reaction mechanisms for the formation of these phases are discussed.

4:40 PM

(ICACC-S12-048-2013) Synthesis of HfB_2 Powders for Aerospace Applications

P. Zheng*, S. Venugopal, A. Paul, B. Vaidhyanathan, J. Binner, Loughborough University, United Kingdom

HfB_2-based ceramics are considered to be potential materials for aerospace applications. Several synthesis routes have been developed including solid-state carbothermal/borothermal reduction, electrochemical, mechanical alloying, self-propagating high-temperature synthesis, polymer precursor route and the sol–gel method, of which, solid-state carbothermal/borothermal reduction has been reported as a commercial route. However, the resulting particle size is generally of the order of 30-40 μm and subsequent grinding to reduce the particle size introduces impurities. The present work is focused on synthesizing sub-micron sized HfB_2 powders via two inexpensive sol-gel routes: one based on carbothermal/borothermal reduction and the other based on borothermal reduction alone. Ethanol was used as a medium to dissolve Hf, B and C containing precursors. These two routes successfully yielded high-purity sub-micron sized HfB2 powders. The particle size of the finest powder obtained was less than 1 μm in size and was achieved by using phenolic resin as the carbon source. This method has been scaled up with a view to produce 50 g rather than 5 g batches of the powder. The phase purity, particle size and agglomerate size of the powders produced have been characterised using XRD, FEGSEM and TEM and the oxidation temperature and oxidation products were also analysed using TGA and high temperature XRD.

5:00 PM

(ICACC-S12-049-2013) Erosion-resistant Cr2AlC and Ti2AlC coatings (Invited)

C. Leyens*, Technische Universität Dresden, Germany

In aero engines, coatings are facing severe attack under multiple loading conditions. Sand erosion, e.g., can cause great damage to turbine hardware in the compressor, while hot corrosion and oxidation are of concern in the hotter parts of the engines. Today, coatings are widely applied to protect high pressure turbine airfoils, however, their use in the compressor and the low pressure turbine is scarce yet. Due to their inherent nanolaminate structure, Ti2AlC and Cr2AlC MAX phases deposited as thin coatings have proven to be erosion resistant in harsh environments. The paper will review recent developments in synthesis of these types of coatings, findings on their microstructure and the resulting properties. Depending on the deposition conditions the texture of MAX phase coatings can be tailored and adjusted to the erosion attack. Post-deposition heat treatments can further improve the erosion resistance of the coatings caused by phase transformation. Laboratory erosion tests revealed that the failure mode of MAX phase coatings is primarily governed by layerwise failure rather than spallation of the whole coating as found for other coating architectures. At elevated temperatures the coating systems tend to interdiffuse with the substrate alloys such as nickel-base superalloys, titanium alloys and titanium aluminides which appears to limit the useful lifetime at temperatures beyond 800°C.

5:20 PM

(ICACC-S12-050-2013) Synthesis of epitaxial MAX phase thin films by thermal annealing

T. Cabioch*, A. Drevin-Bazin, M. Beaufort, M. Alkazaz, University of Poitiers, France; P. Eklund, IFM Linköping University, Sweden; J. Barbot, University of Poitiers, France

By using two different techniques, based on the thermal annealing of layers or multilayers deposited at room temperature, the synthesis of epitaxial thin films of Ti_3SiC_2 and Ti_2AlN were achieved. In the first approach, the formation of the MAX phase thin films is based on interdiffusion processes between the substrate and the deposited layer. TiAl thin films deposited onto (0001) and (11-20) 4H-SiC single crystals, were annealed at 1000°C for 10 minutes allowing to obtain epitaxial $Ti_3(Si,Al)C_2$ thin films. For both substrates, basal planes from the Hexagonal SiC substrate and that of the MAX phase are parallel allowing one to obtain $Ti_3(Si,Al)C_2$ thin films having their basal plane parallel or perpendicular to the substrate surface. For the second approach, Ti/AlN multilayers, deposited onto various substrates, were annealed up to 800°C and characterized in situ by X-Ray diffraction. The formation of the MAX Phase Ti_2AlN is observed at 550-600°C and, single-phased, epitaxial layers can be obtained after a thermal annealing at 750°C for multilayers deposited onto 4H-SiC (0001) and Al_2O_3 (0001) single crystals.

5:40 PM

(ICACC-S12-051-2013) Study the parameters of Ti2AlC and Ti3AlC2 MAX phases fabrication by Mechanically Activated Self-propagating High temperature Synthesis

A. Sedghi*, Imam Khomeini International University, Islamic Republic of Iran; R. Vahed, Imam Khomeini International University, Islamic Republic of Iran; A. Razaghian Arani, Imam Khomeini International University, Islamic Republic of Iran

The MAX phases in the Al–Ti–C ternary system that named TACs ceramics such as Ti2AlC and Ti3AlC2 combines a unique combination of properties of metals and ceramics, including low density, high elastic modulus, easy machinability, excellent thermal shock resistance, high mechanical strength, good plasticity and good thermal and electrical conductivity which lead to using them as high-temperature structural and functional materials. TACs compounds were synthesized by different methods which one of them is called MASHS (Mechanically Activated Self-propagating High temperature Synthesis). This process has some special parameters and these parameters have been studied in this research. Samples fabricated by short duration ball milling (MA) of reactants (Ti, Al, C, TiC as starting material) which were followed by self-sustaining combustion (SHS) in microwave furnace. The fabricated compounds had been investigated by XRD and SEM and formation of these MAX phases as well as their structure and morphology were examined. This study shows TACs could be achieved by MASHS but some impurity such as TiC and TiAl intermetallics were revealed during synthesis which it's possible to remove them by optimization of raw materials and processing conditions.

S13: Advanced Ceramics and Composites for Sustainable Nuclear Energy and Fusion Energy

Joining / Irradiation and Environmental Effects I / Fabrication and Processing of Ceramic Functional Materials

Room: Ponce DeLeon
Session Chairs: Yutai Katoh, Oak Ridge National Laboratory; Josef Matyas, Pacific Northwest National Lab

1:30 PM

(ICACC-S13-020-2013) Glass-ceramics as joining materials for nuclear applications (Invited)

M. Ferraris*, V. Casalegno, S. Rizzo, M. Salvo, Politecnico di Torino, Italy; D. Blagoeva, NRG, Netherlands

Joining of SiC/SiC composites and generally speaking SiC-based materials for nuclear applications can be of interest for both future thermo-nuclear fusion reactors and new generation fission reactors components. In both cases, the main issues are extreme thermo-mechanical loads on the joined components, their resistance to high temperatures, neutron irradiation and harsh chemical environment, as well as not completely known service conditions and requirements. Three silica and non-silica based glass-ceramics have been used to join SiC and SiC/SiC by a pressure-less joining technique. Bending strength has been measured on glass-ceramic joined SiC/SiC before and after neutron irradiation at the High Flux Reactor in Netherlands, within the EU project EXTREMAT. Preliminary results showed almost the same bending strengthsbefore and after irradiation at 820 °C. Finally, the behaviour of glass-ceramics as joining materials for SiC/SiC was investigated before and after fast neutron irradiation. The same glass ceramic structure and phases were observed before and after neutron irradiation at 820 °C.

2:00 PM

(ICACC-S13-021-2013) A Novel Composite Brazing Approach for Joining Silicon Carbide

E. D. Herderick*, EWI, USA

Silicon carbide has been investigated for numerous applications including nuclear fuel rod cladding. One of the key enabling technologies for this application is a joining approach which would provide a hermetic seal of an end cap to a silicon carbide tube. This joint must be able to withstand elevated operating and accident condition temperatures in a reactor coolant environment under high neutron flux for an extended period of time. In this work, results for a new approach for joining silicon carbide will be presented. This approach consists of a composite metal system that is damage tolerant and straightforward to manufacture. Joints were characterized using optical and electron microscopy and their shear strengths evaluated. Joined assemblies survived thermal cycling tests that mimic in service reactor conditions and accident temperature conditions. Additionally, joined assemblies remained intact after nearly 6 months of irradiation in the MIT research reactor under PWR primary water conditions of 300°C, 1000 ppm B and 7 ppm Li at saturation pressure. Further work on integrating mechanical interlocking approaches with the composite braze will also be presented.

2:20 PM

(ICACC-S13-022-2013) Evaluation of Engineered Microstructures for Enhanced Reliability in Nuclear Grade Joints

H. Khalifa*, C. P. Deck, C. Hill, C. A. Back, General Atomics, USA

Silicon carbide and silicon carbide fiber reinforced 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. Laboratory work presented here focuses on low activation joint materials that behave similarly under reactor operating conditions to the SiC-SiC composites they join. SiC components have been joined using SiC-based materials with varying compositions and morphologies of low-activation additives and fillers. Joint strength was evaluated using the single lap offset (SLO) and Iosipescu shear test methods to assess the effect of the additions on the densification and Weibull parameters of different joining processes. While SLO is a commonly used test method, specimen asymmetry and frictional contributions make measurements of the joint performance collected by this method difficult to interpret. Iosipescu testing employed here has been adapted to generate uniform shear strain across the joint interface and mitigate stress singularities through reliable sample alignment and specimen face loading. Data generated using test methods will be compared, and test fixture design features critical for accurate characterization will be discussed.

2:40 PM

(ICACC-S13-023-2013) Radiation Stability of Silicon Carbide Joints Made by Various Bonding Methods

Y. Katoh*, Oak Ridge National Laboratory, USA; T. Hinoki, Kyoto University, Japan; M. Ferraris, Politecnico di Torino, Italy; C. H. Henager, Pacific Northwest National Laboratory, USA

Joining is among the key technologies required for integrating silicon carbide ceramic and composite components for high radiation services. For instance, high temperature blanket for fusion reactors will require extensive adhesive joining that withstands intense neutron irradiation at temperatures approaching 1000°C. Silicon carbide-based light water reactor cladding will require hermetic end plugging that confines gaseous fission products in nuclear environment. While various joining methods have been proposed and developed for silicon carbide to operate in non-nuclear environments, none of those technologies has demonstrated adequate radiation resistance. In the recent international collaboration among the present authors, specimens of silicon carbide in monolithic or fiber composite forms joined together by various bonding methods were subjected to neutron irradiation in High Flux Isotope Reactor up to ~4 displacement per atom at 500 and 800°C. Results from the mechanical properties evaluation for the irradiated specimens will be presented. Although none of the joining materials used has been anticipated or previously proven to be inherently radiation-resistant, the result implied that the properties of irradiated joint may not necessarily be bound directly to the radiation stability of the joining agents as the bulk material.

3:20 PM

(ICACC-S13-024-2013) Effect of irradiation and chemical interaction on select MAX phases for Gen IV reactors (Invited)

D. J. Tallman*, G. W. Bentzel, Drexel University, USA; E. Hoffman, R. Sindelar, G. Kohse, Savannah River National Lab, USA; M. W. Barsoum, Drexel University, USA

Gen IV nuclear reactors require new materials that can withstand harsher environments than in current reactors. The Mn+1AXn (MAX) phases are a group of layered machinable ternary compounds, where M is an early transition metal, A is a group 13 to 16 element, and X is C and/or N. These compounds possess mechanical properties atypical for ceramics, notably thermal conductivity, oxidation resistance, and plasticity at high temperatures. Data about their irradiated properties are required to fully realize their potential. The MAX phases must also show chemical inertness with cooling media and structural components of the new reactor designs. Research is thus ongoing to characterize their irradiated properties, and the chemical interaction between MAX phases and reactive media (Na, Pb-Bi, etc.). Comparison of pre- and post-irradiated characterization of samples will be presented, including TEM analysis of microstructure, electrical resistivity, chemical compatibilities, fuel/fission product diffusivities, and thermal properties.

3:50 PM

(ICACC-S13-027-2013) Oxidation behavior of UO2 in air

K. Suzuki*, Japan Atomic Energy Agency, Japan; A. T. Nelson, Los Alamos National Laboratory, USA; T. Sunaoshi, Inspection Development Company, Japan; K. J. McClellan, Los Alamos National Laboratory, USA; M. Kato, Japan Atomic Energy Agency, Japan

In a reactor core or a spent fuel pool loss of coolant accident, fuel cladding may be breached and cause rapid oxidation of UO2 pellets. Oxidation of UO2 results in pulverization of the pellet and significant evaporation of UO3, possibly leading to spread of nuclear material to the environment. Therefore, understanding the oxidation behavior of UO2 is an important factor in modeling the evolution and consequences of nuclear accidents. In this study, the oxidation behavior of UO2 pellets and powders in air was investigated over a wide temperature range. Isothermal oxidations were carried out using a thermogravimetric analyzer from 673 to 1923K. Oxidative pulverization was observed below 1073K. The weight gain rate at 773K was larger than that at 873K, suggesting the oxidation mechanism might change in this regime. Rapid weight loss was observed above 1723K. The vapor pressure of each phase in the U-O system was calculated, indicating that volatilization of UO3 was likely responsible for the measured weight loss. The evaporation rate of UO3 for a urania pellet was then evaluated. The same tests were repeated for UO2 powders to investigate the surface area and species diffusion effects on oxidation. The results of these measurements are then combined to develop the framework for a mechanistic kinetic model describing oxidation of UO2 in accident-relevant environments.

4:10 PM

(ICACC-S13-029-2013) Silver-functionalized silica aerogel: A novel benchmark for capturing and immobilization of iodine-129 from fuel reprocessing off-gas

J. Matyas*, G. Fryxell, Pacific Northwest National Lab, USA

Release of volatile radioiodine from nuclear fuel reprocessing plants and its safe storage have to be controlled to meet the Environmental Protection Agency and Nuclear Regulatory Agency regulations for emissions and disposal. This requires the development of a material exhibiting high selectivity and sorption capacity for iodine-129, and when consolidated, a durable waste form. We have developed silver-functionalized silica aerogels with maximum sorption capacity 48 mass % and decontamination factors in excess of 10,000. In addition, our preliminary densification tests showed that the iodine-loaded aerogels retained more than 92 mass% of the iodine when sintered at 1200 °C for 30 min at moderate pressure. In this presentation, we will discuss the results of sorption and densification studies with these aerogels.

4:30 PM

(ICACC-S13-030-2013) Mechanical Properties of Porous Silicon Carbide Composites Following Exposure at Elevated Temperature in Air

T. Hinoki*, K. Shimoda, Kyoto University, Japan; S. Maeta, N. Konishi, GUNZE LIMITED, Japan; K. Toyoshima, Kyoto University, Japan; T. Kawahara, A. Sato, GUNZE LIMITED, Japan

Novel conceptual silicon carbide composites were developed applying porous silicon carbide matrix. The composites consist with just silicon carbide fiber and crystalline porous silicon carbide matrix without fiber/matrix interphase like carbon. The silicon carbide matrix was formed with carbon powder by liquid phase sintering or reaction sintering method. The porous silicon carbide matrix was formed following decarburization process. The composites showed pseud-ductile behavior and complicated fracture behavior due to frictional stress at debonded fiber/matrix interface. The porous silicon carbide composites were exposed at elevated temperature up to 1200C in air. The mechanical properties were characterized by flexural test, tensile test, diametral compression test and double-notched shear test. Mean flexural strength of the porous silicon carbide composites was 274 MPa following exposure at 1100C and no apparent degradation was observed compared to flexural strength of the as-received material.

4:50 PM

(ICACC-S13-031-2013) Modifications of Micro-structure and Pore Morphology of Lithium Orthosilicate Pebbles during Sintering

D. Mandal*, D. Sen, S. Mazumder, S. Ramnathan, Bhabha Atomic Research Centre, India

Lithium orthosilicate, enriched in Li6 isotope, is one of the contenders for tritium generation for future fusion reactors. It will be used in pebble form with some desired specifications viz. density, porosity, grain size, thermal conductivity etc. Sintering is one of the most important steps is used to achieve these required specifications. The morphological modifications and change in microscopic structure in lithium orthosilicate pebbles during sintering have been investigated using small angle neutron scattering (SANS), helium pycnometer, mercury porosimeter and electron microscopy. The experimental details and results viz. variation of a) pebble density b) porosity (open and close); c) surface area d) grain size d) variation of pore size with the duration of sintering etc. will be discussed in this paper.

FS1: Geopolymers and Chemically Bonded Ceramics

Porosity II

Room: Coquina Salon A
Session Chair: Sylvie Rossignol, CEC GEMH ENSCI

1:30 PM

(ICACC-FS1-009-2013) The influence of curing conditions on mechanical strength and porosity of geopolymers (Invited)

H. Engqvist*, B. Cai, T. Mellgren, Engineering Sciences, Sweden; S. Bredenberg, Orexo AB, Sweden

Geopolymers have been suggested to be used as construction, waste treatment and even drug delivery material due to its excellent mechanical strength, acid resistance and biocompatibility. The aim of this study is to investigate the influence of temperature, time and humidity during curing on mechanical strength and porosity of geopolymers. The geopolymer was synthesized by mixing metakaolin, waterglass and de-ionized water until a homogenous paste was obtained. The following molar oxide ratio was used: Al2O3/SiO2=0.353, Na2O/SiO2=0.202, H2O/SiO2=2.977. The paste was molded into cylindrical rubber moulds (6 12 mm) and cured under different temperatures (ambient temperature, 37°C and 90°C), humidity and time (24, 48 and 96 hours). The compressive strength was determined using a universal testing machine. Helium pycnometer was used to measure the porosity. Via x-ray diffraction the phase composition of the cured samples was determined. Higher curing temperature increased the compressive strength after 24 hour but did not affect the strength for longer curing times. In general, the samples cured in moisture had higher mechanical strength than those cured in air. More metakaolin remained in samples cured under high temperature, while for samples cured under low temperature for longer time showed a higher conversion to geopolymer. Curing time did not show much influence on the total porosity.

2:00 PM

(ICACC-FS1-010-2013) Effects of pore evolution on the mechanical properties and microstructure of Inorganic Polymer Cement-Aggregate systems

E. Kamseu*, University of Modena, Italy; C. Leonelli, University of Modena and Reggio Emilia, Italy; V. M. Sglavo, University of Trento, Italy

The work describes the mechanical and microstructural changes that occur in inorganic polymer cement when different grade of fine siliceous aggregates are added. The flexural strength of the inorganic polymer cement that goes from 4 MPa to 4.2, 4.8 and 6.8 MPa respectively for 20 wt% of quartz sand, nepheline syenite and ladle slag addition. The significant improvement of the strength upon 28 to 90 days of curing (9.1 MPa for ladle slag and 10.0 MPa for nepheline syenite) demonstrated that appropriate siliceous aggregates can be identified to produce homogeneous mortars and concretes with reduced pore-size and pore volume, improving hence the strength. The increase in content of the ladle slag from 20 to 60 wt% did not further improve the flexural strength as in the case of nepheline syenite where an increase in the flexural strength to 10 MPa was measured. The samples with high flexural strength presented dense and homogeneous matrices as results of the absence of larger pores, intensive microcracks which are generally at the origin of poor mechanical properties of geopolymers. It was concluded that the reaction of the inorganic polymer cement with fine aggregate is limited by saturation in Ca and Si available in pores solution.

2:20 PM

(ICACC-FS1-011-2013) Use of industrial sludges to produce geopolymer foam

E. Prud'homme*, P. Michaud, GEMH-ENSCI, France; E. Joussein, GRESE, France; S. Rossignol, GEMH-ENSCI, France

Nowadays the production of industrial waste is increasingly important. Manufactures produces important quantity of waste such as sludges. This by-product can be easily upgraded in geopolymer material, which has a good ability to integrate a large variety of recycled materials. The present paper proposed to study the formation mechanisms and the parameters influencing the formation of porosity inside foam containing a small amount of sludge. The impact on formation of two parameters is investigated, which are clay amount and additives. The synthesis of foam is realized by mixing alkali hydroxide and silicate, various amounts of clay, sludge and eventual additives. All samples are treated at moderated temperature. The introduction of sludges leads to the formation of gas and consequently to porosity formation in material. Their characterization is realized in terms of structural properties (SEM observations, FTIR, density, viscosity) and of use properties (mechanical and thermal measurements). The introduction of a small amount of sludge permits to keep the geopolymerisation reaction unchanged. Clay and additives allow adjustment of properties for particular application. From all analysis an optimal insulating composition can be stated. The final materials present very good properties in terms of thermal properties (0.085 W/m/K). It allows to consider the use of this material in the construction field.

2:40 PM

(ICACC-FS1-012-2013) Optimization of Gas Adsorption Porosimetry for Geopolymer Analysis

B. E. Glad*, W. M. Kriven, University of Illinois at Urbana-Champaign, USA

Gas adsorption porosity measurement of geopolymers is required for quantitative understanding of the mesoporous structure, but the complex nature of the geopolymer system makes analysis difficult. A systematic investigation of geopolymer gas adsorption results was conducted to optimize the use of this measurement technique. The investigation revealed that degassing time, degassing temperature, adsorbent choice, maximum analysis pressure and inert gas exposure all affect the observed isotherm. Variations in these choices can result in up to ≈100% deviation of surface area and NLDFT pore size distribution measurements for an identical sample. This deviation can occur even when reasonable measurement practices are utilized, as it is caused by complex surface-adsorbent interactions atypical for most ceramics. These surface interactions are examined in detail, and quantitative methods for accounting for them are developed. The value of gas adsorption porosimetry data in exposing geopolymer microstructure is examined at length.

Mechanical Properties

Room: Coquina Salon A
Session Chair: Miladin Radovic, Texas A&M University

3:20 PM

(ICACC-FS1-013-2013) Chemically Bonded Phosphate Ceramics Subject to Temperatures up to 1000 C

H. A. Colorado*, J. Yang, UCLA, USA; C. Hiel, Composite Support and Solutions Inc., USA

In this paper chemically bonded phosphate ceramic (CBPC) composites are studied when exposed to temperatures up to 1000 C. Different raw materials including wollastonite and fly ash were used to consolidate the matrix. Glass, graphite, Basalt and SiC fibers have been used as reinforcements. CBPCs were synthesized at room temperature and further thermal processing was performed after the manufacturing. Samples were placed in a furnace at different temperatures (up to 1000C) to determine the effect of these exposures on bending strength. The characterization was conducted by optical and scanning electron microscope and by x-ray diffraction. The thermal stability of the samples was also evaluated by Thermo-gravimetric analysis.

3:40 PM

(ICACC-FS1-014-2013) Mechanical Properties and Microstructure of Potassium-based Geopolymer with Chamotte Particulate Reinforcement

S. Musil*, W. M. Kriven, University of Illinois at Urbana-Champaign, USA

Geopolymers are an inorganic polymeric material composed of alumina, silica, and alkali metal oxides. Monolithic geopolymer is brittle and susceptible to dehydration cracking at elevated temperatures. The addition of a reinforcing phase can not only improve strength and toughness, but can also maintain the structural integrity of the material at elevated temperatures. For this study, potassium-based geopolymer is reinforced with varying weight percent of chamotte particles. Chamotte is kaolin grade clay calcined at 1350oC to produce 38% crystalline mullite, as well as metastable cristobalite and quartz. Chemical composition of the chamotte is nearly identical to that of the metakaolin used to create the geopolymer, however its crystalline nature prevents reactivity with the potassium water glass and it remains as a particulate reinforcement. Flexural strength is evaluated at room temperature and in-situ at elevated temperatures to just below the leucite crystallization temperature. Reinforcement with 25 weight percent chamotte has shown a three-fold increase in room temperature flexural strength. Flexural strength is also evaluated at room temperature after heating above the leucite crystallization temperature to determine if the glassy phase of the chamotte acts as a self-healing mechanism during the dilatational and destructive crystallization to leucite.

4:00 PM

(ICACC-FS1-015-2013) Optimized cesium substitution in potassium-based geopolymers for enhanced mechanical properties

A. J. Steveson*, W. M. Kriven, University of Illinois at Urbana-Champaign, USA

Cesium-based geopolymers have shown great promise in high strength, high temperature applications, but precursors remain prohibitively expensive for industrial use. Low levels of cesium substitution in potassium-based geopolymers have been previously shown to stabilize the cubic leucite formed upon heating to about 1100°C. In the pursuit of economical fully-stabilized cubic leucite, thermal evolution of cesium-substituted potassium-based geopolymer ((K_1-x Cs_x)_2O.Al_2O_3.4SiO_2.11H_2O, x=0.1, 0.15, 0.2, 0.25, 0.3) during heating was studied by differential thermal analysis and thermal gravimetric analysis. Further, mechanical properties have been investigated via high temperature four point bend testing from 100°C to 1500°C in order to determine the temperature range of usefulness in structural applications.

4:20 PM

(ICACC-FS1-017-2013) Static and Dynamic Properties of Potassium-Based Geopolymer as Measured by Different Techniques

S. Cho*, University of Illinois at Urbana-Champaign, USA

The processing and microstructure of potassium-based geopolymer have been studied by various techniques. However, the mechanical properties such as Young's and shear modulus lack systematic research. Split Hopkinson Bar (SHPB), impulse excitation (IE) and ultrasonic measurements were made to determine the dynamic properties. In addition, conventional static methods such as microindentation, compression and four-point bending tests were applied to compare and analyze the significantly different test results among the techniques. Since the geopolymer contained a significant amount of dispersed water, the dynamic properties varied within a wide range depending on the different drying conditions. Therefore, the appropriate drying process of the cured geopolymers was determined for the precision of each measurement.

4:40 PM

(ICACC-FS1-018-2013) Influence of the interaction between different metakaolins and reinforcements on the mechanical properties of geopolymers

A. Autef*, E. Joussein, CEC-GEMH, France; G. Gasgnier, Imerys Ceramic Center, France; S. Rossignol, CEC-GEMH, France

Geopolymers materials are currently the object of numerous studies worldwide because of their low environmental impact. Geopolymers are inorganic binders with silicon and aluminum synthesized by alkaline activation of alumino-silicate at room temperature. The aim of this work is to study the role of reinforcements (sand) on the mechanical properties of geopolymers obtained with three different metakaolins. Geopolymers were synthesized from a mixture containing alkaline silicate solution and three various metakaolins. Several compositions containing various rates of amorphous silica and sand were attacked by alkaline solution. The metakaolin was added to the alkaline mixture and the consolidation took at room temperature. Compression tests were realized to determine the mechanical properties of the strengthened materials. Moreover, the influence of the sand was performed by spectroscopy e.g. in situ FTIR. SEM observations were realized to evidence interactions between sand and geopolymer matrix. First results show that whatever is the introduced sand rate the mechanisms of formation are identical for a given metakaolin. Furthermore, the addition of sand within the geopolymer matrix allows improving the mechanical properties of final materials. Finally, the addition of crystalline species (sand) decreases dissolution and polycondensation kinetics.

5:00 PM

(ICACC-FS1-019-2013) Evaluation of Geopolymer Concretes at Elevated Temperatures

K. Kupwade-Patil*, S. Badar, E. N. Allouche, Louisiana Tech University, USA

Geopolymers is an emerging class of cementitious binders which possess a potential for high-temperature resistance that could possibly be utilized in applications such as nozzles, aspirators, and refractory linings. Geopolymer concrete (GPC) was prepared using eleven types of fly ashes obtained from four different countries. GPC was subjected to 2600°F using an oxy-acetylene torch to examine the effect of elevated temperature for rocket plume trench applications. In addition, GPC was subjected to thermal shock tests using ASTM C 1100-88. The GPC samples, prepared with Tabular alumina, were kept in at 2000°F and immediately quenched in water. GPC specimens prepared with certain fly ashes exhibited signs of expansion along with cracking and spalling, while GPC prepared with specific Class 'F' fly ash showed superior resistance to thermo shock. A microstructural analysis revealed that the resistance of GPC at elevated temperatures was dependent on the calcium oxide content, the Loss of Ignition (LOI) of the Fly Ash, the Crystalline to Amorphous ratio of the GPC, and the formation of zeolitic phases such as sodalite, analcime, and chabazite. The work indicates that the chemical composition and particle size distribution of the fly ash, the type of fly ash (Class 'C' & 'F'), and the geopolymerization process play a vital role in determining the suitability of geopolymer concrete for high temperature applications.

FS4: Advanced Ceramic Materials and Processing for Photonics and Energy

Advanced and Nanostructured Materials for Photovoltaics, including Solar Hydrogen

Room: Oceanview
Session Chairs: Gunnar Westin, Uppsala University; Alberto Gasparotto, Padova University and INSTM

1:30 PM

(ICACC-FS4-010-2013) Inorganic and organic solar cell degradation mechanisms (Invited)

G. Fanchini*, University of Western Ontario, Canada

Keeping maintenance costs low is of paramount importance for the future of solar cells. Recent improvements have given as much as 8% photoconversion efficiency in polymeric organic photovoltaics (OPV) while efficiencies ~15% were obtained several decades ago in inorganic photovoltaics prepared form hydrogenated amorphous silicon (a-Si:H). Such figures indicate that these technologies have the potential to further penetrate in the market, but limitations are posed by poor knowledge of the processes leading to the degradation of photoactive layers. Staebler-Wronski (SW) effect, leading to the formation of dangling bond defects in a-Si:H under illumination, was observed in 1977, but the mechanism that allows such material to self repair and revert defect formation has not yet been fully understood. In OPVs, while several architectures for encapsulating the active layer against the oxygen diffusion have been proposed, their development relies on a trial-and-error approach. In this presentation, we review our recent work on solar cell degradation and show how photothermal deflection spectroscopy can be used to design a-Si:H solar cells with mitigated SW degradation. In OPVs, the decrease of the efficiency in harsh environment will be linked to the incorporation of paramagnetic oxygen and the formation of paramagnetic centers. Our work aims at solar cells with mitigated degradation and improved durability.

1:50 PM

(ICACC-FS4-011-2013) Photoinduced properties of Multiferroics (Invited)

R. Nechache*, University of Rome Tor Vergata, Italy

Driven by a rapid depletion of fossil fuel resources and a rise of environmental concerns, scientists have start to investigate candidate materials for thin films photovoltaic (PV) cells as a critical step for alternative and sustainable energy production. The availability of lower band gap magnetic-ferroelectric oxides (i.e. multiferroic) Bi2FeCrO6 (BFCO) presents an alternative pathway for highly efficient separation of photoexcited carriers. As ferroelectric, multiferroic (MFs) material, which exhibit strong bulk photovoltaic effect, have advantages compared with traditional semiconductor-based solar energy conversion materials: no need to any p/n junction and no limitation of the photo-voltage. Furthermore, the electron-electron interaction governing the magnetic ordering in MFs, leads to a smaller gaps resulting in an improvement of the photocurrent generation process. MFs offer a fundamentally different route to enhance the solar energy conversion efficiency and show potential for visible-light PV devices. Here we review recent progress of our group in the exploration of novel oxide materials – both thin film and heterostructure – in pursuit of two major research thrusts: MF and solar energy conversion.. We will present, the controlled growth and characterization of MF BFCO thin films and heterostructures via pulsed laser deposition. The investigation of the optical and PV properties of this material will be discussed in details.

2:10 PM

(ICACC-FS4-013-2013) Strain Induced Solar Power Conversion Efficiency Enhancement in Periodic Stacking of Multiferroic Bilayers

J. Chakrabartty*, R. Nechache, F. Rosei, INRS, Quebec, Canada, Canada

Nanostructured multiferroic perovskite is a promising candidate for solar photovoltaic application due to its lower band gap and bulk photovoltaic effect. The co-existence of ferroelectricity and magnetism in it seems to be responsible for charge separation and lowering the band gap, respectively. Over investigated multiferroic BiFeO3 represents the higher open circuit voltage with lower short circuit current. But double perovskite multiferroic Bi2FeCrO6 can improve the short circuit current as well. The charge transfer between Cr and Fe improves the short circuit current that leads more photo current in photovoltaic (PV) efficiency. As a consequence of finding new engineering mechanism for efficiency improvement in multiferroic material, periodic stacking of multiferroic bilayer, BiFeO3/BiCrO3 bilayer in this case is the new addition in this field. Lattice mismatch between substrate and films induces strain that helps to stabilize the epitaxial single phase of each film. More interestingly, this strain plays a vital role to enhance Fe and Cr cationic ordering at the interfacial area of bilayer like similar fashion of Bi2FeCrO6 thin film. Here in this report, we will discuss in particular, the growth, optical absorption and thickness dependent photovoltaic (PV) properties of BiFeO3/BiCrO3 bilayer thin films deposited by pulse laser deposition technique.

2:30 PM

(ICACC-FS4-014-2013) Engineering Metal Oxide Structures for Efficient Photovoltaic Devices (Invited)

I. Concina*, G. S. Selopal, CNR-IDASC SENSOR Laboratory & Brescia University, Italy; N. Memarian, Semnan University, Islamic Republic of Iran; V. Galstyan, G. Sberveglieri, A. Vomiero, CNR-IDASC SENSOR Laboratory & Brescia University, Italy

Third generation solar cells promise to have several benefits as compared with their traditional counterparts, between which the possibility to access to green energy thanks to the use of non toxic materials that should guarantee for improved efficiency while maintaining acceptable long term stability. Most performant dye sensitized solar cells (DSCs) are currently exploiting a film of nanoparticulate TiO2 as photoanode, but an impressive effort is being made to seek alternative materials and structures. Herein we present the use of: i) TiO2 self-standing nanotubes grown on plastic substrate and integrated on flexible solar devices; ii) a mixed network of ZnO nanowires and TiO2 nanoparticles attempting to exploit the advantages provided by each structure, i.e. higher electron mobility in quasi 1D structures and surface area suitable for high dye loading, with reciprocal benefit; iii) hierarchically assembled ZnO structures for high efficient completely ZnO-based DSC, built up according to three main aims, namely: high optical density of the sensitized layer, high light scattering of the active layer and inhibition of the back electron transfer between anode and electrolyte. Emphasis will be given on both the advantages provided by the mentioned photoanode configurations and simple and environmental friendly preparation approaches.

3:10 PM

(ICACC-FS4-015-2013) Photoelectrochemical water splitting using an all-solid-state cell with gaseous reactants

K. O. Iwu, T. Norby*, A. Galeckas, A. Kuznetsov, University of Oslo, Norway

A solid-state proton conducting polymer-ceramic composite was used as electrolyte in a photoelectrochemical (PEC) cell. It was equipped with composite photoanode nanostructures of semiconducting oxides with suitable band gaps, carbon nanoparticles, carbon paper, and polymer electrolyte. The photoanode reactants were gaseous methanol and water vapour. Upon irradiation with UV rich light the all-solid-state and gaseous cell generated considerable photovoltages at open circuit as well as loaded or driven photocurrents. The results and functioning of the cell are interpreted in light of the syntheses, chemistry, nanostructures, and optical properties of the oxides employed, and the concept of all-solid-state PEC solar hydrogen is discussed.

3:30 PM

(ICACC-FS4-008-2013) Investigation of the Effect of Porosities on the Efficiency of DSSCS Produced by Using Nano-sized TiO2

N. Bilgin*, METU, Turkey; J. Park, Atilim University, Turkey; A. Ozturk, METU, Turkey

Titania under light gives free radicals and destroys organic contaminations. Also by applying on mirrors, house walls and textile products, one can benefit its self-cleaner property. The main reason of using titania in the dye-sensitized solar cells (DSSC) is that, it is easy to product porous TiO2. Using porous materials in DSSCs is important because it forms a transmission way for free electrons. Also porous structure lets more dye absorption from the surface. The reasons lead to choose titania are that, it is chemically stable, non-toxic and cheap. In this study, pastes which include sizes of 20 nm and 200 nm TiO2 nano-particles were mixed in different amounts. XRD and SEM analysis has been done to investigate the microstructure of TiO2,. Also to determine the efficiency of the cells I-V curves have been drawn. It's observed that using 40%(wt.) 20 nm and 60%(wt.) 200 nm shows best efficiency while keeping all the other parameters fixed.

3:50 PM

(ICACC-FS4-012-2013) One dimensional multiferroic materials for solar energy conversion

S. Li*, R. Nechache, F. Rosei, EMT-INRS, Canada

One-dimensional (1D) inorganic semiconductor nanostructures are among some of the most attractive nanomaterials for photovoltaic devices owing to their extraordinary performance and processing benefits, such as a direct path for charge transport resulting from the lateral confinement of electrons in the axial direction, and large surface areas for light harvest due to the unique geometry of such nanostructures. Ferroelectric materials have drawn significant attention for photovoltaic applications owing to their efficient ferroelectric polarization-driven carrier separation, as compared with traditional silicon based bipolar junctions solar cell. Among all the ferroelectric materials, multiferroic BiFeO3 (BFO), with a desirable narrow band gap energy of 2.2 ~ 2.8 eV, has been identified as an excellent candidate for photovoltaic devices in the visible light region recently. In this study, we report on the photovoltaic performance of mixed P3HT/BFO nanostructure bulk heterojunction devices consisting of randomly oriented single crystalline BFO nanowires. We demonstrate a significant photocurrent enhancement and power conversion efficiency improvement with up to 60% under the AM 1.5 solar illumination after introducing BFO nanowires.

Advanced and Nanostructured Materials for Sensing and Electronics

Room: Oceanview

Session Chair: Mauro Epifani, CNR-IMM

4:30 PM

(ICACC-FS4-018-2013) Tailoring nanoscale sensing devices through chemical functionalization of graphene and ZnO nanowires (Invited)

K. Balasubramanian*, T. Kurkina, V. Pachauri, S. Sundaram, R. S. Sundaram, Max Planck Institute for Solid State Research, Germany; F. Re, M. Masserini, Universita degli Studi di Milano Bicocca, Italy; K. Kern, Max Planck Institute for Solid State Research, Germany; K. Kern, Ecole Polytechnique Federale de Lausanne, Switzerland

On-chip devices based on nanostructures show promise for many applications. For example, biosensors based on few carbon nanotubes can detect DNA down to attomolar concentrations. In order to achieve such a high performance, chemical functionalization of nanostructures plays a key role. Here we demonstrate how chemical functionalization can be judiciously utilized to tailor nanosensors. First, the talk focusses on the fabrication of site-specific sensing devices based on ZnO nanowires (ZnONWs) or graphene. ZnONW devices are obtained using a direct hydrothermal growth method, while graphene devices are prepared by chemical anchoring of reduced graphene oxide. Both ZnONW and graphene devices can be operated efficiently as liquid-gated field-effect transistors. Utilizing electrochemical functionalization ZnONWs are decorated with metal nanoparticles. These nanowire-nanoparticle hybrids pave way for a new class of sensing devices, where the active element comprises of the metal-semiconductor junction. Finally we show the use of graphene devices for the immunodetection of amyloid beta peptide that is implicated in Alzheimer's diseases. By tailoring the graphene surface with antibodies we attain sensitivity to the peptide in the low femtomolar range. The talk concludes with future prospects for the use of chemical functionalization in realizing nanosensors.

4:50 PM

(ICACC-FS4-019-2013) Advanced polymer-ceramic nanocomposites for tunable RF and microwave device applications (Invited)

H. Srikanth*, University of South Florida, USA

Polymer composites loaded with soft ferrite particles are viable materials for tunable RF and microwave applications such as microwave absorbers, inductors, phase shifters and circulators. Polymers offer a number of advantages as host materials due to their ease of processing, flexibility and piezoelectric properties, in some cases. A well known problem in polymer nanocomposites is particle agglomeration into non-uniform clusters during the processing stages of thick films. We demonstrate how this challenge can be overcome by using different surfactants on the nanoparticle surfaces that prevent particle diffusion and clustering. Our experiments in recent years have led to the demonstration of superparamagnetic response in large-area spin coated films up to 20 microns thick for cutting down hysteretic and eddy current losses for soft RF and micrwave device applications. Microwave and RF measurements were conducted on polymer nanocomposites of various loadings using a cavity resonator. We have also extended this approach to novel high-aspect ratio nanostructures –such as uniformly dispersed spinel ferrite nanoparticles inside carbon nanotube templates, which in turn are embedded into polymers. In all of these materials, we have shown magnetic field dependent tunable microwave absorption using a resonant microstrip transmission line.

5:10 PM

(ICACC-FS4-020-2013) All-alkoxide based solution deposition and properties of spinel and perovskite films, and multi-layer structures (Invited)

G. Westin*, A. Kumar, K. Lashagari, A. Pohl, K. Olof, Uppsala University, Sweden; K. Jansson, Stockholm University, Sweden

Thin films of complex composition oxides such as perovskites and spinels containing Mn, Fe, Co and Ni are of high importance for many technological applications including fuel-cells, electrodes, IR sensors and electro-magnetic response materials including multi-ferroics. Solution based processes offer cost efficient alternatives to CVD and PVD, and can be used to coat very large and complex shape substrates required for some applications. Here all-alkoxide based routes to spinels and perovskite films and coatings are described. Reactive mixed or heterometallic single source alkoxide precursors may offer very low preparation temperatures and highly epitaxial films. The conversion of the gel to oxide by heat-treatment is described in detail based combined data from a wide range of techniques including; TGA, DSC, TEM-EDS, SEM, XRD and IR spectroscopy. The effect of the precursors and heat-treatment parameters on the final spinel or perovskite film will be discussed. For example the single source precursor, CoFe2(OtOBu)8 allowed for formation of phase pure nano-crystalline CoFe2O4 at temperatures below 300oC and crystallites grow to ca 100 nm at 1000oC. The electric and magnetic properties of the spinel and perovskite films, as well as multi-layer perovskite-spinel-perovskite films will be descried and related to the film microstructures.

Engineering Ceramics Summit of the Americas

Ceramics for Energy and Environmental Systems

Room: Coquina Salon G

Session Chairs: Kevin Plucknett, Dalhousie University; R. Muccillo, IPEN

1:30 PM

(ICACC-ECSA-015-2013) Reflections on the present and future of the ceramic refractory area (Invited)

V. C. Pandolfelli*, UFSCar, Brazil

Refractory is a mature field regarding importance but also in terms of the average age of professionals working in the area. Perhaps the most difficult aspect is not for the young generation to see the refractory area with our eyes, but the opposite. As mature people we are more reluctant to changes, whereas the present generation with their energy and dreams want to be convinced. Were we any different? The problem is not trying to understand young people, because it is clear what they want! The battle is for us to present them with the refractory area in a way that they can be attracted! For example, why not thinking and showing the challenges of refractory energy saving issues from an integrated point of view? High emissivity paints, slag foaming, advanced foaming spray insulating, novel ceramic burner designs made by 3D printing, etc, can be part of a holistic view of refractory subjects that will help the environment, the society and make us feel useful! How about the courses that are taught? Are we concerned with the importance of the transversality of the knowledge? We have arguments and history to change the old and current "Dirty-Messy-Polluting" image of the refractory area for a "Clean-Green-Challenging" one. The problem is that we are expecting the young generation to see the importance of refractory on their own, whereas the other professionals are marketing their area better.

2:00 PM

(ICACC-ECSA-016-2013) Ceramic Hot-Surface Ignition Systems for Natural Gas Clean Engines: A Case Study of Successful Industry-University R&D in Canada (Invited)

T. Troczynski*, UBC, Canada

Westport Innovations of Vancouver, BC, Canada is a world leader in development of High-Pressure Direct-Injection (HPDI) clean-combustion natural gas engine technology. The engines currently use natural gas as the primary fuel along with a small amount of diesel (~ 3%) as an ignition source. Second-Generation injection and combustion technology uses instead ceramic hot-surface ignition (in the form of "Glow Plug" GP), in order to simplify overall system design and lower its costs. A silicon nitride GP is one candidate, but they fail prematurely due to redistribution of sintering additives in Si3N4/Yb2O3 under the influence of electric field. In this work we will overview the collaborative R&D between Westport and Ceramics Group at UBC. The results of modeling of ceramic GP in direct and alternate electric fields and model verification against experimental results of GP evaluations in-lab and in-engine will be presented

2:30 PM

(ICACC-ECSA-017-2013) Advanced Ceramics for Mineral Processing and Energy Generation and the Technology Importance for Ceramic Manufacturing (Invited)

E. Medvedovski*, Consultant, Canada

The use of advanced ceramics, composites and coatings in the mineral, metallurgical, chemical processing and alternative energy generation continually grows owing to the development of materials with improved properties and their technologies in accordance with particular application requirements. The examples of the successful development and processing of wear, corrosion and thermal shock resistant ceramics, composites and coatings (e.g. fine grained materials and materials with specially designed grain size and phase distribution), as well as the materials, which can be used for alternative energy generation (e.g. for thin film photovoltaics, thermoelectrics and some others), will be discussed. The demands for products with high reliability and complex shapes for a variety of applications require novel and optimized processing. The starting materials selection (from nano- to even hundreds micron particles with special particle size distributions), colloidal processing and forming method development allow managing the required shapes, densification at the thermal treatment and, finally, ceramic structure, properties and reliability of products. Some examples of the technology importance on the components for mineral processing and energy generation will be discussed.

3:20 PM

(ICACC-ECSA-018-2013) Recent developments on electric-field assisted sintering ceramic materials (Invited)

R. Muccillo*, E. N. Muccillo, IPEN, Brazil

In the last few years many experiments have been reported on coupling the effects of heat and of applying an electric field with or without pressure. Considerable shrinkage has been obtained by simply heating a ceramic green pellet under an external electric field or applying an electric field at temperatures well below the temperature required for attaining full density. Mass transport as well as charge transport might be considered. The electrical behavior of the ceramic material as well as its geometrical dimensions and shape have to be taken into account for the suitable choice of the electrical parameters. The impedance spectroscopy technique is of utmost importance for the evaluation of the bulk and interfaces (mainly grain boundaries) resistivities before, during and after sintering. The experimental setup for flash sintering ceramic materials to chosen shrinkage values, consisting of a dilatometer connected either to a power supply or to an impedance analyzer, will be described in detail along with scanning electron microscopy and scanning probe microscopy images of zirconia-based solid electrolytes after conventional and electric-field-assisted sintering. Even though most of the published results are in electroceramics, mainly solid electrolytes, the technique does not preclude its application to any ceramic material, provided proper experimental arrangements are available.

3:50 PM

(ICACC-ECSA-019-2013) Recent Developments in Cermets and Hard Boride Coatings (Invited)

K. P. Plucknett*, Dalhousie University, Canada

Current research in the areas of ceramic-metal composites (or cermets) and boride coating development at Dalhousie University are reviewed. Two families of cermets are described, the first based on titanium carbonitride with a ductile nickel aluminide binder, and the second utilising titanium carbide with a variety of stainless steel binders. The sliding wear and aqueous corrosion behaviour of these materials will be outlined. In addition, recent work on the development of boride coatings on titanium alloys will be discussed, including the effects of the coatings on tensile behaviour.

4:20 PM

(ICACC-ECSA-020-2013) Using material science to prepare novel tailored ceramic materials to improve the performance of hydrocarbon processing units (Invited)

T. Szymanski*, Saint-Gobain NorPro, USA

The continuing mandate that oil refiners simultaneously increase production using heavier and "dirtier" oil feedstocks and produce cleaner and cleaner fuels yields more difficult conditions for all refinery operations. This is especially true for hydrotreating processes. These increasingly demanding conditions often cause increases in pressure drop over the catalytic or absorbent reactor during its operating lifetime. These pressure drop increases can result in higher operating costs and decreased product quality. Engineering these fixed bed hydrocarbon conversion reactors with novel tailored ceramic materials can minimize or prevent this pressure drop increase and also insure lower overall system pressure drops and longer service life.

4:50 PM

(ICACC-ECSA-021-2013) Properties and Growth Mechanism of Transparent and Conductive Indium Tin Oxide Nanowires (Invited)

E. P. Arlindo, J. A. Lucindo, M. O. Orlandi*, UNESP- Araraquara, Brazil

1D materials has been the main focus of many studies due to the possibility to produce high performance devices. Between them pure inorganic materials, such as In2O3 and SnO2, have attracted special attention due to their interesting properties. However, doping can modify the intrinsic properties of materials, which is interesting for many applications. As an example, the system Indium Tin Oxide (ITO) has a metallic behavior depending on the In/Sn ratio, and it contrasts with the semiconductor behavior of pure oxides. Besides, as ITO system has high transparence in the visible range, that can be used to produce optoelectronic devices. In this work we synthesized ITO nanostructures from vapor phase using the carbothermal reduction process with co-evaporation of oxides. Using this method we found that it is possible to control the In/Sn ratio in the nanostructures, so controlling its properties. After the synthesis a wool-like material was collected inside the tube, and the collected materials were fully characterized. The XRD data showed that is possible to grow structures in the SnO or In2O3 phases, and the structures are one-dimensional with square cross-section; i.e. nanowires. The XRD and TEM data showed that the nanowires in the In2O3 phase grow in the [100] direction and are single crystalline. A model based on vapor-liquid-solid (VLS) process was used to explain ITO nanowires growth.

5:20 PM

(ICACC-ECSA-022-2013) Magnetoelectric coefficient in oxide electrodes buffered lanthanum modified bismuth ferrite thin films grown by chemical method (Invited)

A. Z. Simões*, J. A. Varela, E. Longo, UNESP, Brazil

This paper focus on the magnetoelectric coupling (ME) at room temperature in lanthanum modified bismuth ferrite thin film (BLFO) deposited on SrRuO3-LaNiO3 and LaSrCoO3 buffered Pt/TiO2/SiO2/Si (100) substrates by the soft chemical method. BLFO film was coherently grown at a temperature of 500°C. The magnetoelectric coefficient measurement was performed to evidence magnetoelectric coupling behavior. Room temperature magnetic coercive field indicates that the film is magnetically soft. The maximum magnetoelectric coefficient in the longitudinal direction was close to 12 V/cmOe for the SrRuO3-buffered Pt/TiO2/SiO2/Si (100) substrates . Dielectric permittivity and dielectric loss demonstrated only slight dispersion with frequency due the less two-dimensional stress in the plane of the film. Polarization reversal was investigated by applying dc voltage through a conductive tip during the area scanning. We observed that various types of domain behavior such as 71° and 180° domain switchings, and pinned domain formation occurred.

Friday, February 1, 2013

S3: 10th International Symposium on Solid Oxide Fuel Cells (SOFC): Materials, Science and Technology

Mechanical/Thermal Properties

Room: Coquina Salon H
Session Chairs: Teruhisa Horita, AIST; S. Elangovan, Ceramatec, Inc.

8:00 AM

(ICACC-S3-056-2013) The mechanical behavior of solid oxide fuel cell substrates in relevant environments

A. Shyam*, D. McClurg, A. Pandey, T. Rosa, E. Lara-Curzio, Oak Ridge National Laboratory, USA; R. Goettler, LG Fuel Cell Systems Inc., USA

Techniques for the measuring the mechanical properties such as Young's modulus, strength, fracture toughness and slow crack growth resistance of porous substrates for solid oxide fuel cells (SOFCs) were developed and will be discussed. The microstructure of the substrate consists of a porous composite of cubic magnesium oxide (MgO) and spinel (MgAl2O4) phases. The slow crack growth behavior of the porous magnesia magnesium aluminate (MMA) material was determined by slow crack growth testing. The slow crack growth resistance of MMA is much improved compared to conventional Ni-YSZ substrates under SOFC operating conditions. Implications of improved slow crack growth behavior on the long term reliability of SOFC stacks will be discussed.

8:20 AM

(ICACC-S3-057-2013) Thermal Residual Stress and Biaxial Strength of (Y2O3)0.08(ZrO2)0.92 / (Sc2O3)0.1(CeO2)0.01(ZrO2)0.89 Multi-layered Electrolytes for Intermediate Temperature Solid Oxide Fuel Cells

Y. Chen*, N. Orlovskaya, University of Central Florida, USA; T. Graule, J. Kuebler, Empa, Swiss Federal Laboratories for Materials Science and Technology, Laboratory for High Performance Ceramics, Switzerland

Multi-layered (Y2O3)0.08(ZrO2)0.92 / (Sc2O3)0.1(CeO2)0.01(ZrO2)0.89 (YSZ/SCSZ) electrolytes have been designed and manufactured via tape-casting, laminating and sintering, so that the inner SCSZ layers provided superior ionic conductivity and the outer YSZ skin layers maintained good chemical and phase stability. After sintering, the thickness of YSZ outer layers were ~30 μm, the thickness of SCSZ inner layer varies from about 30 μm, 60 μm and 120 μm for Y-SC-Y, Y-2SC-Y and Y-4SC-Y designs, respectively. The thermal residual stresses were calculated by the mismatch of coefficients of thermal expansion of each layer. It was found the compressive stress in outer layers and tensile stress in inner layers at 800 °C. The residual stresses can be controlled by adjusting thickness ratio of the layers. The biaxial flexure strength of layered electrolytes was tested via a ring-on-ring method at RT and 800 °C. The applied load and the normalized applied load at the fracture showed an improved strength in Y-xSC-Y type electrolytes at 800 °C in comparison to electrolytes with single YSZ or SCSZ composition; whereas at RT, the Y-xSC-Y type electrolytes showed lower strength. The residual stresses due to the thermal expansion might play an important role in the flexure strength of layered electrolytes.

8:40 AM

(ICACC-S3-058-2013) Evaluation of crack mechanism of SOFCs in redox cycle at high temperatures using X-CT method

T. Kushi*, K. Fujita, Tokyo Gas Co., Ltd., Japan

Solid Oxide Fuel Cells (SOFCs) are attracting considerable attentions such as energy conversion devices. It is claimed that improving the durability of SOFCs is particularly important for its commercialization. Mechanical damage is one of the most serious problems that may cause degradation or even destruction of the cell. One of the typical reasons for the mechanical damage is redox cycle. The mechanical damage mechanism in redox cycle on the practical SOFCs is often complicated because of the delicate balance of the cell designs, the seal technique and the material composition. Thus, it is important to evaluate the mechanical damage mechanism of the SOFCs at the operating conditions. Currently, there are a lot of reports on the relationship between redox cycle and mechanical crack. However, there are few reports that observed the in situ mechanical damage in redox cycle. In this report, we evaluated the crack and deformation induced by stress and strain of the anode supported cells in redox cycle using X-CT method. The crack and deformation was investigated by the visual images of the cell at high temperatures and reduction/oxidation atmospheres. It was found that cracks occur at re-oxidation stage after exceeding the certain deformation value. This paper discusses further mechanical damage mechanisms observing relationship among crack, stress and strain.

9:00 AM

(ICACC-S3-059-2013) Thermal diffusivity/conductivity of Zirconia before, during and after Sintering

E. Post*, NETZSCH Geraetebau GmbH, Germany

A zirconia green body was investigated by means of the Laser Flash technique (LFA) regarding the thermal diffusivity (TD)/ thermal conductivity (TC) before, during and after sintering. The TD/TC values were corrected for temperature-dependent length changes measured by dilatometry. Usually, the dilatometer measurements are performed at a dynamic heating rate. The temperature profile of LFA measurements is different since isothermal temperature steps are required where the shots were taken. This means temperature treatment of the LFA and dilatometer sample varies and shrinkage during the isothermal steps is usually not taken into account for the length correction. In this paper, the influence on the TD/TC results are discussed using the length change data from dynamic dilatometer measurements and dilatometer measurements with an identical temperature profile like that for LFA measurements.

Electrolysis etc

Room: Coquina Salon H
Session Chairs: S. Elangovan, Ceramatec, Inc.; Teruhisa Horita, AIST

9:20 AM

(ICACC-S3-060-2013) Operating strategies to counteract degradation in SOEC systems

J. B. Hansen*, Haldor Topsøe A/S, Denmark; J. U. Nielsen, M. F. Madsen, Topsoe Fuel Cell A/S, Denmark

SOEC technology offers a highly efficient option for converting renewable electricity into a variety of products such as hydrogen or carbon based synthetic fuels. State of the art SOEC cells and stacks do, however, still suffer from higher degradation rates than SOFC systems. This paper will discuss various strategies for counteracting the performance degradation on a system level. In principle four strategies can be employed: Increase cell voltages, decrease current density, lower steam and carbon dioxide conversion per pass or increase operating temperatures. The consequences on a sytem level will be examined by means of modelling. Examples from hydrogen and methanol production as well as biogas upgrading will be given.

10:00 AM

(ICACC-S3-061-2013) Testing and Analysis of Solid Oxide Electrolysis Stacks

S. Elangovan*, J. Hartvigsen, Ceramatec, Inc., USA; P. Singh, University of Connecticut, USA

The potential for producing high purity hydrogen at high electrical efficiency and recent progress in solid oxide fuel cell performance have been the motivation for increased research activities in solid oxide electrolysis cells (SOEC). Performance degradation of SOEC is a major technical challenge that needs to overcome for practical implementation of SOEC devices. Research activities at Ceramatec over the last three years have resulted in identifying many of the chief sources of degradation. Many of the changes relating to air electrode composition, current collection materials, and seals have resulted in significant improvement to stack performance stability as borne out by tests both at Ceramatec and at independent sites. Tested stacks have been analyzed at the University of Connecticut's Center for Clean Energy Engineering to identify changes to the morphology and chemistry of various stack components to provide additional insight that can be used for further improvements to stack performance and stability. Stack test and analysis results will be presented.

10:20 AM

(ICACC-S3-062-2013) Thermal imaging of Solid Oxide Cells during co-electrolysis of carbon dioxide and steam

D. J. Cumming*, R. H. Elder, D. C. Sinclair, University of Sheffield, United Kingdom

Carbon dioxide recycling to form synthetic fuel has the potential to address two of the problems facing global energy supply: the depletion of fossil fuels resources and the issue of climate change caused by carbon dioxide emission. If the energy source for a carbon dioxide recycling process is renewable then a carbon neutral fuel cycle is created. Activation and reduction carbon dioxide is not a simple process. However, high temperature co-electrolysis using a solid oxide cell (SOC) offers several advantages and has shown promise for large scale CO_2 recycling. There has been a large scale research effort in recent years on SOCs under fuel cell operation but co-electrolysis is poorly understood and far from optimised. Materials and system improvements are critical for the efficient production of clean fuel. Thermal imaging has been shown to be a useful tool for the in situ characterisation of SOCs. In this work we report the in-situ thermal observation and comparison of a solid oxide cell operating in steam electrolysis and co-electrolysis modes. State of the art electrolyte supported and electrode supported cell are characterised and compared. With this approach we hope to gain a better understanding of electrode processes occurring in the SOC during co-electrolysis.

10:40 AM

(ICACC-S3-063-2013) Propane driven hot gas ejector for anode off gas recycling in an SOFC-system

C. Immisch*, A. Lindermeir, R. Dietrich, CUTEC Institut, Germany

External reforming allows the use of hydrocarbon fuels like propane for power generation with SOFC. Especially reforming via anode off gas recycling (AOGR) enables electrical system efficiencies > 60 %. A hot gas ejector using propane bottle pressure as motive power is developed for hot AOGR and deployed in a 1 kW SOFC-system with minimized heat and pressure losses. To achieve high impulse energy of the propellant gas a Laval nozzle was chosen as ejector primary nozzle. This enables acceleration of the motive gas stream to supersonic speed for sufficient recycle ratios. An ejector prototype with adjustable nozzle position, mixing channel diameter and -length was experimentally characterized and the optimal design parameters were determined. In addition, ejector behavior at elevated temperatures was tested. The tests show that the ejector performance is highly sensitive to the backpressure caused by the anode and the reformer. A mixing channel diameter of 2 mm was found as optimum; the favorable distance between nozzle and mixing channel was independent of the backpressure. Influence of temperature on the ejector performance is rather small. Propane stability tests proof a viable nozzle inlet temperature for the propane feed of 600 °C. The presentation will figure out, that a supersonic ejector is a feasible solution for hot AOGR in small SOFC-systems, promising electrical system efficiency over 60 %.

11:00 AM

(ICACC-S3-064-2013) Progress in Development of Solid Oxide Fuel Cells with Silver Based Composites

A. Sarikaya*, V. Petrovsky, F. Dogan, Missouri University of Science and Technology, USA

Performance and stability are critical issues affecting the realization of the solid oxide fuel cell (SOFC) technology. Microstructures of the conventional Ni-yttria stabilized zirconia (YSZ) anode, YSZ electrolyte and YSZ-lanthanum-strontium manganite (LSM) cathodes play a significant role satisfying the requirements of stable SOFCs with high performance. Microstructural development of each component was investigated in detail and their relationships with the polarization mechanisms were identified. Utilization of the obtained understanding allowed achieving relatively high power densities ($>1.7W/cm^2$) at 800^oC using a diluted fuel (10% H_2 in Ar). Implementation of the developed, stable Ag based composites to the cathode side of the SOFCs led to further reduction of the cathode polarizations as well as the current collection resistances. The relationships between processing, microstructural development, electrochemical performance and stability of the SOFCs will be presented. Obtained novel results will help achieving a better understanding of the impact of microstructural engineering on the development of high performance SOFCs.

11:20 AM

(ICACC-S3-065-2013) Aqueous processing routes for new SOFC materials

M. C. Verbraeken*, M. Cassidy, J. T. Irvine, University of St Andrews, United Kingdom

Doped strontium titanates are of interest as conductive ceramic backbone material in SOFC anodes. Porous scaffolds of these materials can then be impregnated with electrocatalysts to obtain good anode performance. In this work we are producing anode supports using A-site deficient $a_{0.20}Sr_{0.25}Ca_{0.45}TiO_3$ ($LSCT_{A-}$) through an aqueous tape casting process. Apart from being environmentally friendly, aqueous processing also allows a wider range of polymeric pore formers, which in turn allows for a more precise control of the porous scaffold's microstructure and hence performance. Both dense and porous ceramics have thus been produced, with good flatness. The next stage of this work is to screen print electrolyte layers onto green aqueous tapes and subsequently co-sinter. Conventional organics based inks have proven to be incompatible leading to de-wetting problems. We are therefore developing new inks based on more polar solvent systems. A submicron 8-YSZ powder is used as the electrolyte material. Dispersions in both isopropanol as well as glycerol-propylene glycol (PG)-water mixtures will be discussed, as well as the effect of binder (PVP) concentration on the rheological behaviour of vehicles and inks. SEM analysis of the ceramics after co-firing has shown reasonably good adherence between anode support and electrolyte. Matching of the shrinkage rates of both materials (LSCTA- and 8-YSZ) means minimal warping occurred.

11:40 AM

(ICACC-S3-066-2013) Proton conducting lanthanum tungstates for ceramic fuel cells and gas separation membranes

T. Norby*, University of Oslo, Norway

In a quest for Ba-free proton conducting ceramics, lanthanum –rich lanthanum tungstates (La/W = 5.3-5.7) have been investigated in several European projects, both as fuel cell electrolytes and mixed conducting gas separation membranes. The work has led to a new understanding of the materials' unique crystal structure, defect structure, and actual stability ranges. For proton ceramic fuel cells (PCFCs) the material has been applied as micron-thin dense membrane with functional anode on a 3rd generation alloy substrate, and cathodes with promising performance have been demonstrated. Operation under very reducing conditions and proper doping yields mixed proton-electron conduction and potential use in hydrogen permeable membranes. The presentation provides a review of recent progress on the fundamentals and applications of proton conducting lanthanum tungstates for fuel cells and membranes.

S5: Next Generation Bioceramics and Biocomposites

Ceramics for Medical and Dental Applications

Room: Coquina Salon C
Session Chair: A. Cuneyt Tas, University of Illinois at Urbana-Champaign

8:00 AM

(ICACC-S5-022-2013) Processing and Microstructure-Property of Multi Stage Spark Plasma Sintered Hydroxyapatite- Calcium Titanate Biocomposite

P. K. Mallik*, K. Balani, B. Basu, Indian Institute of Technology, India

In view of the limited fracture toughness of hydroxyapatite (HA), significant efforts in the research of biomaterials have invested to develop tough HA-based composites. One of the strategies in the current research is to develop a HA-calcium titanate (CT) biocomposites using innovative multi-stage spark plasma sintering (MSSPS) technique that can mimic the function and properties close to that of natural bone. The experimental results revealed that 99% theoretical density and equiaxed grains of 1-2 μm could be achieved for HA-CT composite using MSSPS. Phase analysis using x-ray diffraction revealed an absence of α and β-tricalcium phosphate (Ca3(PO4)2) or CaO phase which is also supported by Fourier transformed infra-red spectroscopy. Elastic modulus of 46-135 GPa is observed using nanoindentation, and fracture toughness 0.6-1.5 MPam1/2 is obtained using single-edge-V-notched beam (SEVNB) in the HA-CT biocomposites. In addition, flexural strength of 99-250 MPa and diametrical tensile strength 17-36 MPa insinuate that HA-CT composites can serve as potential functional and biological material for bone implants.

8:20 AM

(ICACC-S5-024-2013) Calcium metal to synthesize amorphous or cryptocrystalline calcium phosphates

A. Tas*, Yeditepe University, Turkey

Metallic calcium was never used before as the calcium source in synthesizing biomaterials. Amorphous calcium phosphate (ACP) was synthesized at room temperature, in synthetic mineralization solutions which contained Na+, K+, Mg2+, Cl-, HCO3- and HPO42- ions at concentrations similar to those found in human blood plasma, by using calcium (Ca) metal as the only calcium source. The experimental conditions leading to the formation of PCA (cryptocrystalline or poorly crystallized apatite) or CaCO3 were also determined when using metallic Ca in aqueous synthesis in the mineralization solutions. The formation of calcium phosphate (CaP) in synthesis solutions was immediately initiated by the addition of calcium metal granules (or shots), at appropriate amounts, into the solutions while the solutions were being continuously stirred in glass bottles at room temperature (22 C). The synthesis reactions were reaching completion in less than 30 minutes with the final solution pH values ranging from 9 to 12, without a necessity for any external pH adjustment in the form of any strong base (such as NH4OH, LiOH, NaOH or KOH) additions. ACP or PCA powders are useful for dentin and enamel remineralization applications or orthopedic (bone) defect-filling applications.

8:40 AM

(ICACC-S5-025-2013) Energetics of Rare Earth Doped Apatite-Based Materials

S. Hosseini*, A. Navrotsky, UC Davis, USA; C. Drouet, Institut Carnot CIRIMAT, France

Calcium phosphate apatites analogous to bone minerals, $Ca_{10-x}(PO_4)_{6-x}(HPO_4)_x(OH)_{2-x}$ are attracting interest for medical applications such as bone and teeth replacement. The apatite structure has the ability to accommodate many types of mineral ions or small organics. In this regard, calcium phosphates doped by lanthanide ions, with luminescent properties, are of interest for medical imaging applications. In this study, calcium phosphate materials, non-doped and doped with lanthanide ions (Eu^{3+}, Er^{3+}, Nd^{3+}, and Tb^{3+}), have been synthesized by coprecipitation at 80 - 100 ^oC under controlled pH and time. To study the thermodynamic stability of these materials, enthalpies of formation have been measured by high temperature oxide melt solution calorimetry using molten $3Na_2O.4MoO_3$ solvent at 973 K. The enthalpies of formation from oxides, $\Delta H^o_{f\text{-}oxides}$, for hydroxyapatite, $Ca_{10-x-y}Eu_y(PO_4)_{6-x}(HPO_4)_x(OH)_{2-x}$ are: -2283.2±13.0, -2247.8±11.4, -2256.4±14.6, -2119.3±13.0, -2110.1±10.6, and -2042.6±5.4 kJ/mol for y=0, y=0.01, 0.02, 0.04, 0.07, and 0.1, respectively. Characterization shows the existence of a second phase, lanthanide hydroxide, for all samples containing more than 2% dopant. The general trend in formation enthalpies as a function of Eu/(Eu+Ca) indicates that the apatite phase becomes less stable as the dopant content increases.

9:00 AM

(ICACC-S5-026-2013) Investigation of Effect of Polymers on Calcium Oxalate Crystallization

M. Oner*, B. Akin, Yildiz Technical University, Turkey

Crystallization studies of calcium oxalate (CaC2O4, CaOx) have been of interest to engineers and urologists for many years. Hence its precipitation is of particular interest not only for fundamental research concerning for biomineralization but also their importance in industrial applications. Much of our knowledge of molecular influences on oriented crystallization has come from the study of biomineralization. Biological mineralization leads to formation of hard tissues in many species by precipitation of minerals within polymeric tissue matrices and calcium containing salts are major mineral components. In this study, the effects of polymeric additives on the crystallization of calcium oxalate have been investigated in aqueous solutions. Poly(Vinylphosphonic acid-co-4-Vinylimidazole), (Poly(VPA-co-4-VIm)), with different acid contents, Vinylphosphonic acid (VPA) and Ethylene glicol methacrylate phosphate (EGMP) with different N,N-Methylene bis acrylamide (MBA) contents have been synthesized for using as additives. The effect of polymers on the rate of crystallization of calcium oxalate has been determined by recording the change of solution conductivity versus time. The polymer architecture and acid contents of the polymers were found to be important parameters in controlling of calcium oxalate crystallization.

9:20 AM

(ICACC-S5-028-2013) Production of Potassium Titanate Whisker Reinforced Dental Composites

D. Kapusuz*, Middle East Technical University, Turkey; J. Park, Atilim University, Turkey; A. Ozturk, Middle East Technical University, Turkey

One of the novel methods for exceeding the mechanical strength of amalgam without losing aesthetics is the loading of ceramic reinforcers into dental resins. Potassium titanate (K2O.nTiO2) whiskers (KTW), have high potential to be used as alternatives to current fillers in commercial dental polymers. This study includes the synthesis of KTW and introducing them to UDMA-TEGDMA resins by light curing. The aim is to produce self-cleaning, mechanically strong restoratives that can replace amalgam. Solvothermal methods were used to synthesize KTW in different morphology. Phase and morphological analyses were done by using XRD, FE-SEM and TEM. Compositions of 30-70, 50-50, and 70-30 mole % of UDMA-TEGDMA matrices were reinforced by 5-50 wt % of KTW with and without silanization of KTW. Compression, hardness and wear tests were performed on the composites. Results showed that only 5 wt% of KTW loading increased the hardness of 50-50% UDMA-TEGDMA composites from 600 to 1000 HV without silanization. In addition, the wear rate of the polymers decreased significantly by reinforcement. Methylene Blue (MB) degradation tests were applied both on the whiskers and the composites to state and compare their photo-activity. The whiskers degraded MB totally in 90 min. Their addition into bulk composites decreased the rate of degradation; however, the total degradation was still much higher than the unreinforced composites.

10:00 AM

(ICACC-S5-030-2013) Perfluorodecalin containing bioceramics and bone regeneration (Invited)

F. Tamimi*, P. Comeau, McGill University, Canada; D. Le Nihouannen, University of Bordeaux, France; Y. Zhang, D. Bassett, S. Khalili, McGill University, Canada; U. Gbureck, University of Wuzburg, Germany; S. D. Tran, K. Svetlana, J. E. Barralet, McGill University, Canada

Perfluorodecalin (PFD) is a chemically and biologically inert biomaterial and as many perfluorocarbons, is also hydrophobic, radiopaque and can dissolve high concentrations of gasses such as oxygen. In this article we have demonstrated, both in vitro and in vivo, that PFD may significantly enhance bone regeneration. Firstly, the potential benefit of PFD was demonstrated by prolonging the survival of bone marrow cells cultured in anaerobic conditions. These findings translated in vivo, where PFD incorporated into bone-marrow-loaded 3D-printed scaffolds substantially improved their capacity to regenerate bone. Secondly, in addition to biological applications, we have also shown that PFD improves the radiopacity of bone regeneration biomaterials, a key feature required for the visualization of biomaterials during and after surgical implantation. And finally we have shown how the extreme hydrophobicity of PFD enables the fabrication of highly cohesive self-setting injectable biomaterials for bone regeneration. In conclusion perfluorocarbons would appear to be highly beneficial additives to a number of regenerative biomaterials, especially those for bone regeneration.

10:20 AM

(ICACC-S5-023-2013) Enhancement of hydroxiapatite precipitation on PDLLA scaffolds functionalized with diazonium chemistry

H. Mahjoubi*, M. Cerruti, McGill University, Canada

Scaffolds made with synthetic polymers such as polyesters are commonly used in bone tissue engineering but due to their hydrophobic properties their surface is not ideal for cell adhesion and growth. Surface modification of these materials is thus crucial for enhancing the scaffold integration in the body. Different wet chemistry surface modification techniques have been developed to improve scaffold biocompatibility, such as hydrolysis that can be used to bind several functional groups, but they often change the scaffold properties because they degrade the polymer. Here we show that diazonium chemistry can be used to modify the surfaces of Poly(D,L-lactic acid) scaffolds with phosphonate groups, using a simple 2-step method. By changing reaction time and impregnation procedure we were able to tune the concentration of phosphonate groups present on the surfaces of the scaffolds. Phosphonate groups should be able to enhance nucleation and growth of hydroxiapatite (HA) by attracting calcium cations. To test this, we immersed the scaffolds in simulated body fluid, and characterized them with SEM, XPS, XRD, Raman, and FT-IR spectroscopy. Our results showed that HA precipitates faster and in larger amounts on phosphonate-modified PDLLA scaffolds than on bare PDLLA. This work shows that diazonium chemistry can be used as a tunable scaffold surface modification technique.

10:40 AM

(ICACC-S5-027-2013) Surface modification of sol-gel-derived 45S5 Bioglass® for incorporation in polylactic acid (PLA)

E. Rezabeigi*, P. Wood-Adams, R. Drew, Concordia University, Canada

Submicron bioactive glass particles are known to produce better composite scaffolds in comparison with larger particles. Surface modification of these submicron particles can result in better dispersion and improved adhesion to the polymeric matrix of the scaffold. This subsequently promotes bioactivity and ensures good mechanical properties of the final framework. In the current study, submicron 45S5 Bioglass® powder was synthesized via a novel sol-gel route and subsequently, surface functionalized with methacryloxypropyltriethoxysilane. The surface modified bioactive glass was then characterized and the efficiency of this surface treatment was evaluated with PLA providing an appropriate material for fabrication of scaffolds for bone regeneration.

S11: Next Generation Technologies for Innovative Surface Coatings

NEXT Generation Coating

Room: Coquina Salon E
Session Chairs: Jun Akedo, National Institute of Advanced Industrial Science and Technology (AIST); Sang Sub Kim, Inha University

8:00 AM

(ICACC-S11-013-2013) Grain orientation control of bismuth layer-structured ferroelectrics and bismuth based perovskite oxides thick films prepared by aerosol deposition method (Invited)

M. Suzuki*, J. Akedo, National Institute of Advanced Industrial Science and Technology (AIST), Japan

Bismuth layer-structured ferroelectrics (BLSFs) has been regarded as a promising material for applications involving ferroelectric memories and piezoelectric devices operating at high temperatures due to its large spontaneous polarization (Ps) and high Curie temperature (TC). Also, (Bi,Na)TiO3 (BNT) is an attractive piezoelectric material1 because BNT has a high TC of 320 °C and a large Ps. It is of great interest to control crystallographic orientation of grains in the form of polycrystalline ceramics and films for achieving superior properties. An aerosol deposition (AD) method, which is based on room temperature impact consolidation (RTIC) phenomena, is attracting attention because it can form thick ceramic layers of simple or complex compositions at a room temperature. In this study, ceramic thick films of SrBi2Ta2O9 (SBTa), Bi4Ti3O12 (BiT), SrBi4Ti4O15 (SBTi), which are BLSFs family, and BNT were deposited on glass and Pt/Ti/YSZ substrates by AD method, and their microstructure and polarization properties were investigated. One possible reason is that the control of particles shape leads to obtain grain oriented thick films in the AD method.

8:30 AM

(ICACC-S11-014-2013) Atomic layer deposition of buffer and transparent conducting oxide layer for CIGS solar cell (Invited)

J. Kim*, H. Kim, J. Kim, H. Yu, SK innovation, Republic of Korea

There have been increasing demands for buffer and transparent conducting oxides (TCO) grown by atomic layer deposition (ALD) in CIGS thin film solar cell. We evaluated ultrathin ZnS and Zn(O,S) as a buffer layer depending on the thickness and the composition, where ALD ZnO was also used as transparent resistive oxide (TRO). ZnS showed the almost same level of efficiency as chemical bath deposition (CBD) CdS. In Zn(O,S), efficiency was strongly dependent on the composition. Device of low level of S showed low Voc that can be explained by the negative conduction band offset (CBO), while S-rich Zn(O,S) exhibited low Jsc because of the large positive CBO. We could obtain the efficiency gain of 0.7% by process optimization. Especially, Jsc was improved because the total thickness of buffer/TRO stack was decreased down to 50nm. Our interest in further ALD work is tied to innovative materials development, like doped ZnO. Recently, it has been reported that amorphous Zn-Sn-O or Zn-Mg-O show the superior device performance. Furthermore, a single-step ALD buffer/TRO process is far more attractive, and has been the direction of advanced emitter, since we can reduce the capital investment by eliminating sputter TRO process. Details on the growth behavior and electrical properties of ALD buffer and TCO films will be given and compared to the conventional process.

9:00 AM

(ICACC-S11-016-2013) Highly Sensitive Chemiresistive Sensors Using Oxide Fibers Based on Interface Engineering

S. Kim*, Inha University, Republic of Korea

There has been growing interest in one-dimensional oxide nanomaterials, because of their fundamental scientific interest and potential applications in a variety of functional devices. More recently, oxide nanofibers synthesized by electrospinning have been extensively studied for the use of chemical gas and bio sensors. In this presentation, various kinds and types of oxide nanofibers synthesized by an electrospinning method are discussed in light of microstructure and capability in gas sensing. In particular, the roles of interfaces including grain boundaries, interfaces between core and shell, inner and outer surfaces are discussed in terms of sensing performances.

9:20 AM

(ICACC-S11-017-2013) Development of Porous TBC Systems with Enhanced Durability using TriplexPro 210 Technology

M. R. Dorfman*, C. Dambra, J. Medrano, D. Chen, M. Nestler, Sulzer Metco (US) Inc, USA

Over the last few years, there has been a great deal of R&D looking at alternative chemistries to traditional 7-8 wt% Yttria Stabilized Zirconium oxide (YSZ) coating systems. The main reason for this is that engine temperatures have been increasing and coating surface temperatures greater than 1200°C for prolonged periods of time will result in: 1) accelerated phase destabilization, 2) increased surface sintering, and 3) cracking and spallation. However, many existing engines still see service temperatures that do not exceed 1200°C. For these engine components, legacy YSZ materials will still be used for application cost reasons. This program has evaluated several different YSZ materials in developing a cost efficient, mechanically durable YSZ system using TriplexPro technology. Key areas studied include the effects of powder properties and spray parameters on coating microstructure and performance. The program also reviews application cost verses performance. Key testing included: 1) burner rig testing, 2) Furnace Cyclic Testing (FCT), 3) thermal conductivity, and 3) metallographic analysis. Technical results showed that high purity agglomerated and sintered and/or HOSP YSZ powders can be manufactured and sprayed to produce porous coatings with improved thermal cyclic performance.

9:40 AM

(ICACC-S11-018-2013) Enhancement of energy conversion efficiency of porous TiO2 thin films for DSSC application

H. Kim*, T. Hwang, KITECH, Republic of Korea

Dye-sensitized solar cells (DSSCs) are drawing many attentions as a next generation solar energy-harvesting device due to its simplicity of fabrication and the possibility of making flexible device. Amongst all the proposed designs of DSSCs, the flexible device requires a few technical requirements such as low-temperature curable porous TiO2 thin films. However, the low-temperature processability inevitably brings about the loss of efficiency due to a low degree of necking between the TiO2 nanoparticles. Therefore, an appropriate network former or binder that polymerize at a low temperature is considered as one of the most wanted parts for the flexible DSSC device in everyday life. Addition to the binder, some special skills to further increase the efficiency is also the hot topics. In this study, we prepared flexible TiO2 thin films on ITO-coated PEN films by a sol-gel chemical method, which comprised a low-temperature curing at 120 C. Hydrolyzed titanium isopropoxide was used as a network former and colloidal silica nanoparticles of 10 nm were also used as an auxiliary binding agent.

10:00 AM

(ICACC-S11-015-2013) Linearly aligned diamond fillers in polysiloxane/diamond composite films with enhanced thermal conductivity

T. Nakayama*, Nagaoka Univ of Tech, Japan

The relocation of diamond fillers was performed in polysiloxane-based composite films under different electric fields. The microscale diamond filler particles were dispersed by sonication in a prepolymer mixture of polysiloxane, followed by high-speed mixing. The homogeneous suspension was cast onto a polyamide spacer of microscale thickness and subjected to three different electric fields: AC, DC, and switched DC, before the mixture became cross-linked. Analysis revealed that self-assemblies of linearly aligned diamond fillers (LADFs) were fabricated in the composite film, connecting the film planes as bridges with different thicknesses depending on the applied electric field. Composites with assemblies of LADFs exhibited enhanced thermal conductivity and electrical insulation, and are attractive for application as thermal interface materials in the semiconductor industry.

Innovative Surface Coating

Room: Coquina Salon E
Session Chairs: Masahiro Yoshimura, National Cheng Kung University; Do-Geun Kim, Korea Institute of Materials Science

10:20 AM

(ICACC-S11-019-2013) Growing Integration Layer [GIL] Strategy: Direct Fabrication of Hierarchically Structured Ceramic Coatings on Metallic Materials in Solution (Invited)

M. Yoshimura*, National Cheng Kung University, Taiwan

In the fabrication of Hierarchically Structured Ceramic/Matal coating and joining, the most difficult problem is how to overcome weak interfacial bonding and poor adhesion of ceramic layers by their cracking and /or peeling arising from their intrinsic brittleness. We have proposed a novel concept and technology of the formation "Growing Integration Layer" [GIL] between ceramics and metallic materials to improve the adhesion performance. Those GIL(s) can be prepared via integration of ceramic film formation from a component of the metallic materials by chemical and /or electrochemical reactions in a solution at low temperature of RT-200 C. BaTiO3 and SrTiO3/TiOx GIL films on Ti plates formed by hydrothermal-electrochemical method showed good adhesion. CaTiO3/ Al2O3/Ti2Al GIL films on TiAl exhibited excellent adhesion and anti-oxidation performances: they could be sustained for 10 times cyclic oxidation test at 900 C in air for 5 hrs. The GIL strategy is effective for many metallic alloys and bulk metallic glasses because they generally contain active component(s). On a Ti-base Bulk Metallic Glass, we could succeed to prepare bioactive titanate nano-mesh layer by hydrothermal-electrochemical techniques at 90-120 C.The GIL methods are applicable for various functional and structural Ceramics/Metal Layers and Composites.

10:50 AM

(ICACC-S11-020-2013) Influence of oxygen content on the hardness and electrical resistivity of Cr(N,O) thin films

A. Sato*, T. Endo, K. Suzuki, T. Suzuki, T. Nakayama, H. Suematsu, K. Niihara, Nagaoka University of Technology, Japan

Chromium nitride (CrN) use as a coating material on cutting tools is a superior material with a high oxidation resistance, a low friction coefficient and good seize resistance. Chromium oxynitride (Cr(N,O)) thin film was prepared for improvement of the hardness of the CrN thin film. However, their electric characteristics have never been measured. Above all, the electrical resistivity is an important parameter when we apply this thin film as a contact sensor. Therefore, the purpose of this study is to investigate effects of oxygen content on the hardness and electrical resistivity of Cr(N,O) thin films. Cr(N,O) thin films were deposited on Si(100) substrates by pulsed laser deposition. A Cr (purity: 99.9%) metal target and nitrogen plasma from an RF radical source was used. The compositions of the thin films were analyzed by Rutherford backscattering spectroscopy and electron energy-loss spectroscopy. The thin films were found to contain up to 35 at.% oxygen. Additionally, Cr(N,O) thin films were confirmed to keep NaCl type structure by X-ray diffraction. We revealed that the electrical resistivity of Cr(N,O) thin film was increased gradually with increasing the oxygen content in the range of keeping NaCl type structure.

11:10 AM

(ICACC-S11-021-2013) XPS analysis for tribological behavior of CrMoN film prepared by hybrid PVD

Y. Oh*, Y. Yang, KICET, Republic of Korea; I. Lyo, Hyundai & Kia, Republic of Korea; S. Park, Hyundai Hysco, Republic of Korea; D. Lim, Korea University, Republic of Korea

Current industrial requirement for tools, forming dies with hard coatings such as CrN, TiN is not limited for high hardness only. In particular tribology is noteworthy property for protective films of forming tools to reduce energy. In the solid state tribology system, surface oxidation is believed to lower the frictional force between films and counter material. Metal ions, in the form of multi-compositional films, can be a role of lubricant during the wear. Tribological behavior of CrMoN film with respects to the surface chemistry was investigated by using X-ray photoelectron spectroscopy (XPS). All of films were prepared from hybrid PVD system consisted of DC unbalanced magnetron (UBM) sputtering and arc ion plating (AIP) sources. Tribological property of films was evaluated by friction coefficient using Ball-on-disk type tribometer. The chemistry of wear track analyzed by energy dispersive spectroscopy (EDS) and XPS. The friction coefficient was measured as 0.4 for CrMoN film which is lower than that of monolithic CrN film. EDS & XPS results implies that the formation of oxide layer on coating surface which was identified as molybdenum oxide phases known as solid lubricant during the wear test.

11:30 AM

(ICACC-S11-022-2013) Preparation of Cr-Si-N single crystal thin film with epitaxial growth by pulsed laser deposition

T. Endo*, K. Suzuki, A. Sato, T. Suzuki, T. Nakayama, H. Suematsu, K. Niihara, Nagaoka University of Technology, Japan

Cr-Si-N thin films having nanocomposite structure consisting of nanosized CrN crystallites with B1(NaCl type) structure and an amorphous SiNx phase have been improve the hardness and tribological properties more than that of CrN. It is thought that solubility of Si atoms in the CrN lattice with six coordination is limited, since Si is to be easy to form four coordination due to sp3 hybridized orbital. However, whether Si is contained in the nanosized CrN crystal has not been clear. In this work, Cr-Si-N single crystal with B1 structure by epitaxial growth have deposite on MgO(100) substrate using pulsed laser deposition. Cr-Si-N single crystal were prepared by irradiation of third harmonic light from a Nd:YAG pulse laser onto rotating targets of Si and Cr. The added amount of Si in the thin films was controlled by varying the ratio of surface area of Si for Cr. Nitrogen plasma from an RF radical source was supplied up to 1.3×10-2 Pa. The prepared thin films were characterized by X-ray diffraction, energy dispersive X-ray spectroscopy and electron energy loss spectroscopy. According to these results, it was found that the thin films were Cr-Si-N single crystal with B1 structure when the contents of Si in the thin films were 0-5 at.%. Compared the contents ratio of Cr and N, Cr contents is less than that of N. It is suggested that there is some possibility of being formed (Cr,Si)N.

11:50 AM

(ICACC-S11-023-2013) Fabrication and characterization of porous TiO2 films for photocatalytic removal of VOC

J. Park*, T. Hwang, KITECH, Republic of Korea

Photocatalysis of porous TiO2 thin films has long been the subject of extensive studies. In spite of numerous achievements in the academic field, industrial implementation of photocatalytic removal of VOCs such as Benzene and Toluene, and irritating odor is still a hot topic especially when it comes with the industrial air-conditioner, where active carbon is used yet. Substitution of active carbon by TiO2 is believed to be much advantageous, since the photocatalytic TiO2 would provide the longer operation lifetime due to a completely different removal mechanism, decomposition instead of adsorption. In this study, we employed two ways of porous TiO2 thin films preparation, sol-gel method and anodization, which are currently accepted as a feasible candidate for the mass-production of porous TiO2 layer on metal meshes. Porous TiO2 films were sol-gel prepared on stainless-steel meshes, and TiO2 thin films were also fabricated on Ti wires through an anodization process. With the intention of enhance the photocatalytic efficiency of the films, metal nano-dots were incorporated by a photo-reduction of metal salt, and the their effects on photocatalytic properties of TiO2 thin films were also investigated in view of electron-hole recombination retardation.

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

Methods for Improving Damage Tolerance,Oxidation and Thermal Shock Resistance I

Room: Coquina Salon F
Session Chair: Luke Walker, The University of Arizona

8:00 AM

(ICACC-S12-052-2013) Behaviors of Ceramic Matrix Composites (CMCs) and ultrahigh temperature ceramic (UHTC) Coatings at High Temperature Environments (Invited)

S. Dong*, X. Zhang, Y. Ding, L. Gao, H. Zhou, Z. Wang, P. He, Y. Kan, Shanghai Institute of Ceramics, CAS, China

Carbon fiber reinforced CMCs, like C/SiC composites, have many outstanding thermomechanical properties coupled with low densities. These properties make the materials suitable for many high temperature applications. However, due to the instability of C/SiC composites in oxidizing environments at elevated temperatures, UHTC matrices and UHTC coatings need to be developed to improve the oxidation resistance in extreme environments. UHTCs like ZrC, HfC, ZrB2, HfB2 introduced into carbon fiber preforms can potentially improve the properties of CMCs at ultrahigh temperature. Polymer impregnation and pyrolysis (PIP) and melt infiltration (MI) are the effective processes to introduce the compounds containing Zr and Hf into matrix by a high temperature pyrolysis and an in-situ reaction. Chemical vapor Infiltration (CVI) is another way to form the UHTCs matrix. Because the thermal expansion coefficients of UHTC phases are higher, a combined HfC and SiC matrix is preferred to reduce the microcracks. This method is also used to form the multilayered UHTCs surface coatings with HfC, HfB2 and SiC. Oxidation resistances of C/UHTCs and UHTC coatings at higher temperature are conducted using arc jet tests. The ablation property and oxidation resistance are improved significantly by UHTC modified matrix and UHTC coatings.

8:30 AM

(ICACC-S12-053-2013) Development of Novel Processing Methods for Next Generation Ultra-High Temperature ZrB_2-SiC Fiber Reinforced Composites

B. J. Lai*, J. L. Watts, G. E. Hilmas, W. G. Fahrenholtz, Missouri University of Science and Technology, USA

Ceramic matrix composites (CMCs) based on a zirconium diboride (ZrB_2) matrix reinforced with silicon carbide (SiC) fibers were prepared utilizing a novel combination of processing methods. Specifically, tape casting along with polymeric precursor impregnation and pyrolysis (PIP) were investigated. A standard colloidal processing technique was used for preparation of ZrB_2-based tape casting slurries, which utilized zirconium disilicide ($ZrSi_2$) as a sintering additive to allow for densification at temperatures in the range of 1400 to 1650°C. Incorporation of $ZrSi_2$ permits for appreciable densification in this temperature range consistent with the maximum use temperature of numerous commercially available SiC fibers. This study focused on fabrication and testing of SiC fiber-reinforced CMCs utilizing a dense ZrB_2-$ZrSi_2$ matrix phase. Specimens were prepared by stacking and lamination of slurry infiltrated/coated continuous fiber tow, followed by hot-pressing to near theoretical density. Mechanical performance was evaluated by four point bending to determine strength, modulus, and work of fracture. Specifically, Hi-Nicalon with an interfacial boron nitride (BN) coating displayed an average max flexural strength of 265 MPa and a work of fracture of 3.5 kJ/m^2. Microstructural analysis was also conducted to determine fiber-matrix interactions.

8:50 AM

(ICACC-S12-054-2013) Fabrication and Characterization of Continuous SiC Fiber Reinforced HfB_2-SiC Composites

C. J. Leslie*, E. Boakye, K. Keller, M. Cinibulk, AFRL, USA

The extreme operating conditions of hypersonic flight require materials with high temperature capability and high thermal conductivity, such as ultra high-temperature ceramics (UHTCs). Among the most common UHTCs are the diborides of Hf and Zr. These ceramics, typically combined with up to 30% SiC, have been studied extensively in monolithic form, demonstrating excellent high-temperature strength and oxidation resistance. However, poor damage tolerance significantly limits the use of these as monolithics. The most effective approach to improving the fracture toughness of ceramics is with the addition of fiber reinforcements. In the work presented here, continuous SiC fiber reinforced HfB_2-SiC composites were developed using slurry infiltration and polymeric precursor impregnation techniques. The matrix infiltration techniques were initially developed using commercially available partially densified SiC/SiC woven preform panels. A process was subsequently developed for fabricating these composites through infiltration of SiC fiber cloth laminates. The mechanical and thermal properties of these composites were evaluated and compared to both monolithic HfB_2-SiC materials and conventional SiC/SiC and C/SiC CMCs.

9:10 AM

(ICACC-S12-055-2013) Development and Evaluation of SiC Fiber Reinforced ZrB2 Based Composites for use in Extreme Environments

J. Watts*, G. Hilmas, W. Fahrenholtz, Missouri S & T, USA

Previous research has demonstrated that zirconium diboride (ZrB_2) based composites are candidates for use in extreme environments such as hypersonic flight. The fracture toughness and thermal shock resistance of these composites, however, are limiting factors in their future use in aerospace components. The current study has focused on the development of continuous SiC fiber reinforced ZrB_2 based matrix composites. Commercially available Sylramic IBN and Hi-Nicalon fibers, both having a silicon-doped boron nitride coating, were used as the fiber reinforcing phase to produce composite architectures. A matrix material consisting of ZrB_2 with 10 vol% $ZrSi_2$ was developed allowing for a lower sintering temperature to avoid damage to the SiC fibers. The composites were hot pressed at 1500°C under a 32 MPa load for ~1 hour to achieve near theoretical densities. The presentation will discuss the processing procedures used to infiltrate/coat the SiC tows with matrix material, the development of leading edge components for testing in simulated atmospheric re-entry conditions, as well as the results of preliminary thermal shock testing.

Methods for Improving Damage Tolerance,Oxidation and Thermal Shock Resistance II

Room: Coquina Salon F
Session Chair: Laura Silvestroni, CNR-ISTEC

9:50 AM

(ICACC-S12-056-2013) Study of SiC fiber-matrix interaction in ultra-high temperature ceramics by transmission electron microscopy

L. Silvestroni*, S. Diletta, CNR, Italy

In the last few years ISTEC activity has been focused on the development of toughened ultra-high temperature ceramics, in order to fill the gap of the low intrinsic fracture toughness of this class of materials. Toughness improvement from 3.5 to around 6 MPam1/2 has been achieved through the addition of SiC short fibers, by varying processing methods, sintering additives, thermal treatments and type of fiber. In turn, all these parameters affect fiber integrity and the matrix/fiber interface chemistry, ultimately affecting the mechanical properties. The aim of this study was to understand how the sintering additive or specific treatments on the fiber can control the interface fiber/matrix. Transmission electron microscopy was mainly used as fundamental technique for the characterization at nanoscale level of the fiber morphology and interface with the matrix. A comparison between the evolution of the Hi Nicalon fiber versus the Tyranno type in ZrB2 matrices is presented, evidencing that different thermal stability and chemical inertness may affect the local and global microstructure. Relevant mechanical properties are also reported and related to the microstructural features.

10:10 AM

(ICACC-S12-057-2013) High temperature oxidation resistant ceramic matrix composites by reverse infiltrated ultra high temperature ceramic-coated carbon-carbon composites

L. S. Walker*, E. L. Corral, The University of Arizona, USA

Carbon-Carbon (C-C) composites have ideal mechanical properties for high temperature structural components on aerospace vehicles however they lack necessary oxidation resistance. A two-step approach has been developed that improves the oxidation resistance of both the bulk C-C and forms a protective surface coating. Infiltrations of ultra high temperature ceramics (UHTCs) into C-C composites by liquid based precursors significantly improve the oxidation response of the bulk composite with minimal infiltration cycles forming a self protective substrate. The matrix infiltrated C-C substrate can then coated with a controlled surface layer of UHTCs to isolate oxidation on the surface of the coating. The two-step process creates a damage tolerant high temperature oxidation resistant ceramic matrix composite without long heat treatment cycles. Coatings were designed and optimized isothermally using dynamic non-equilibrium TGA at 1600°C then tested using an oxy-acetylene ablation torch at >1600°C. The oxidation response of the coating is dictated by the coating chemistry and can be related to bulk oxidation of dense UHTCs with similar composition.

10:30 AM

(ICACC-S12-058-2013) Sub-micron HfB2 Powder Protected Cf – Preform

S. Venugopal*, A. Paul, Loughborough university, United Kingdom; P. Zheng, B. Vaidhyanathan, J. Binner, Loughborough University, United Kingdom; A. Heaton, P. Brown, DSTL, United Kingdom

There is considerable interest in ultra high temperature ceramics owing to the need for materials that can cope with the extreme temperatures generated during hypersonic flight. HfB2 has been identified as a promising ultra high temperature ceramic for such applications. However, the lack of availability of HfB2 as fine powder hinders its application in this field. A high sintering temperature and poor impregnation in the case of composites are disadvantages of the existing available coarse HfB2 powders that are typically 1-2 μm in size. Loughborough University has gained experience and the capability to make HfB2 powder with a particle size of 400-500 nm. This powder which is synthesized in house has been thoroughly characterised using XRD, FEGSEM, TEM and SIMS. It has also been impregnated into a 2D carbon fibre preform using vacuum impregnation and the resulting composite tested for its oxidation resistance using an existing oxyacetylene torch facility at the University. A combination of commercial coarse and our fine powder mixture was also used to impregnate the carbon fibre preform and the composite similarly tested and the performance compared with the composite made from only the finer powder. Loughborough's synthesized powder has also been sintered using spark plasma sintering and the sintering parameters compared with that of the commercial powder.

10:50 AM

(ICACC-S12-059-2013) The Effect of WO_3 on Sinterability and Properties of ZrO_2 Ceramics

M. Kazemzadeh Dehdashti*, W. G. Fahrenholtz, G. E. Hilmas, Missouri University of Sience and Technology, USA

The effect of WO_3 additions on the liquid phase sintering behavior of ZrO_2 and ZrO_2-B_2O_3 ceramics was studied. These systems were selected based on the oxide scale that forms when ZrB_2 ceramics containing W additions are oxidized at elevated temperatures. The addition of W has been shown to improve oxidation resistance, but the mechanism has not been investigated. Zirconia specimens with additions of B_2O_3 and/or WO_3 were sintered in a $MoSi_2$ box furnace at temperatures ranging from 800-1400 °C for 2 hours in air. Density measurements revealed that the addition of WO_3 reduced the temperature for the onset of densification and resulted in higher densities of the zirconia ceramics. In addition, specimens containing WO_3 had smaller grain sizes and less porosity. It was concluded that WO_3 acts as a liquid phase sintering aid and improves the sinterability of ZrO_2 ceramics.

11:10 AM

(ICACC-S12-060-2013) Influence of precursor ZrC powders on the properties of the spark plasma sintered ceramic composite materials

N. Voltsihhin*, I. Hussainova, D. Yung, Tallinn University of Technology, Estonia; E. Cura, S. Hannula, Aalto University, Finland

The main objective of the research was to sinter ultrahigh temperature ceramics based on ZrC powders supplied by different companies with the help of spark plasma sintering furnace and to reveal different ZrC powders' influence on the properties of the bulk body. In this study two different zirconium carbide powders were used for fabrication of carbide based ceramic composite materials. One of the powders was nanosized and another had initial particles of micronsize. XRD measurements were made to determine the chemical composition of the grades before and after sintering. ZrC powders were combined with ZrO2, TiC and Mo powders. Spark plasma sintering technique was used for densification of mixed powders and the process parameters were optimized to obtain the near theoretical densities. Densification behavior was different for compositions containing micronsized and nanosized ZrC powders. The research has revealed a great influence of the precursor powders together with sintering parameters on the properties of the final composite specimens. Initial ZrC nanopowder showed some impurity peaks in the XRD observation. Micronsized ZrC based composites has demonstrated higher densities and mechanical properties.

11:30 AM

(ICACC-S12-061-2013) Thermomechanical Properties of Shape Memory Alloy (NiTi) and MAX (Ti3SiC2) Phase Interpenetrating Composites

A. Kothalkar, R. Benitez, L. Hu*, M. Radovic, I. Karaman, Texas A&M University, USA

A shape memory alloy (SMA) - MAX phase composite, namely NiTi - Ti3SiC2, was processed using rapid consolidation technique of NiTi and Ti3SiC2 powder mixture via spark plasma sintering (SPS). The microstructure of the composite was characterized using scanning electron microscopy (SEM) to study the distribution of NiTi, Ti3SiC2, and any other reaction phases. Differential scanning calorimeter was employed to ascertain martensitic phase transformation in the composite after sintering. The composite was thermomechanically trained through thermal cycling under constant stress to introduce residual stresses in the composite. Two-way shape memory effect (TWSME) was confirmed after the training. Damping behavior, implying the energy dissipation per loading-unloading cycle under increasing compressive stresses, of NiTi, Ti3SiC2, as processed and trained NiTi-Ti3SiC2 composites were investigated. The trained composite exhibited the highest energy dissipation per cycle followed by as processed composite, which in itself had higher damping than either the pristine MAX phase or any other metal – MAX phase composites reported in the literature to date.

S13: Advanced Ceramics and Composites for Sustainable Nuclear Energy and Fusion Energy

Irradiation and Environmental Effects II & III

Room: Ponce DeLeon
Session Chairs: Tatsuya Hinoki, Kyoto University; Weon-Ju Kim, Korea Atomic Energy Research Institute

8:00 AM

(ICACC-S13-032-2013) Environmental Effect on the Oxidation of CVD SiC Ceramics and Composites (Invited)

W. Kim*, D. Kim, J. Park, Korea Atomic Energy Research Institute, Republic of Korea

High purity silicon carbide (SiC) ceramics have excellent high temperature mechanical properties, chemical stability, irradiation resistance, and low radioactivity under neutron irradiation. Owing to these superior physical/chemical properties, the SiC ceramics in monolithic and composite forms are being considered as various components for fusion and advanced fission reactors. One of the major life-limiting factors of structural ceramic components is associated with the oxidation or corrosion in coolant media. Under a normal operation or an accident condition of very high temperature reactors, SiC undergoes a passive or active oxidation by a reaction with impurities contained in the He coolant depending on the partial pressure of the oxidants and temperature. In this study, we investigated oxidation behavior of CVD β-SiC and SiCf/SiC composites at various temperatures in He environments with different partial pressure of oxidants. The microstructure, surface chemistry, and surface roughness of the oxidized specimens were characterized using scanning electron microscopy, X-ray photoelectron spectroscopy, and atomic force microscopy, respectively.

8:30 AM

(ICACC-S13-033-2013) Biaxial mechanical behavior of SiC_f/SiC composite tubes

F. Bernachy-Barbe*, L. Gelebart, CEA, France; J. Crepin, Mines ParisTech, France; M. Bornert, Ecole des Ponts ParisTech, France

Modeling the anisotropic behavior of SiC/SiC composites tubes (candidates as fuel cladding of 4th generation Gas-cooled Fast Reactors) requires biaxial mechanical tests along with a characterization of damage mechanisms. On account of the lack of available data on this last generation of SiC/SiC composites (with Hi-Nicalon S fibers), biaxial tension-torsion tests were conducted. Monotonous and cyclic tests were performed on 2D braided CVI SiC/SiC tubes elaborated at CEA. For each test, the load was applied with a constant (axial stress / shear stress) ratio. A Digital Image Correlation procedure was developed to measure the three components of the strain at the surface of the tube. In addition, acoustic emission (AE) was recorded. These mechanical tests allowed to evaluate the macroscopic mechanical behavior and failure criteria in the axial stress / shear stress plane. Moreover, damage onset criteria were defined using AE or strain evolution. From a microscopic point of view, post-failure observations allowed to obtain statistical data about the density and orientation of matrix cracks. Some information about the damage development was acquired through the evolution of AE parameters (amplitude, energy…). Finally, a phenomenological damage model was proposed to reproduce the biaxial mechanical behavior of the composite. Its few parameters were identified from our experimental data.

8:50 AM

(ICACC-S13-034-2013) Dimensional changes and flexural behavior of neutron irradiated 2D carbon fiber reinforced SiC matrix composite

C. Shih*, Y. Katoh, Oak Ridge National Laboratory, USA; J. Steinbeck, Physical Sciences Inc., USA

The effects of neutron irradiation on the dimensional changes and flexural behavior of a 2D carbon fiber reinforced-polymer derived SiC matrix composite were investigated in order to determine its applicability as reactor core components for high temperature gas cooled nuclear reactors. Rectangular flexure bend bars were put into the High Flux Isotope Reactor in Oak Ridge National Laboratory at a nominal irradiation temperature of 800°C until neutron doses of up to 9.3 × 1025 n/m2 were reached. Dimensional measurements, 4 point- ¼ point flexural test (ASTM C1341-06), sonic modulus (ASTM C1259-08), and optical and scanning electron microscopy were utilized to evaluate the effect of neutron irradiation on the composite. The composite experienced shrinkage in the length and width directions while swelling in the thickness direction. Pseudo-ductile to brittle transformation of the fracture mode was observed following irradiation. Flexural strength decrease of up to 54% was observed while flexural modulus increased. Sonic modulus showed a ten-fold increase following irradiation. While this result is considered erroneous in its exact magnitude, it hints at major degradation of the composite's structural integrity. Microstructural examination revealed dimensional instability of carbon fibers that ultimately results in composite deformation and structural damage.

9:10 AM

(ICACC-S13-035-2013) Tensile and Interfacial Properties of Unidirectional Advanced SiC/SiC Minicomposites

K. Ozawa*, T. Nozawa, H. Tanigawa, Japan Atomic Energy Agency, Japan; Y. Katoh, L. L. Snead, Oak Ridge National Laboratory, USA

A silicon carbide (SiC) matrix composite is a promising candidate for nuclear fusion energy applications. In order to design a damage tolerant composite, fiber/matrix interfacial property with and without irradiation effects should be thoroughly and systematically understood. This study aims the effects of different fibers and interphases on tensile and interfacial properties of non-irradiated SiC/SiC minicomposites which have high crystalline and near stoichiometric fibers. Unloading-reloading cyclic tensile tests were conducted to estimate interfacial properties for unidirectional SiC/SiC minicomposites reinforced by Hi-Nicalon Type-S (HNLS) or Tyranno-SA3 SiC fibers via CVI process were conducted. The interfacial properties were also evaluated by the fiber push-out test. HNLS minicomposites with the 240- or 1150-nm-thick PyC interphase (hereafter TypeS-240 and TypeS-1150, respectively) exhibited the pseudo-ductile fracture behavior. Based on the hysteresis loop analysis, the sliding stress estimated for the TypeS-1150 appeared to be about 0.7 times as that for the TypeS-240. This tendency was also confirmed by the fiber push-out test. Tensile failure behavior of the unidirectional minicomposites with interfacial properties will be presented specially emphasis on the case with relatively rough SiC fiber composites, contributing to the design of the damage tolerant composites.

9:30 AM

(ICACC-S13-036-2013) The Use of Additives to Improve SiC-SiC Composites for Nuclear Applications

C. P. Deck*, H. E. Khalifa, C. Hill, C. A. Back, General Atomics, USA

Silicon carbide fiber reinforced, silicon carbide matrix (SiC-SiC) composites intended for nuclear applications are traditionally fabricated using chemical vapor infiltration (CVI) in order to obtain high purity, β-phase SiC with good neutron irradiation tolerance. However, the use of additives and modified fabrication processes could allow improved control over the composite structure, and enable a material to be engineered with more desirable macroscopic properties. These additives are of high purity, and therefore are not expected to undergo the irradiation induced swelling and degradation that often compromises materials in harsh nuclear environments. In this study, SiC-SiC composite samples with additives were fabricated and compared to baseline composites containing only woven continuous fiber. Modifications to the baseline process were investigated, with the goal of retaining the ultimate strength and stability of the cladding, while reducing fabrication time. Characterization and measurements of the samples show that the amount and distribution of SiC additives can be used to tailor the mechanical and thermal properties of the resulting composite. In addition to the traditional CVI fabrication method, composites with additives were also produced using the nano-infiltrated transient eutectic (NITE) approach, producing a high density, low permeability composite material.

10:10 AM

(ICACC-S13-037-2013) Microstructural behavior of SiC/SiC composites under ion irradiation environment (Invited)

N. Chaabane*, M. Le Flem, T. Vandenberghe, S. Urvoy, CEA Saclay, France; P. Dumas, Synchrotron SOLEIL, France; Y. Serruys, CEA Saclay, France

Microstructural changes of SiC fiber reinforced SiC matrix (SiC/SiC) composites (Tyranno S (TS), Tyranno SA3 (TSA3) and Hi-Nicalon type S (HNS)) after 12 MeV Au ion irradiation at room temperature and 800 °C up to 0.05 and 1 dpa doses. Damaged materials were investigated by Raman spectroscopy and Atomic Force Microscope analyses on the irradiated surface and by Transmission Electron Microscopy along the beam penetration. Damages were mainly located at amorphous zones in the matrix, as well as in all the fibers themselves, detected after 1 dpa irradiation at room temperature. TS fiber shrinkage is suggested and consistent with AFM analyses of the composite surface highlighting a 350 nm step height among SiC matrix and TS fibers. On the opposite, the advanced SiC fiber (TSA3 and HNS) did not shrink and showed a superior dimensional stability. The formation of the amorphous layer was confirmed by Raman spectroscopy results. However, the amorphisation occurrence and the different behaviors of the TS fibers (shrinkage) and the matrix (swelling), were both limited at higher irradiation temperature (800 °C): irradiation defect annealing resulted in the occurrence of a slightly disordered material evidenced by Raman, and in less discrepancies in volume changes of matrix and fibers. At this scale of observation, the Pyrolitic carbon interphase appeared unaffected under these irradiation conditions.

10:40 AM

(ICACC-S13-038-2013) Radiation effects in thick Gd2O3 films used for neutron detection

D. Grave*, Z. Hughes, J. Robinson, D. Wolfe, Penn State University, USA

Gadolinium's excellent neutron capture cross section makes Gd containing materials appealing for use in solid state neutron detection. Process-structure-property relations were developed for thick Gd2O3 films deposited by electron beam physical vapor deposition

(EB-PVD) for use in novel radiation detectors. Incorporation of the Gd2O3 films into both silicon based devices and aluminum gallium nitride (AlGaN) / gallium nitride (GaN) high electron mobility transistor (HEMT) structures on silicon carbide (SiC) has been achieved. GaN HEMTs utilizing Gd2O3 as the dielectric allow for multi-mode sensing by measuring changes in both oxide conductivity and HEMT channel resistance due to injection of electrons from neutron interactions within the dielectric under irradiation. Film structural and electrical properties will be linked to device performance in thermal neutron, high energy neutron, and gamma ray fields. Particular attention will be given to degradation of the structural and electrical properties of the films as well as challenges for HEMT device stability under irradiation.

11:00 AM

(ICACC-S13-039-2013) Magnesium phosphate cements for nuclear waste encapsulation

W. Montague*, Imperial College London, United Kingdom; M. Hayes, National Nuclear Laboratory, United Kingdom; L. J. Vandeperre, Imperial College London, United Kingdom

Nuclear waste streams consist of a diversity of physical and chemical forms, requiring a toolbox approach in the application of materials to their disposal. MKPC (Magnesium Potassium Phosphate Cement) is an alternative candidate to Portland cement for encapsulation of specific wastes where lower free water content, lower internal pH or the immobilisation of radioactive isotopes as low-solubility phosphates minerals are desired properties. This work was aimed at allowing improved mix design for the tailoring of the MKPC properties to the requirements of specific waste streams through modelling of strength-formulation relationships within the MKPC/PFA(pulverised fly ash) system. This is achieved utilising theoretical density calculations and compressive strength development data for a variety of formulations, with free water content, density and porosity measurements compared for model validation. Measured compressive strength values for the system have reached as high as 61 ± 5 MPa at 90 days of age.

11:20 AM

(ICACC-S13-040-2013) Dimensional stability of graphite under ion-irradiation

M. Nonaka*, S. Kondo, T. Hinoki, Kyoto University, Japan

Graphite is expected to be used as the core structural material for VHTR. Isotropic polycrystalline graphite generally shows unique fluence dependence of the dimensional change under neutron irradiation, where they first contract and thereafter expand. The turnaround point is considered as an application limit. Ion-irradiation may be suitable for understanding the basic information of the dimensional stability of the graphite because of the highly controllable and fast damage rates. The purpose of this study is to clarify how dimensional change of each crystalline axis depends on irradiation conditions. Samples, highly oriented pyrolytic graphite, were polished parallel to either a-axis or c-axis. The surfaces were irradiated with 5.1MeV Si^{2+}ion. Because the ion range is limited to ~2.75μm from the irradiate surface, specimens were curved due to the strain mismatch between irradiated region and unirradiated region. Atomic force microscope was used for determine the irradiated curvature. The specimens with surface parallel to c-axis curved in a convex way due likely to the significant expansion of c-axis direction. Although the other sample was expected to curve in a concave way due to the a-axis contraction, it was very limited or absent. It indicates that the contraction rate of a-axis was significantly smaller than that of c-axis.

11:40 AM

(ICACC-S13-041-2013) Temperature dependence of the contraction rates of the nuclear-grade graphite

S. Kondo*, T. Hinoki, Kyoto University, Japan; M. Okuda, T. Takagi, IBIDEN CO., LTD., Japan

Irradiation-induced dimensional change in nuclear graphite is one of the key concerns for its use in structural components of high-temperature gas-cooled reactors. The behavior is somewhat unique in that the transition from contraction to expansion is found at a given damage level depending on the temperature. Although recent highly crystalline, well graphitized, and pure materials are believed to show moderate contraction rates, the irradiation data is very limited to low fluence, specific temperature, and a few materials. Testing by ion-irradiation with highly controllable and accurate irradiation conditions is suitable for understanding such temperature- and fluence-sensitive phenomena. The objectives of this work are to clarify and to compare the temperature dependence of the contraction rates of various graphites. Samples provided by more than one company were irradiated with Si-ions 400-800°C in DuET at Kyoto University. Because the ion range was limited to few microns, increase in the amount of crack opening was observed due to the tensile stress induced within the irradiated region. The shrink was estimated by comparing the crack opening between irradiated and unirradiated samples, in which the contraction was clearly observed at all the temperatures as demonstrated in neutron experiments reported. Most samples showed comparable contraction rates in identical irradiation conditions.

FS1: Geopolymers and Chemically Bonded Ceramics

Novel Applications

Room: Coquina Salon A
Session Chair: Claus Rüscher, Leibniz University Hannover

8:00 AM

(ICACC-FS1-020-2013) Basic research on geopolymer gels for production of green binders and hydrogen storages (Invited)

C. H. Rüscher*, L. Schomborg, A. Schulz, J. C. Buhl, Leibniz University Hannover, Germany

Geopolymer gels could be optimised for binders possessing high mechanical strength. Two further applications will be reported. i.) NaBH4 crystals could easily be recrystallized within a geopolymer type matrix. The handling of the NaBH4 containing geopolymer gel is easy even under moisture. Highest contents of NaBH4 are about 72 wt% which can be used in a rather controlled reaction for hydrogen release. Ii.) The disadvantage and the main reason that a breakthrough for large scale applications of NaBH4 as a hydrogen storage did not come is, however, that the production of NaBH4 is very energy consuming and costly. There seems to be no way for a reload or recycle of the material. Some recent results showed, however, that the reaction behind the hydrogen release could be controlled separately, opening the possibility to reload hydrogen. The key point for this will be discussed: These are the enclosure of the BH4-anion in the cages of the sodalite during crystallisation from the geopolymer gel. The nanosized up to microsized crystals of BH4-SOD are also enclosed or contain a geopolymer type matrix. This matrix is of very importance since it contains and transports the water to the entrance windows in the sodalite cages for the consecutive hydrogen release reactions. It also helps to achieve the relevant concentration gradients for the strictly diffusion controlled processes.

8:30 AM

(ICACC-FS1-021-2013) Low density geopolymers containing silver nanoparticles with biocide activity (Invited)

B. Cabal*, Nanomaterials and Nanotechnology Research Center (CINN-CSIC-UO-PA), Spain; B. E. Glad, W. M. Kriven, University of Illinois at Urbana-Champaign, USA; F. Rojo, National Center for Biotechnology (CNB-CSIC), Spain; R. Torrecillas, Nanomaterials and Nanotechnology Research Center (CINN-CSIC-UO-PA), Spain; J. S. Moya, Materials Science Institute of Madrid (ICMM-CSIC), Spain

Biocidal ceramics have obvious utility in water purification and other biomedical applications, and ionic silver has long been used as a safe antibacterial agent. Here, synthesis of biocidal geopolymers is investigated. Porous Na-based geopolymers were developed from using a synthetically nanostructured biocidal metakaolin (metakaolin-nAg, developed here) and waterglass. The metakaolin-nAg was synthesized as a powder, starting from salts and decorated with silver nanoparticles following reduction of the metal. Porous Na-based geopolymers decorated with these silver nanoparticles were compared to controls. The samples were ≈70% porous with ≈5 μm diameter pores (determined using mercury intrusion porosimetry). As cast geopolymer composites were also heat treated to effect conversion to a stronger glass ceramic. All samples were fully characterized by chemical analysis, XRD, NMR, UV-V spectroscopy and TEM. To investigate the antibacterial and antifungal effect of these geopolymers, biocide tests were performed inoculating Escherichia coli (Gram-negative bacteria), Micrococcus luteus (Gram-positive bacteria) and Issatchenkia orientalis (yeast). This procedure opens the possibility to design a new family of low cost biocides with a large spectrum of applications.

9:00 AM

(ICACC-FS1-022-2013) Mechanical Characteristics of Natural Fiber-Reinforced Geopolymer Composites

J. Low*, T. Alomayri, Curtin University, Australia

Natural fiber reinforced composites have attracted much attention recently because of their desirable properties in improved fracture toughness, high modulus, low density, recyclability and renewability. In fact, the use of natural fibers in geopolymer composites has the potential to produce materials with higher specific strength and specific modulus due of their low density. In this paper, geopolymer composites reinforced with cotton fibers have been fabricated and investigated. The influence of cotton fibers dispersion on the mechanical and fracture properties of these composites have been characterized in terms of hardness, impact strength, flexural strength and fracture toughness. The failure micromechanisms and energy dissipative processes in these composites are discussed in terms of microstructural observations.

9:20 AM

(ICACC-FS1-023-2013) Green Composite: Processing, Mechanical Properties and Microstructure of Sodium-based Geopolymer Reinforced with Chemically Extracted Corn Husk Fibers (Invited)

S. Musil*, University of Illinois at Urbana-Champaign, USA; P. Keane, W. M. Kriven, Keanetech LLC, USA

Geopolymers are an inorganic polymeric material composed of alumina, silica, and alkali metal oxides. Geopolymers have shown promise as a low cost, environmentally friendly structural material. The addition of a reinforcing phase vastly improves the strength and toughness of the composite. For this study, sodium-based geopolymer is reinforced with chemically extracted corn husk fibers via a paste and weave approach followed by cold press and 50 degrees C curing. Corn husk fibers (CHF) are a low cost, abundant and sustainable resource. They show moderate strength and high elongation to failure equating to high work of rupture for a natural fiber which acts as a toughening mechanism for this biocomposite. CHF are chemically extracted from corn husks using a 10:1 NaOH:H2O room temperature alkali bath with manual agitation for 30 minutes and are rinsed with water to neutralize the pH. Composite tensile and flexural strength are determined for both quasi-aligned and randomly oriented fibers. Composite microstructure is also evaluated with the SEM focusing on fiber continuity and fiber/matrix interface.

10:00 AM

(ICACC-FS1-024-2013) Ceramic Wall Tile Development by Geopolymerization (Invited)

F. Kara*, G. Korc, M. Vicent, K. G. Suzuk, T. Seiffarth, Anadolu University, Turkey

Ceramic tile manufacturing process is energy intensive process and energy cost is about 30% of the total manufacturing cost. Thus, there is a great need to reduce the energy consumption and associated CO2 emission in the tile industry. Although one obvious route would be to reduce firing temperatures and times with associated incremental improvement, different approach is needed to have substantial impact on energy saving and geopolymerization can be an answer to this. Geopolymers are inorganic polymers typicaly formed by reaction between a solid aluminosilicate and sodium silicate solution under highly alkaline conditions. These materials are energy efficient ceramic-like materials which form and harden at ambient temperatures. The objective of this study is to develop an energy efficient manufacturing process by transforming the geopolymer technology into the traditional ceramic tile production. Ceramic tiles are produced at 1100-1200 °C, whereas the geopolymers require 25-150 °C temperature to get the desired strength. In the study, metakaolin, metakaolin and perlite based geopolymer compositions containing different fillers were prepared by using conventional ceramic tile dry processing route. The results shows that the wall tiles with required properties can be produced by geopolymeric route.

Construction Materials

Room: Coquina Salon A
Session Chair: Kwesi Sagoe-Crentsil, CSIRO

10:30 AM

(ICACC-FS1-025-2013) Use of local geomaterials for water harvesting in Jordan (Invited)

H. Rahier*, M. Esaifan, J. Wastiels, Vrije Universiteit Brussel, Belgium; H. Khoury, University of Jordan, Jordan

A 5 year project was conducted to develop alkali activated cements form Jordanian local resources. The main use of these materials in this project was for making water ponds for agriculture use. An important issue was developing low energy impact materials that can be produced on site with limited tools that can be locally bought. In the first stage a selection of raw materials has been made. Some Jordanian kaolinitic soils (containing 65% kaolinite) can be activated with strong alkaline solutions (NaOH or KOH based). The composition and cure procedure was optimized. As the optimal amount of water is close to the plastic limit of the kaolinite a special mixer with horizontal shaft was designed. The best mixing was obtained when first mixing the sand or filler with the liquid and then adding the clay. Tiles were pressed in a press used for cement tiles. The stones were cured at 45°C in large furnace for 21 days. In the field this furnace could be replace by a green house. A pond was created with these tiles. The mortar used to place the tiles and to fill the joints between the tiles, is a geopolymer consisting of metakaolinite and sodiumsilicate solution. The reason for switching to metakaolinite is that filling the joints with the plastic unheated clay was not possible. The metakaolinite based geopolymer has lost the plasticity and can be poured and used as a mortar.

11:00 AM

(ICACC-FS1-026-2013) Serviceability, durability and chemical factors governing Geopolymer concrete performance (Invited)

K. Sagoe-Crentsil*, S. Yan, T. Brown, CSIRO, Australia

The serviceability, structural behavior and overall durability of Geopolymer concretes are largely controlled by chemical and microstructural properties of the binder matrix phase. In particular, the role played by Si content of feedstock materials and the effects of curing conditions on durability performance have been assessed in this study. Although matrix permeability varies with strength, it was observed that concrete mixtures with equal compressive strengths do not necessarily produce equal levels of permeability. However, fairly good correlation exists between strength and initial surface absorption measurements. Measured mean gas permeability coefficient values of 6.19E-17m2 at 300kPa gas pressure obtained for medium-strength fly ash based concrete specimens also compare favorably with equivalent grade reference OPC samples. The effects of fly ash chemical composition and curing parameters were further observed to alter the evolution of matrix capillary porosity and distribution. The Paper examines such chemical and processing factors on key durability parameters including steel reinforcement corrosion and long-term engineering performance.

11:30 AM

(ICACC-FS1-027-2013) Optimization and Characterization of Geopolymer Concrete using Response Surface Methodology (Invited)

M. Dhakal, K. Kupwade-Patil*, Louisiana Tech University, USA; A. Agarwal, Indian Institute of Technology (IIT), India; E. N. Allouche, Louisiana Tech University, USA

The current study uses a statistical approach known as Response Surface Methodology (RSM) to optimize the constituents for the production of engineered geopolymer concrete (E-GPC). The RSM method was used to optimize the influence on strength and porosity using four variables such as calcium oxide, amorphous to crystalline ratio, particle size distribution of the fly ash, and activator solution to binder ratio. The models suggested a possible relation between the four variables to achieve a desired engineering E-GPC in terms of strength and porosity. Microstructural characterization was carried out using scanning electron microscope (SEM), X-Ray Diffraction (XRD), and Fourier Transform Infrared Spectroscopy (FTIR). The characterization revealed information related to crystalline to amorphous content of E-GPC, zeolitic crystalline phases, and the bonds between Si and Al to examine the effect of hydrated sodium alumino silicate hydrate (N-A-S-H) on strength of geopolymeric gels. Optimization of geopolymer concrete, using RSM and microstructural study, helped in designing an engineering E-GPC in terms of strength, porosity, workability, and setting time for specific civil infrastructure applications.

FS4: Advanced Ceramic Materials and Processing for Photonics and Energy

Multifunctional Materials

Room: Oceanview
Session Chairs: Francois Legare, INRS; Mohamed Chaker, INRS

8:00 AM

(ICACC-FS4-021-2013) Priorities for Ceramics Education and Research (Invited)

L. D. Madsen*, National Science Foundation, USA

Current research priorities in the United States are being guided by the reauthorized America Competes Act and the recommendations made in the Rising above the Gathering Storm, Revisited (2010 report). The underlying fundamentals are education, employment, competitiveness and economic prosperity. Efforts attracting funding from the US National Science Foundation will include: (i) strengthening of education, (ii) transformative advances in manufacturing, (iii) promotion of innovation, and (iv) diversifying representation in the sciences and engineering. Two opportunities will continue: Scalable Nanomanufacturing (SNM) – an effort aligned with a National Nanotechnology signature initiative, and Innovation Corps – a program designed to guide the output of scientific discoveries closer to products that benefit society. The Materials Genome Initiative had its first competitions and is now into year two. Ceramic research activities with a contemporary focus can occupy a central position providing that relevance and importance to national priorities is evident.

8:30 AM

(ICACC-FS4-022-2013) Core-shell Carbon Nanotubes Structures and its applications (Invited)

D. Chua*, National University of Singapore, Singapore

Carbon nanotubes have attracted much attention due to their unique properties, such as the nanometer-size diameter, good structural integrity, high electrical and thermal conductivity, and chemical stability. As of today, several different applications have been reported, such as nanotube transistors, electron emitters, nanotube ropes etc have been reported. In this research, we demonstrate that carbon nanotubes can also be used as a base template for other materials to build on, forming hybrid nanostructures which can effectively extend its applications. Using carbon nanotubes as a base template allows the formation of structural shell to form on the top. This hybrid form is able to demonstrate new physical and material properties. As such, by carefully designing the shell on carbon nanotubes core, one can significantly enhance various engineering applications. A few applications will be reviewed here. For example, metal oxide tip-coated carbon nanotubes (such as MoO3 and WO3) have proved to be excellent schottky electron emitters while platinum coated carbon nanotubes formed excellent catalytical activity for PEM fuel cell applications. Other metal-oxide composites such as ZnO can have dual-functional properties allowing good electron emission with photoluminescence properties. We further demonstrate that these hybrid structures can be extended into biomedical materials as seed layer for hydroxyapatite growth.

8:50 AM

(ICACC-FS4-023-2013) Multifunctional inorganic nanomaterials: from design to energy and environmental applications (Invited)

A. Gasparotto*, Padova University and INSTM, Italy; D. Barreca, CNR-ISTM and INSTM, Italy; D. Bekermann, G. Carraro, C. Maccato, Q. Simon, Padova University and INSTM, Italy

The development of emerging technologies occurred in the last decades has been largely enabled by the ability to design novel inorganic nanomaterials boasting improved, or even unpredicted, functional properties. Thanks to the increasing degree of control over composition, structure and morphology a plethora of advanced systems and devices has been developed through the tailored bottom-up assembly of various 0D, 1D, 2D and 3D architectures. Basing on our recent research activity, the present contribution will introduce the potential of Chemical Vapor Deposition (CVD) and Radio Frequency- (RF) Sputtering for the synthesis of oxide-based nanosystems with controlled size, shape, and topology. After a thorough chemical and physical system characterization aimed at shedding light on the nucleation, growth and assembly processes, the functional properties of the target nanomaterials will be presented and discussed. Focusing on some selected case studies, the impact of material design on the resulting functional behavior will be highlighted, with particular regard to the sustainable production of energy, environmental remediation and gas sensing applications.

9:10 AM

(ICACC-FS4-024-2013) Si-nanowire devices by controlling Si nanowire growth (Invited)

N. Quitoriano*, McGill University, Canada

Semiconductor-nanowire-based devices are typically made by first growing the nanowires, removing them from their growth substrate and then dispersing them onto a new substrate, upon which the devices are made. Believing that this approach is difficult to reproduce on mass, we adopt a hybrid top-down and bottom-up approach to grow semiconductor nanowires in-place and then utilize them for devices. Using this hybrid approach, we demonstrate metal-oxide-semiconductor, field-effect transistors, as well as nano-cantilever-based, differential-mass sensors. To demonstrate these devices, Si nanowire growth directions and locations have been engineered. The growth direction control has been achieved by growing the nanowire against an oxide surface while the nanowire locations are controlled by controlling the location of the Au, colloid catalyst, using the built-in field from a pn junction.

9:50 AM

(ICACC-FS4-025-2013) Modification of the Electrical Conduction Properties of the Grain Boundaries of Nanocrystalline Mixed Conducting Ceramics (Invited)

G. Gregori*, M. C. Göbel, P. Lupetin, J. Maier, Max Planck Institute for Solid State Research, Germany

Grain boundaries (GB) have a profound impact on the electrical transport properties of ceramics. This is particularly relevant for nanocrystalline materials due to (i) the large volume fraction of boundaries and (ii) the possible occurrence of a mesoscopic situation (in which no unaffected bulk properties are present in the material). In this context, an intriguing aspect is represented by the possibility of modifying the grain boundary properties. A viable strategy in this sense is given by locally doping the boundaries (GB decoration). In this contribution, a number of results will be presented to illustrate the perspectives (and also the limitations) of such an approach.

10:10 AM

(ICACC-FS4-026-2013) Multifunctional titania materials: from surface modification to nanocrystal inclusion, and related applications (Invited)

M. Epifani*, CNR-IMM, Italy

Titanium dioxide features a broad range of properties and applications, including gas-sensors and energy-harvesting devices. Important features include low cost, natural abundance, chemical inertness and low toxicity. Specific properties can be enhanced by providing the starting TiO_2 host with suitable modifications. It is then important that the TiO_2 host is simply prepared and post-processed. This possibility is offered by wet chemical colloidal synthesis techniques. This work will first review the development of a two step hydrolytic-solvolithic synthetic process for TiO_2 nanocrystals. Then two modifications will be detailed, resulting in different final material morphology and applications. In the first case, surface deposition of V_2O_5 species will be described, including the investigation of the actual placement of the V ions. The preparation and testing of supercapacitor devices will be reviewed, showing the effect of combining stable TiO_2 core with suitable property-modifying surface modifications. In the second case, the synthesis of Pt-modified TiO_2 nanocrystals will be described, including the rational choice of the Pt precursor and the investigation of the composite structure. The results of the sensing tests will show the importance of well-dispersed catalyst nanocrystals in the improvement of the device performance.

10:30 AM

(ICACC-FS4-030-2012) Synthetic strategies for creating CdSe/polymer hybrid materials for photovoltaic applications (Invited)

K. Mazzio, K. Okamoto, C. Luscombe*, University of Washington, USA

A key application which is currently attracting a lot of interest for semiconducting polymers is their use in organic photovoltaic devices. The main drive for developing organic photovoltaic devices is the potential for lower cost associated with their manufacturing, because of the fact that organic semiconducting polymers can be solution processed. The processes of light absorption, exciton dissociation, charge transport (without recombination), and charge extraction widely recognized as the critical issues underpinning organic solar cell performance. It remains a major challenge to find an effective way to optimize these four requirements simultaneously in organic photovoltaics. Organic photovoltaic devices are classified as excitonic solar cells, where strongly bound electron-hole pairs known as excitons are generated upon light absorption. Unlike Si and other inorganic semiconductors, in which photoexcitation produces free charge carriers directly or delocalized (Wannier) excitons with small binding energies (~10 meV), light absorption in current organic/polymer semiconductors creates Frenkel excitons with large binding energies (~0.4-1.0 eV) and small diffusion lengths (5-20 nm).

11:00 AM

(ICACC-FS4-029-2013) Room temperature ferromagnetism in Cobalt and Europium implanted Zinc Oxide thin films

J. Lee*, G. Xing, The University of New South Wales, Australia; T. Chen, The Chinese University of Hong Kong, China; P. Photongkam, Synchrotron Light Research Institute, Thailand; M. Ionescu, Australian Nuclear Science and Technology Organisation, Australia; Y. Zhang, S. Li, The University of New South Wales, Australia

Spintronics is a new discipline which has recently become one of the key research areas connected to magnetic-recording and semiconductor industries. Major ongoing research focus on doping of transition metals (TM) group into ZnO which demands stringent criteria. However till date, there is no direct evidence to such criteria fulfilled. In this work, we present a study of TM and rare earth codoped ZnO films. The films are prepared through the implantation of Cobalt (Co) and Europium (Eu) as co-doping scheme in ZnO epitaxial film. Ion depth distributions of elements were characterized by using ion beam analysis (IBA). The crystalline structure was analysed using x-ray diffraction (XRD). X-ray photoelectron spectroscopy (XPS) was used to characterize the charge state of the Co ions in the films. Within the detection limit of XRD and XPS, we can rule out the metallic Co as the observed source of ferromagnetism. In order to explore the origin of ferromagnetism, 0.5%-4% of Europium is implanted into Co doped ZnO films. The samples were annealed in Argon atmosphere, 600oC and 1 atm. Magnetic measurements were carried out on the as implanted samples and annealed samples. All the samples showed ferromagnetism with Curie temperature above room temperature. We also showed that Co substitution can be enhance by inducing Eu codoping though X-ray Absorption Fine structure Spectroscopy (XAFS) study.

11:20 AM

(ICACC-FS4-027-2013) Effect of annealing on the dielectric properties of amorphous silicon carbonitrides ceramic

H. Gong*, L. An, University of Central Florida, USA

A polymer-derived ceramic (PDC) made from polysilazane modified with different amounts of methacrylic acid (MAA) was investigated. The dielectric properties of the obtained ceramics which had been annealed in air at the temperature from 1000 to 1300 °C were studied. With a proper MAA loading level and annealing temperature, high dielectric constants were observed. PDCs are kind of percolation composites, comprising of SiCN amorphous matrix and self-assembled carbon nanoclusters which serve as the electrode surfaces of numerous small capacitors. The capacitors network gives the composites high dielectric constant. Annealing process could control the conductivity of the matrix and the dispersion of carbon nanoclusters. XRD, NMR, EPR and Raman were used to characterize the structure of the SiCN ceramics. Such materials are potential candidates for applications of storing charge and electrical energy.

Engineering Ceramics Summit of the Americas

Ceramics for Energy and Aerospace Systems

Room: Coquina Salon G
Session Chairs: Hua-Tay Lin, Oak Ridge National Laboratory; Michael Halbig, NASA Glenn Research Center

8:00 AM

(ICACC-ECSA-023-2013) Automated Creep Rupture Water Vapor Degradation Model for Gas Turbine Hot Section Ceramics (Invited)

M. K. Ferber*, H. Lin, ORNL, USA; M. van Roode, MvR Institute of Technology, USA

A rapid excel-based routine was developed to estimate temperatures and stresses for coated and uncoated ceramic combustor liner components for gas turbines. The temperature gradients occurring across the combustor liner were estimated using a simplified heat transfer analyses. The resulting surface temperature of the outer most component was then used to calculate recession. The heat transfer analyses followed by the recession calculation were subsequently repeated until the desired time at temperature was obtained. The model was applied to silicon carbide monolithics and SiC/SiC and oxid/oxide based ceramic matrix composites with or without protective coatings. A 2D FEA capable of coupled heat and structural analyses was then used validate the results.

8:30 AM

(ICACC-ECSA-024-2013) A Miniature Ceramic Gas Turbine Engine Architecture Designed for Long Life and High Reliability (Invited)

M. Vick*, U.S. Naval Research Lab, USA

Ceramics could enable small gas turbine engines (3 - 30 kWe) to reach much higher fuel efficiencies. This could enable turbines to penetrate new markets, such as residential combined heat and power or range extenders for hybrid automobiles. Cost presently seems to be an obstacle to the use of ceramic matrix composites, but monolithic ceramic components can be mass produced at low cost and high precision by injection molding. However, the life and reliability of existing materials are severely limited by water vapor erosion, slow crack growth, and other processes. This talk will explore a new ceramic turbine engine architecture that employs three strategies – low blade speeds, a low pressure ratio, and a high degree of recuperation – to mitigate these life-limiting processes, potentially enabling a small engine to achieve a life exceeding 10,000 hours at a reliability level above 99 percent. To realize this vision, a compact, high effectiveness ceramic recuperator is needed. A novel primary surface microchannel heat exchanger designed to meet this need will be described, along with results from computer simulations and tests that were conducted to estimate its performance, and a survey of viable ways to manufacture it at low cost.

9:00 AM

(ICACC-ECSA-025-2013) Ceramic Microturbines for Small-Scale Distributed Energy Applications (Invited)

H. Lin*, M. Ferber, Oak Ridge National Laboratory, USA

Microturbine engine could provide a high quality, reliable, and less expensive electricity alternative to potentially replace the needs for the construction of large, central power plants, and high and congested voltage transmission lines. The application of microturbines for distributed energy applications has been under development for a number of years in the United States (US) and other countries. One limitation of most commercial microturbine systems is the relatively low electrical thermal efficiency, which ranges from 20 to 30%. The strategies, which could be implemented to significantly improve engine performance, are to increase the turbine inlet temperature and/or air/fuel pressure. Advanced ceramic materials have been considered as enabling technology for significantly improving the performance of microturbine engines. While silicon nitride and silicon carbide ceramics have demonstrated considerable promise for this application due to their superior high-temperature mechanical performance and oxidation resistance, relatively little effort has been placed on utilizing these materials in microturbine engines. This paper will describe the work that has been done in this area and also currently ongoing ceramic microturbine projects in the US. The challenges that remain to be addressed for environmental degradation (recession) and future prospects would be presented and discussed.

9:20 AM

(ICACC-ECSA-026-2013) Thermal Protection Materials and Systems: Successes and Challenges (Invited)

S. M. Johnson*, NASA Ames Research Center, USA

Thermal protection materials and systems (TPS) are used to protect space vehicles and their contents from the heat generated during entry into a planetary atmosphere. The materials used for this application must withstand both thermal and structural stresses while contributing as little mass to the vehicle as possible. Tailoring materials to specific applications and conditions is critical to ensuring that TPS is both efficient and reliable. This talk will review the classes of materials (both reusable and ablative), property needs and some recent successes, including the recent entry into Mars. The challenges expected form future missions and the materials needs will be discussed, and some recent approaches to developing new materials will be presented. The importance of modeling, both for developing materials and understanding and predicting behavior will be stressed.

10:10 AM

(ICACC-ECSA-027-2013) Ceramic Matrix Composite Component Development and Demonstration For Applications in Aircraft Turbine Engines (Invited)

M. C. Halbig*, M. H. Jaskowiak, J. D. Kiser, D. Zhu, NASA Glenn Research Center, USA

Ceramic matrix composite (CMC) components and environmental barrier coatings (EBCs) are being developed in the NASA Environmentally Responsible Aviation (ERA) Project for aircraft turbine engine applications. The goal of the ERA Project is to explore and mature alternate aircraft designs and technologies which have the potential to decrease noise, emissions, and fuel burn to allow achievement of the midterm goals as described in the National Aeronautics Research & Development Plan. To help meet the goals of the ERA Project, three different types of CMC components are being matured. These include a CMC combustor liner, a CMC high pressure turbine vane, and a CMC exhaust nozzle. Advanced EBCs specifically tailored to the needs of the CMC combustor and vane are also being developed. The primary objectives are to address manufacturability of the complex-shaped components and to evaluate their performance under engine operating conditions. Results of flat panel and component testing will be compared to ensure that materials properties are not significantly reduced during scale-up of processing toward full size components. Major challenges to be addressed are in component fabrication, component cooling design, heat transfer characterization, test stand integration, and testing under relevant engine operating conditions.

10:30 AM

(ICACC-ECSA-028-2013) SiC/SiC Ceramic Matrix Composite: Challenges and Opportunities in the Turbine Engine Industry (Invited)

A. Chamberlain*, J. Lane, Rolls-Royce Corporation, USA

Airlines and government agencies are creating more aggressive requirements for future gas turbine engines. These requirements include: reduced specific fuel consumption, reduced weight, reduced emissions, and increased performance. Achieving these targets requires increased engine operating temperatures, reduced cooling air usage, and higher overall pressure ratios. This combination has pushed single crystal nickel alloys and high efficiency cooling schemes to operational limits. This limitation has resulted in the increased demand for the development of SiC-based ceramic matrix composites (CMCs) and their supporting technologies. SiC-based CMCs systems have the potential to provide component operating temperatures approaching 1650°C with minimal or no cooling air, which will enable the achievement of future customer requirements. The successful insertion of CMCs into turbine engine requires significant development in various areas in order achieve full benefit. These areas include: high temperature materials, environmental coatings, lifing, joining, and ceramic – metallic interface.

11:00 AM

(ICACC-ECSA-029-2013) Advanced Non-Oxide Ceramics in Energy Generation and Conservation (Invited)

B. Mikijelj*, Ceradyne Inc., USA

Several applications for non-oxide ceramics in oil/gas exploration and generation industries will be shown. They integrate ceramics with metals, combining each material's best properties. Progress in hot pressing-derived complex channel ceramic structures for heat exchange applications and micro-chemical reactors and challenges in the area will be discussed. Examples of specialty glass frits in SFC and Solar panels as well as bio-active glass uses in dental applications will be described.

11:30 AM

(ICACC-ECSA-030-2013) Ceramic, gas-separation membranes for advanced energy applications (Invited)

C. Lewinsohn*, Ceramatec, Inc., USA

Certain oxide materials conduct both electronic and ionic species and are called "mixed-conducting" materials. In particular, materials that conduct either oxygen or hydrogen can be used as gas separation membranes in a number of advanced energy applications. A general review of typical materials and the principles of using them for gas separation will be presented. Applications in gasification with carbon capture and sequestration, gas-to-liquids fuel processing, and hydrometallurgical refining will be reviewed. Engineering issues related to practical device design will be described. An overview and progress in current demonstration projects will also be presented. This technology development has been supported in part by the U.S. Department of Energy under Contract No. FC26-98FT40343. The U.S. Government reserves for itself and others acting on its behalf a royalty-free, nonexclusive, irrevocable, worldwide license for Governmental purposes to publish, distribute, translate, duplicate, exhibit and perform this copyrighted abstract.

Author Index

*** Denotes Presenter**

Author Index

Author Index