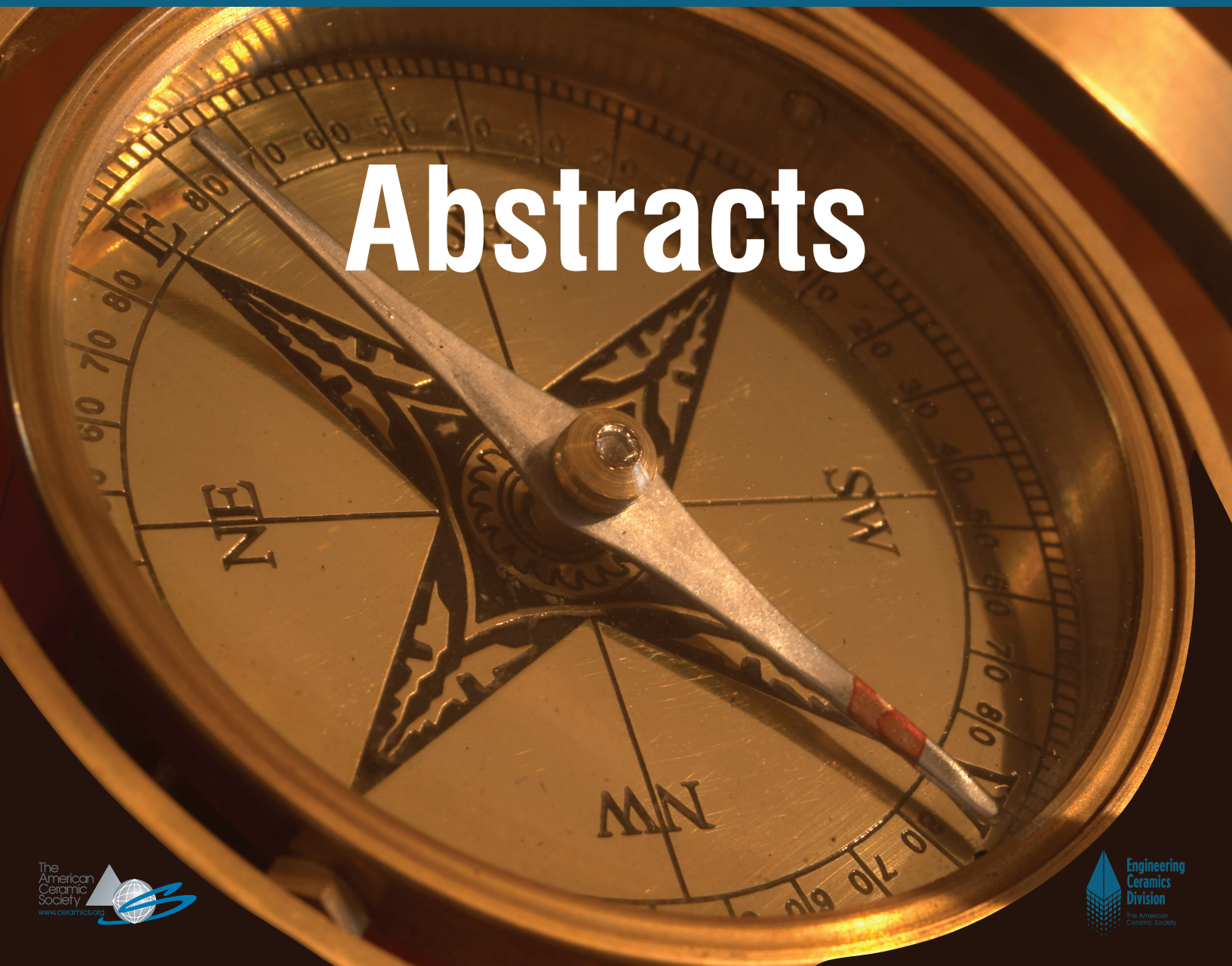
35TH INTERNATIONAL CONFERENCE AND EXPOSITION ON

ADVANCED CERAMICS AND COMPOSITES

Hilton Daytona Beach Resort & Ocean Center ✦ Daytona Beach, FL, USA ✦ Jan. 23-28, 2011

Organized by The American Ceramic Society and The American Ceramic Society's Engineering Ceramics Division



Abstracts

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Introduction

This volume contains abstracts for more than 800 presentations during the 35th 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 presenting author and the page number on which their abstract can be found.

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The American Ceramic Society

35th International Conference & Exposition on Advanced Ceramics and Composites

ABSTRACT BOOK

January 23-28, 2011
Daytona Beach, Florida

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Monday, January 24, 2011

Plenary Session

Room: Coquina Salon D
Session Chairs: Dileep Singh, Argonne National Laboratory; Tatsuki Ohji, National Institute of Advanced Industrial Science and Technology

9:00 AM

(ICACC-PL-001-2011) Thermal Protection Materials: From Retrospect to Foresight (Invited)
S. Johnson*, NASA Ames Research Center, USA

Jim Mueller after whom this award is named, had a close connection to thermal protection materials as he worked extensively on the development of what are commonly known as "space shuttle tiles". Thermal protection materials or systems (TPS) are used to protect space vehicles from the heat of reentry into an atmosphere. Although the vehicles and types of materials change with mission scenarios, the core need for efficient and reliable performance remains. The first part of this talk will address some of the history and background of these materials, and will include discussion of both reusable and ablative materials. The second part will discuss ultrahigh temperature ceramic materials (based on diborides of hafnium and zirconium) that have potential use for sharp leading edges, the issues associated with these materials, and the progress being made towards solutions. The history and examples will demonstrate the issues associated with thermal protection (and other materials): the long development times, the need to balance current applications with future needs, continue innovation, and capture knowledge.

9:40 AM

(ICACC-PL-002-2011) Carbon/Carbon Composites to Ceramic Matrix Composites: High End Applications Through Controlled Microstructure (Invited)
L. M. Manocha*, Sardar Patel University, India

Carbon/Carbon composites have been successfully used in many applications during the last four decades. Their tremendous growth potential presents the scientific and technological curiosity as well as many technical challenges, mainly because of big scope in playing with its structure and attaining exotic properties. Carbon/Carbon composites have been developed in India for aerospace and re-entry vehicles through controlled microstructure using liquid infiltration techniques. The recent development of nanomaterials, the so-called carbon nanostructures (nanofibers, nanotubes, nanoparticles, and graphene) have again renewed interest in these composites. Application of carbon nanotubes as reinforcing material is attractive due to their combined mechanical and thermal characteristics, which can improve the thermal properties of composites. This has been achieved through synthesis of multiwall carbon nanotubes (MWCNTs) or their growth on the surface of different substrates, which themselves can be used as reinforcements. These reinforcements affect the microstructure of the carbon matrix and improve thermal properties, oxidation resistance, and fracture toughness of composites.

10:40 AM

(ICACC-PL-003-2011) Opportunities for Advanced Ceramics and Composites in the Nuclear Sector (Invited)
W. E. Lee*, M. Gilbert, R. W. Grimes, Imperial College London, United Kingdom

Ceramics have been crucial to development of fission reactors particularly in UO2 or PuO2/UO2 mixed oxide fuels, in glass & glass composite high level wasteforms & in composite cements to encapsulate intermediate level wastes. Ceramics will continue to play a key role in the near-term expansion of nuclear power via next-step developments of fuels with inert matrices or in layered pebble form, & in wasteforms using alternative composite cements or single or multiphase ceramics which can host Pu & other radionuclides (RN). Longer-term advances for Generation IV reactors which will operate at higher temperatures & with higher fuel burn-up require innovative fuel developments potentially via carbides & nitrides or composite oxide fuel systems containing thermally-conducting fibres or complex layer structures. Future developments in waste treatment will be based on separation technologies for partitioning individual RN along with design & construction of RN-containing ceramic targets for inducing transmutation reactions. Opportunities also exist for ceramics in structural applications in e.g. the Very High Temperature Reactor and in fuel and tritium breeder components of fusion reactors. In all these cases, performance is limited by poorly understood radiation damage and interface controlled processes, which demands a combined modelling/experimental approach.

11:20 AM

(ICACC-PL-004-2011) Nanogenerator and Nano-Piezotronics (Invited)
Z. Wang*, Georgia Institute of Technology, USA

Developing wireless nanodevices and nanosystems is of critical importance for sensing, medical science, environmental/infrastructure monitoring and personal electronics. It is highly desirable for wireless devices to be self-powered without using battery. This is a new initiative in today's energy research for mico/nano-systems in searching for sustainable self-sufficient power sources. It is essential to explore innovative nanotechnologies for converting mechanical energy, vibration energy, and hydraulic energy into electric energy that will be used to power nanodevices. We have invented an innovative approach for converting nano-scale mechanical energy into electric energy by piezoelectric zinc oxide nanowire arrays. As today, a gentle straining can output 2 V from an integrated nanogenerator, using which a self-powered nanosensor has been demonstrated. This is a key step for developing a totally nanowire-based nanosystem. Alternatively, by substituting the gate voltage in a field effect transistor with the piezopotential creating by an external strain, we have fabricated a series of devices that rely on a coupling between semiconductor and piezoelectric properties and are controlled/tuned by externally applied force/pressure, such as diode, strain sensor and strain-gated logic unites, which are a new field called piezotronics.

S1: Mechanical Behavior and Performance of Ceramics & Composites

Fracture Mechanics, Modeling, and Testing

Room: Coquina Salon A
Session Chairs: Rajan Tandon, Sandia National Laboratories; Hagen Klemm, Fraunhofer IKTS

1:30 PM

(ICACC-S1-001-2011) Quantitative Optical Fluorescence Microprobe Measurements of Indentation and Grinding Stresses in Al2O3 and Al2O3/SiC Nanocomposites
R. I. Todd*, S. Guo, X. Huang, University of Oxford, United Kingdom

Cr3+ fluorescence microscopy enables high resolution measurements of near surface stresses in alumina-based ceramics but is complicated because much of the signal comes from below the surface. In this paper, confocal microscopy, multiple peak fitting, and the use of a suitable probe response function (PRF) are used to alleviate this problem. This was applied first to diamond grinding stresses. The mean surface stresses were compressive but on a microscopic scale the stresses were very inhomogeneous, to the extent that strongly tensile stresses were present in some regions. Modelling showed that this was the result of pullout of parts of the plastically deformed surface layer by fracture. The initiation of surface fracture therefore makes further fracture easier, a feedback mechanism which sheds light on the mild-severe wear transition. Measurements of indentation stresses showed that cracking reduced the stresses by well over an order of magnitude compared with literature models for the stresses.

This explains the small plastic zone size in ceramics cf. metals. A new model for indentation stresses is developed that accounts for radial and lateral cracking. The model agrees well with the experimental measurements. The indentation stresses in alumina and in alumina/SiC nanocomposites were the same.

1:50 PM

(ICACC-S1-002-2011) Hertzian Stress Field and Ring Crack Initiation Analysis including the Effect of Friction

R. Tandon*, Sandia National Laboratories, USA; B. Paliwal, Georgia Tech – CNRS (UMI-2958), France

We have conducted analytical modeling and finite element simulations to (a)study the Hertzian indentation problem including friction, and (b) assess the applicability of the technique to determine the fracture toughness of brittle materials. Results suggest that for dissimilar indenter/substrate material combinations, the stress intensity factor for surface crack is extremely sensitive to the friction coefficient and to the Poisson's ratio of the substrate. A correction factor, which computes the stress intensity factor for a surface crack is calculated. Experimental results on glass substrates subjected to different surface treatments and indented with WC indenters, will be presented. Results from the modeling and experiments on the applicability of the method for fracture toughness determination will be presented. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000.

2:10 PM

(ICACC-S1-003-2011) Residual Stress in All-Ceramic Zirconia-Porcelain Crown Measured By Nanoindentation

Y. Zhang, J. C. Hanan*, Oklahoma State University, USA

Residual stress has a role in the failure of crowns. The magnitude and distribution of residual stress in the crown system are largely unknown. Determining the residual stress quantitatively is challenging since the crown has such complex contours and shape. This work explored the feasibility and validity of measuring residual stress of zirconia and porcelain in all-ceramic crowns by nanoindentation. Nanoindentation was performed on the cross section of a crown for porcelain and zirconia at two critical locations, one has the thinnest porcelain and the other has the thickest porcelain. A half crown annealed at 400 °C was used as a reference sample. The residual stress can be determined by comparing the measured apparent hardness of the stressed sample with the reference sample. The nanoindentation impression images were acquired through Scanning Probe Microscope (SPM) equipped with Hysitron. The derived normal contact area value was corrected using measured real area. The magnitude of the residual stress is determined along the thickness of crowns at the two locations for both porcelain and zirconia.

2:30 PM

(ICACC-S1-004-2011) High-temperature characterization of ceramic materials by hot-hardness measurement

H. Klemm*, A. Bales, K. Nake, G. Michael, Fraunhofer IKTS, Germany

A new test facility for the measurement of the hardness at elevated temperatures up to 1500 °C in vacuum has been developed. Hot hardness can be measured with diamond indenter in Vickers and Knoop geometry with test loads between 100 p and 30 kp. A comparison of the temperature dependence of the hardness of various ceramic and metallic materials will be presented. A second interesting feature of the hot hardness test equipment was found to be the possibility to characterize the crack propagation behavior of ceramic materials at elevated temperatures. Si3N4 materials with different high-temperature potential have been tested by Vickers indentation from ambient temperatures up to 1400 °C. Higher crack extension was observed with increasing temperature up to about 1000 °C. At higher temperatures, however, the crack propagation was found to be minor; this seems to be the consequence of crack healing effects in the crack tip. A detailed interpretation of these effects will be provided based on SEM investigations of the crack propagation at elevated temperatures. Finally, correlations to dynamic fatigue experiments on bending bars of these Si3N4 materials at elevated temperatures will be presented.

2:50 PM

(ICACC-S1-005-2011) Slow Crack Growth in Coarse Gain Spinel

J. Salem*, NASA Glenn Research Center, USA

The slow crack growth properties of several spinels were investigated as part of a spacecraft windows program. Previous testing of spinel by using a Vickers indentation resulted in large scatter and poor estimates of crack growth parameters, despite the success of the technique on glass. The scatter was due to the presence of cleavage planes and contaminant formation of irregular indentation cracks. To avoid this interference, constant stress rate testing of 400 grit ground disks was used. This provided a multiplicity of sampled cracks with some being well aligned with cleavage planes. Thus, convergence to limiting flaw size was generated in each specimen, and relatively uniform strength was measured at any stress rate. Coarse grain spinel exhibited more crack growth susceptibility because extensive growth occurs on a cleavage plane rather than on a multiplicity of planes.

3:30 PM

(ICACC-S1-006-2011) Micromechanical Finite Element Simulation of Fracture Behaviour in Silicon Nitride High-Performance Ceramics

J. B. Wippler*, T. Böhlke, Karlsruhe Institute of Technology, Germany

The microstructure of ceramics has an important influence on its fracture toughness. Due to the close interactions between microsturcture and material behaviour on the microlevel, numerical calculations have to be used for a better understanding of the reinforcement mechanisms. They are related to size-, shape- and orientation-distribution of column-like crystals, strength of the intergranular phase and its thermal expansion coefficient. FEM meshes are constructed by a statistical model, taking grain growth, growth hindrance and grain resolution into account. The material behaviour is characterized by cracking and debonding of the grains. The grains are modeled as elastically transverse isotropic. The glassy phase is regarded as elastically isotropic. Cracking of grains is assumed to occure under maximum normal stresses. Debonding at the grain-boundaries is mapped by an interface model. The influence of thermal residual stresses on the fracture behaviour is examined as well. Results from structure generation, thermoelastic and fracture simulations will be presented. All mentioned effects will be incorporated into a model, which will be used for an homogenized material description.

3:50 PM

(ICACC-S1-007-2011) A Novel Proof Test for Silicon-Nitride Balls

M. O'Brien*, A. de la Cruz, The Aerospace Corporation, USA

A novel proof test has been developed for the silicon-nitride balls used in hybrid bearings. The ball is compressed diametrally between two hemispherical conforming dies, which causes the ball's equator to bulge, thereby generating a tensile hoop stress that propagates naturally occurring flaws. The flaw propagation is detected by an acoustic emission transducer. In practice, the ball is repeatedly loaded to the desired proof stress, unloaded, rotated by a small angle and reloaded until the entire ball has successively passed through the equator. The finite element technique is used to calculate the principal stresses in the ball under the applied load. For simplicity, the preexisting flaw is modeled as a half-penny crack. The principal stresses are combined with the crack's stress intensity factor to calculate the proof test's threshold for flaw detection based upon two accepted theories of mixed-mode fracture. The tested balls had preexisting naturally occurring flaws in the range of 100 to 300 micrometers. It is also shown that an angular rotation as large as 30 degrees worked well in practice.

4:10 PM

(ICACC-S1-008-2011) Mixed Mode (I/II) Fracture Behavior of Surface and Chevron Notch Cracks in Diametral Compression

K. Gopalakrishnan*, J. J. Mecholsky, University of Florida, USA

Many applications of ceramics in wear and impact environments involve tensile and shear loading. Often it is convenient to test circular disks for these applications. The diametral compression test, also known as the Brazilian disk test, is used to study the mixed mode fracture behavior of surface and chevron notch cracks in soda lime silica glass disks. The crack turning angles along with the stress intensity factors obtained using the different types of precracks are compared. The sensitivity of the surface and chevron notch type cracks to mixed mode loading is thus analyzed and compared. The mixed mode fracture surface for disks failed from surface cracks is characterized by an absence of the mist region. The twist hackle markings observed on the mixed mode fracture surfaces will be discussed in terms of markings observed in pure mode I loading.

4:30 PM

(ICACC-S1-009-2011) Fractal Geometry Applied to Failure Analysis in Materials

J. Mecholsky*, U. of Florida, USA

Failure of materials affects every aspect of research, material development and production. Fracture surfaces of all materials examined can be characterized using fractal geometry. Fractal geometry is a mathematical tool that quantitatively describes irregular surfaces. Fractal objects, such as fracture surfaces, are characterized by their fractal dimension, D, which is the dimension in which the proper measurement of a fractal object is made. A plane square with "bumps" out of the plane would have dimension, 2.D*, where D* is the fractional part of the fractal dimension. The fractal dimensional increment, D*, is directly related to the fracture energy, γ, during fracture for many materials, i.e., $\gamma = \frac{1}{2} E a_0 D^*$ where E is the elastic modulus and a_0 is a material structural parameter. These equations then provide a link to fracture mechanics and quantitative fractography. Using these tools can aid in identifying toughening mechanisms in new materials, distinguishing poorly fabricated from well prepared material and identifying stress at fracture for field failures. Examples of the application of fractal analysis in research, fracture forensics and solving production problems will be discussed. Examples of each application will be discussed in terms of fracture surface analysis and microstructural characterization.

4:50 PM

(ICACC-S1-010-2011) Protocol for Using Atomic Force Microscopy to Measure the Fractal Dimension in the Mirror Region of Fracture Surfaces

M. Strasberg*, J. J. Mecholsky, University of Florida, USA

Fractal geometry is a unique method for analyzing fracture surfaces in the mirror region of brittle materials. The fractal dimension of a fracture surface relates the tortuosity of the surface to the fracture toughness of the material. Conventional optical techniques are not applicable to the mirror region. Replacing optical techniques with atomic force microscopy (AFM) introduces numerous confounding sources of error specific to tip based microscopy, some of which are unique to the measurement of the fractal dimension: scan rate and tip effects, scan size in relation to correlation length and drift effects, direction and location of imaging, sample tilt, pixel density, and imaging mode. By utilizing variogram analysis with rectangular scans and appropriate selection of other parameters based on the feature size of the particular fracture surface, these errors can be minimized resulting in highly repeatable measurements of the fractal dimension of fracture surfaces. The fractal dimension of the mirror region is determined for soda-lime silica glass, silicon, and silicon nitride as a function of the distance from the crack origin. These results and the topography of the mirror region are compared to the mist and hackle regions. A protocol for measuring the fractal dimension of fracture surfaces in the mirror region using AFM is outlined.

5:10 PM

(ICACC-S1-011-2011) Microcantilever testing of alumina based materials

N. A. Yahya*, R. I. Todd, University of Oxford, United Kingdom

Much recent work on measuring mechanical properties on the microscale has been carried out using a wide range of different tests specimens which are then tested using a nanoindenter as a loading device. This is of great interest as it allows mechanical properties to be measured from much smaller volumes than are required for traditional mechanical tests. It is now possible to measure directly the mechanical properties associated with individual microstructural features such as grains, pores, inclusions and grain boundaries. However, most of the previous work has been on coating materials and metals. Therefore, in our study, this novel concept has been extended to measure the strength and toughness of polycrystalline alumina based materials. Focused Ion Beam (FIB) machining was carried out using 30KeV Ga+ ions to manufacture microcantilevers 15 μm by 3 μm with a triangular cross section in polycrystalline aluminas. A nanoindenter was used to apply the bending load and measure the critical value at which the beam failed, enabling the calculation of bending strength. Thermally etched beams were found to possess a mean fracture strength of ~ 5 GPa. The strengths of unetched specimens will also be presented and preliminary attempts to measure the fracture toughness of individual grain boundaries reported.

5:30 PM

(ICACC-S1-012-2011) Specimen Stress Equilibrium in SHPB Test on Ceramics at High Strain Rate

J. Yuan*, J. Ma, Nanyang Technological University, Singapore; G. Tan, DSO National Laboratories, Singapore

Uniform specimen stress and constant strain rate are critical for the validity of the stress-strain data obtained from SHPB tests on ceramics at a few thousand per-second strain rate. This paper analyzes SHPB test on an elastic specimen so as to provide guidance to achieve SHPB test of constant high strain rate and specimen stress equilibrium. One dimension model of SHPB test is expressed by the wave equation with the initial and boundary conditions. Solution of specimen stress is obtained via Fourier transform; consequently, conditions for specimen stress equilibrium and constant strain rate are derived. With any input stress wave, the equations to evaluate stress equilibrium and strain rate are provided. For the two typical input stress waves, i.e. step and linear ramp rise, stress equilibrium and strain rate are discussed. The analysis provides the results to achieve valid SHPB test on ceramics by adjustment of the specimen dimension, the bar-specimen impedance ratio and the input stress wave.

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

Thermal Barrier Coatings I

Room: Coquina Salon G
Session Chairs: Dongming Zhu, NASA Glenn Research Center; Douglas Wolfe, Penn State University

1:30 PM

(ICACC-S2-001-2011) New Developments in Thermal Barrier Coatings (Invited)

V. Shklover*, A. Bhattacharya, ETH Zurich, Switzerland

New results in synthesis and modeling of prospective TBC systems will be reported. Our strategy for finding new TBC candidate has

been discussed. Approaches and key results obtained will be discussed for TaYSZ, TiYSZ, CaSZ, SrZrO3 and SrTiO3. TaYSZ system was found to be highly tetragonal compared to 7YSZ. Higher tetragonality and defect association of smaller Ta ion and bigger Y ion in the ZrO2 lattice are responsible for the higher stability of TaYSZ system. It was found that YTaO4 forms scheelite structure at high temperature (1400 °C) and gets completely soluble (up to 22 mol%) in ZrO2 above this temperature. 20 mol% YTaO4 doped ZrO2 was found to be present as stable tetragonal phase up to 1500 °C when treated for 4 h. However, minor YTaO4 was observed in all the samples below 1500 °C. TaYSZ samples where YTaO4 was present as minor phase were not stable when treated for 600 h at 1250 °C. It completely decomposed to m-ZrO2 along with YTaO4 separation. However, TaYSZ sample, which was pre-treated at 1500 °C (when all the YTaO4 were dissolved in ZrO2), was stable upon long term annealing at 1250 °C for 600 h. In order to recognize the stable phases in this system at different temperatures, ternary phase diagram has been modeled using THERMO-CALC. In the modeled ternary diagram it was found that the tetragonal solid solution region shows a bend towards higher Yttria content.

2:00 PM

(ICACC-S2-002-2011) Processing of Thermal Barrier Coatings Systems Via Directed Vapor Deposition (Invited)

D. Hass*, B. Gogia, Directed Vapor Technologies International, USA

Thermal barrier coating (TBC) systems are pervasively used in current gas turbine engines to prolong the life of hot section airfoils (blades and vanes). In future engines, the desire for elevated engine operation temperatures is driving interest in next generation TBC systems having better thermo-mechanical durability, reduced top coat thermal conductivity / sintering rate and an increased resistance to high temperature corrosive / erosive environments. Alternative coatings and coating approaches are therefore of interest to potentially improve the performance of these multilayered coating systems. Directed Vapor Technologies International (DVTI), is currently investigating the use of an advanced electron beam vapor deposition approach, Directed Vapor Deposition (DVD), as a method for applying high quality thermal barrier coatings at high rates onto engine components. The DVD process operates in a novel processing environment that employs a supersonic gas jet to "direct" vapor atoms onto components resulting in highly efficient deposition of complex coating structures and compositions. Here, the use of this approach to deposit advanced TBC compositions, microstructures and architectures to achieve a comprehensive thermal barrier coating system that provides improved resistance to spallation during elevated temperature exposures will be discussed.

2:30 PM

(ICACC-S2-003-2011) A TEM and SANS-Study for analysis of phase and morphology of alternative EB-PVD deposited TBC-compositions (Invited)

B. Saruhan-Brings*, German Aerospace Center, Germany; V. Ryukhtin, Helmholtz Zentrum Berlin for Materials and Energy, Germany; K. Kelm, German Aerospace Center, Germany

Electron-beam physical vapor deposition (EB-PVD) of standard (PYSZ) thermal barrier coatings produces tetragonal columnar structure with anisotropic pores. Long-term stability of the ceramic top coat of TBCs can be provided through the development of new materials having ultra-low thermal conductivity, excellent phase stability and improved sintering-resistance. For this purpose two alternative TBC-compositions were produced by EB-PVD-process: Fully yttria (14 wt.%) stabilised zirconia (FYSZ) and pyrochlore (LaZr2O7) both of which yield intrinsically low thermal conductivity values. As-coated and aged samples were analysed by the Laser-Flash technique for their thermal diffusivity which were correlated with the thermal derived changes of coatings. The anisotropic nano-sized pore morphology in FYSZ- and La2Zr2O7-TBCs were analysed by small angle neutron scattering (SANS) method. Pore morphology and phase changes were investigated by advanced SANS and TEM/SEM-analysis on FIB sections, indicating that production of pyrochlore phase by EB-PVD requires some process alteration. Cubic zirconia yields anisotropic pore morphology after high temperature treatment and is present already after coating. TEM and SANS investigations indicate that the pore morphology and microstructure of EB-PVD pyrochlore and fully stabilised zirconia differ significantly from those of PYSZ.

3:20 PM

(ICACC-S2-004-2011) Thermal Conductivity of Thermal Barrier Coatings under High Pressure (Invited)

H. Wang*, Oak Ridge National Lab, USA

Thermal barrier coatings (TBCs) are used in turbine engines as heat shields to allow higher temperature operation. The immediate benefits are higher efficiency and improved engine emission. It is critical to know the thermal conductivity of the TBCs and their evolution as a function of time and temperature. Extensive studies have been conducted in this area. Current status of thermal transport properties of the TBCs will be reviewed. The effect of high pressure on thermal conductivity has not been reported, especially at high temperatures. Since TBCs are porous and the materials in the engine could experience 10-15 atmosphere pressure, thermal conductivity values of the TBCs will be higher than the ones measured at 1 atmosphere. Recently, we used a specially designed high pressure laser flash system to evaluate TBCs up to 1000°C. The high pressure system will be described and results of thermal diffusivity under high pressure will be presented. This work was supported by the High Temperature Materials Laboratory User Program sponsored by the U. S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Vehicle Technologies Program.

3:50 PM

(ICACC-S2-005-2011) Processing-Property Relationships in Plasma-Sprayed Gadolinium Zirconate

Y. Tan*, C. M. Weyant, G. Dwivedi, S. Sampath, Stony Brook University, USA

Alternative materials give the potential for achieving the enhanced thermal and mechanical properties needed for using thermal barrier coatings (TBCs) in turbine engines with increased gas stream temperatures. In order to develop viable coatings, understanding the relationship between plasma spray processing conditions and coating properties is crucial. In this work, pyrochlore zirconates and co-doped materials were fabricated by controlled plasma spray processing. Focus was given to gadolinium zirconate, which has promising properties in its bulk form. Coating process conditions have a significant effect on thermal and mechanical properties. Thermophysical properties including elastic compliance and erosion resistance, were measured to link processing parameters with coating properties. Overall the new coating materials exhibited improved phase stability and sintering resistance. The goal of this work is to better understand fabrication of alternative TBC materials and architectures toward improving thermal and mechanical performance.

4:10 PM

(ICACC-S2-006-2011) The influence of a thermal gradient on the lifetime of YSZ –based TBC Systems

R. Vassen*, D. E. Mack, A. Guignard, D. Stöver, Forschungszentrum Jülich, Germany

Often thermal barrier coatings (TBCs) are tested in isothermal furnace tests. However, in a gas turbine environment the TBCs will see a thermal gradient which might rise up to values of1 μm/K for highly loaded parts as blades and vanes. Only limited information is available on the influence of this gradient on the lifetime of the thermal barrier coatings. In the present investigation gas burner rigs have been used to simulate different gradients in atmospherically plasma sprayed TBCs. By adjusting independently cooling air and gas supply of the burner it was possible to fix different surface temperatures

while keeping the bond coat temperature rather constant. The surface temperatures applied were in the range between 1200 and 1400°C. In addition, different microstructures of the APS topcoat have been investigated. For all topcoats a considerable reduction of lifetime with increasing thermal gradient was found. Microstructural investigations, hardness tests, and sintering experiments on free-standing coatings indicate a pronounced sintering in the hot regions. A simple model will be presented which can explain the reduced lifetime as a result of the higher energy release rate in the coatings with a high thermal gradient.

4:30 PM

(ICACC-S2-007-2011) Dependence of thermal conductivity on gas pressure for thermal barrier coatings in power generation gas turbines

P. C. Howell*, U. Rettig, S. Lampenscherf, Siemens AG, Germany; A. Kulkarni, Siemens Energy Inc, USA

Thermal barrier coatings (TBCs) are made of materials with low intrinsic thermal conductivity, which are applied using air-plasma spraying in order to create a porous microstructure, increasing the phonon scattering and so further reducing the thermal conductivity. However, this porosity means that the gas in the pores also makes a contribution to the thermal conductivity, which is expected to depend on the gas pressure. Modern power generation gas turbines operate at pressures in excess of 20 bar, but so far thermal conductivity data has only been available for ambient pressure. We report for the first time the thermal conductivity of the standard material air-plasma sprayed 8SYZ as a function of gas pressure up to 11 bar, measured using a specially adapted laser-flash apparatus. We investigate how the pressure-dependence varies in samples which were heat treated at different temperatures and so have different characteristic pore sizes, as confirmed by examination of microscope cross-sections. We also examine the relationship to mechanical properties of the same samples. We find that the thermal conductivity of TBC material is significantly higher under gas pressures typical of turbine operating conditions than under ambient pressure. This should be taken into account in gas turbine design, to ensure that the TBC provides the required thermal insulation.

4:50 PM

(ICACC-S2-008-2011) Opportunities for Improved TBC Durability in the CeO_2-TiO_2-ZrO_2 System

J. A. Krogstad*, M. Lepple, C. G. Levi, University of California, Santa Barbara, USA

The mechanical integrity of current thermal barrier coatings is a limiting factor for the operating temperature and lifetime. However, improving the toughness beyond that of traditional YSZ coatings often comes at the expense of other material properties such as phase stability. This is due largely to the fact that most conventional dopants stabilize the cubic phase rather than the tougher tetragonal phase. In this work two isovalent cations are employed, one undersized and one oversized relative to the host cation. Specifically, zirconia has been doped with titania and ceria. Codoping not only stabilizes the tetragonal phase but also results in increased tetragonality. The toughness of the material is thus improved, presumably owing an increased contribution of ferroelastic switching. This has been demonstrated for a range of compositions that are not subject to the deleterious monoclinic phase transformation.

5:10 PM

(ICACC-S2-009-2011) Thermophysical properties and hot corrosion behavior of (Sm1–xYbx)2Zr2O7 thermal barrier oxides in air

J. Ouyang*, S. Li, Z. Liu, Y. Zhou, Harbin Institute of Technology, China

(Sm1–xYbx)2Zr2O7 (x = 0, 0.5, 1.0) powders are prepared by chemical-coprecipitation and calcination method, and then pressureless-sintered at 1700°C for 10h. Sm2Zr2O7 has a pyrochlore-type structure, while SmYbZr2O7 and Yb2Zr2O7 have a defect fluorite-type structure. Thermal expansion coefficient and thermal diffusivity of (Sm1–xYbx)2Zr2O7 are studied by a high-temperature dilatometer and a laser flash diffusivity technique from room temperature to 1400°C. Hot corrosion tests between (Sm1–xYbx)2Zr2O7 and three corrosive agents including V2O5, Na2SO4, and a V2O5+Na2SO4 mixture, are carried out from 600 to 1100°C for 2h and 8h in air, respectively. Different reaction products of ZrV2O7, LnVO4 and m-ZrO2 are identified depending upon the hot corrosion conditions, for example, ZrV2O7 and corresponding LnVO4 at 600oC for 2h and 8h, namely SmVO4, (Sm,Yb)VO4, YbVO4, respectively; ZrV2O7, m-ZrO2 and LnVO4 at 700oC for 2h; m-ZrO2 and LnVO4 either at 800~1100oC for 2h or at 700~1100oC for 8 h. No new products are identified on Na2SO4-coated (Sm1–xYbx)2Zr2O7 at 900~1100oC. However, m-ZrO2 and corresponding LnVO4 are found after (Sm1–xYbx)2Zr2O7 exposed to Na2SO4+V2O5 (mole ratio = 1:1) at temperatures of 600~1100oC. Those results are explained based on phase diagram theory, and the principles for crystal growth are used to illustrate the morphologies of reaction products LnVO4.

5:30 PM

(ICACC-S2-010-2011) Evolution of thermal properties of nanostructured tetragonal yttria-stabilized zirconia with high-temperature aging

A. M. Limarga*, Harvard University, USA; J. Alaniz, J. E. Garay, University of California, USA; D. R. Clarke, Harvard University, USA

The use of 7 wt.% yttria-stabilized zirconia (7YSZ) for thermal barrier coatings (TBC) is based on the superior fracture toughness of the metastable tetragonal phase and its intrinsic low thermal conductivity due to the high concentration of oxygen vacancies present in the material. Even lower thermal conductivity can be achieved by incorporating porosity in the coating during deposition. During high-temperature service, the microstructure and the porosity evolve, leading to the degradation of the thermal protection efficiency of the coating. In this work, we determine the evolution of the thermal properties of the material by evaluating fully dense nanocrystalline tetragonal zirconias prepared by Electrical Current Assisted Densification Process (commonly referred to as Spark Plasma Sintering method). Measurements of thermal properties, coupled with Raman spectroscopy revealed how the properties evolve during high temperature aging due to the growth of the nano-sized grains and changes of point defect arrangement in the structure. These results provide an insight on how to design a new generation of TBC with a superior performance and high temperature stability.

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(ICACC-S2-011-2011) Structures and Thermo-Physical Properties of (LaxGd1-x)2Zr2O7 Pyrochlore Systems for Thermal Barrier Coatings (TBCs)

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

With increasing operating temperatures of gas turbines for higher efficiency, the application of thermal barrier coatings (TBCs) to those parts becomes necessary. Yttria-stabilized zirconia(YSZ) has been one of the most commonly used materials for TBCs due to its low thermal conductivity and thermal compatibility or/and stability with metallic substrates. As thermal requirements are going severe, research on alternatives to YSZ for TBC are being intensively carried out. In this study, phase structures and thermo-physical properties of (LaxGd1-x)2Zr2O7 pyrochlore systems are investigated. (LaxGd1-x)2Zr2O7 systems are comprised by selecting La3+ /Gd3+as A-site ions and Zr4+ as B-site ions in A2B2O7 pyrochlore structures. For the pyrochlore phases among (LaxGd1-x)2Zr2O7 compositions, thermo-physical properties, such as thermal conductivity, thermal expansion coefficient, are examined.

The possibilities of these pyrochlore phases for TBC application are also discussed.

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(ICACC-S2-012-2011) Comparing the Thermal Properties of Lanthanide doped YSZ Films Deposited by APS and EB-PVD for Thermal Barrier Coatings

Y. Oh*, K. Kwak, K. Choi, B. Shim, Y. Yang, S. Kim, S. Lee, H. Kim, KICET(Korea Institute of Ceramic Engineering & Technology), Republic of Korea

Turbines, typical applications of TBCs, operating at higher temperature can improve the energy efficiency and performance. The EB PVD method has been studied as a candidate to fabricate thermal barrier coatings (TBCs) for its superior thermo-mechanical stability at higher operating temperature condition. Furthermore the rare earth zirconate ceramics have also been studied for replacing YSZ due to their lower thermal conductivity and structural stability. In this study, Y2O3 stabilizes ZrO2(YSZ) and Lanthanide doped ZrO2(LZO) were coated on the nickel based super-alloy and graphite sheet by two different coating methods, air plasma spray(APS) and electron beam physical vapor deposition(EB-PVD). Graphite sheet used for fabricate free-standing film samples. To obtain the reliable thermal conductivity of films, we tried to compare the thermal conductivities of as-received film on substrate and free standing film using laser flash method (LFA) up to 1200°C under the N2/H2 gas mixtures.

S3: 8th International Symposium on Solid Oxide Fuel Cells (SOFC): Materials, Science and Technology

Cell and Stack Development

Room: Coquina Salon E
Session Chairs: Narottam Bansal, NASA Glenn Research Center; Prabhakar Singh, Connecticut Global Fuel Center

1:30 PM

(ICACC-S3-001-2011) Recent development of SOFC cell and stack at NTT (Invited)

R. Chiba*, NTT, Japan

NTT is a heavy user of electric power accounting for 1% of Japan's comartial electric power consumption. Most of the power is consumed by data centers and central offices, which are located in the centers of cities. We have been investigating a medium scale SOFC system (several kW - several hundred kW) for base load power generation in such facilities, which can contribute to a reduction of CO_2 emissions. We developed a pinhole free anode supported cell (120mm in diameter) with an alumina doped ZrO_2-Sc_2O_3 (SASZ) electrolyte, an $LaNi_{0.4}Fe_{0.6}O_3$ (LNF) cathode and a Ni-SASZ anode. LNF and SASZ were developed by NTT. LNF has several merits including high electrical conductivity, high thermal expansion compatibility with zirconia electrolyte and very high resistance to chromia poisoning. To improve the cathode performance, a composite active layer consisting of LNF and $Ce_{0.9}Gd_{0.1}O_{1.95}$ is placed between the electrolyte and the LNF current collection layer. This prevents the LNF from reacting with zirconia ($La_2Zr_2O_7$ forming reaction). The cell was tested at 800°C for 6000h and exhibited good voltage retention (-0.4%/1000h) at 0.4A/cm^2. We also fabricated a stack with 40 cells and metallic interconnectors. It operated stably for more than 400h at 800°C with humidified CH_4 (S/C=3.0) fuel (Ufuel=60%) and air (Uair=30%). The maximum efficiency of the stack was 64% (DC, LHV) at Ufuel=85%.

2:00 PM

(ICACC-S3-002-2011) US Department of Energy SECA Program – Overview and Accomplishments (Invited)

S. D. Vora*, US Department of Energy, USA

Solid state Energy Conversion Alliance (SECA) program objectives and recent accomplishments will be presented and discussed. Technology highlights ranging from advanced cell component development to modular stack testing will be described. Systems level technology challenges will be examined and development trend will be reviewed.

2:30 PM

(ICACC-S3-003-2011) Thickfilm and multilayer ceramic technology for innovative fuel cell systems (Invited)

A. Michaelis*, Fraunhofer Institute, Germany

Due to their broad spectra of favourable properties high performance ceramic materials offer enormous potential for product innovation in the field of energy conversion. The joint application of structural and functional ceramic technology allows for unique combination of electronic, ionic (electrochemical) and mechanical properties enabling for development of new highly integrated micro- mechanical systems (MEMS). For this, we apply hybrid and multi layer ceramic technologies such as LTCC (low temperature cofired ceramics) and HTCC (high temperature cofired ceramics). We present a fully integrated PEM (polymer electrolyte membrane) fuel cell system completely manufactured in LTCC technology. For higher power applications in the kW range ceramic SOFC (solid oxide fuel cell) systems are favourable. We apply HTCC related technology for their demonstration. Examples for fabrication of robust electrochemical MEA (membrane electrode assemblies), glass seals and contact interlayers are given. In running long term life tests we operated SOFC stacks for more than 12.000 h with degradation rates below 0.5 % per 1000 h. Both fuel cell types, PEM and SOFC have reached a promising level of maturity and are currently close to commercialization.

Novel Cell/Stack Design and Processing

Room: Coquina Salon E
Session Chairs: Prabhakar Singh, Connecticut Global Fuel Center; Narottam Bansal, NASA Glenn Research Center

3:20 PM

(ICACC-S3-004-2011) Production of current collector supported micro – tubular solid oxide fuel cells with sacrificial inner core

R. De la Torre Garcia, M. Casarin, V. M. Sglavo*, University of Trento, Italy

Micro – tubular solid oxide fuel cells (SOFCs) are excellent candidates for mobile applications. Characteristics as thermal stability and high volumetric power density are enhanced when the diameter of the cell is scaled down. However putting in place a current collector in small tubes (< 2 mm diameter) becomes difficult and sometimes ineffective. Several materials and methods have been proposed to improve the effectiveness of current collectors on the efficiency of micro – tubular cells. An internal straight metal wire within the hole or coiled around the end(s) of the cells are the most frequently used configurations. In the present work, micro – tubular SOFCs with sacrificial inner core and supported by the current collector as support were produced and characterized. A nickel wire was coiled on commercial pencil leads using an engine to regulate the number of turns per centimeter. Dip coating was used to deposit the anode and subsequently the electrolyte layer from ceramic slurries based NiO – YSZ and YSZ respectively. Half cells were hold at 800°C for 1 h in air followed by sintering at 1380°C for 2 h in argon atmosphere. The cathode consists of two layers of LSM – YSZ composite and LSM pure co-sintered at 1150°C. In this way complete cells with less than 2 mm diameter and 35 mm length with a cathode active area of about 1 cm2 were produced.

3:40 PM

(ICACC-S3-005-2011) Novel Planar Concept for SOFC

A. Demin*, H. Nabielek, D. Bronin, Solid Cell Inc, USA; S. Ghosh, RocCera LLC, USA

Ceramic materials utilized for a solid oxide fuel cell (SOFC) allow a wide range of geometrical designs (tubes, plates, boxes). The single cells can be realized with a variety of materials and manufacturing processes. Since the 1980s, SOFC technology has been developed at the Institute of High Temperature Electrochemistry in Ekaterinburg, Russia. Solid Cell Inc was founded in 2006 in New York to commercialize the novel SOFC technology, with early applications targeting kW-class SOFCs for remote power generation. In the conventional planar SOFC design, high standards are required in manufacturing and quality control to guarantee robustness and durability. The main problems of the planar design are great temperature difference across the cell, irregular gas distribution and large sealing perimeter. Tubular SOFCs do not have these disadvantages, but they are inherently expensive due to the required manufacturing methods. Solid Cell has patented a new architecture of a single cell representing the planar cell "compressed" into a box where the footprint of a 50cm2 cell is reduced to 8cm2 with the same power. This is called the Modified Planar Cell or MPC. Low cost CIM technology is used to produce MPCs, with ongoing work funded by NYSERDA. A mini-stack of 3 MPCs was tested for 500 hrs. Its characteristics are close to the rated performance and will be discussed, along with an overview of the process for low cost, high volume manufacturing.

4:00 PM

(ICACC-S3-006-2011) Liquid Tin Anode Advanced Cell Development Performance for Direct Fuel Conversion of Liquid and Solid Fuels

M. Koslowske*, J. Brodie, T. Tao, M. Slaney, L. Bateman, CellTech Power, LLC, USA

CellTech Power's direct fuel Liquid Tin Anode-Solid Oxide Fuel Cell (LTA-SOFC) has been operated on carbonaceous fuels without fuel processing or de-sulfurization. Direct JP-8 and direct solid fuel (coal and biomass) have been the focus of development over the last several years. For complex liquid fuels such as JP-8, the LTA-SOFC has shown high performance 170 mW/cm^2 and high efficiencies >30%. Current efforts are focused on single cell performance in terms of thermal cycling (> 100), longevity (> 1000 hrs), weight reduction and building of direct JP-8 stacks. Direct solid fuel work continues to address the contaminant interaction with the liquid tin. A new capability to feed solid fuel into the test chamber has been added to extend test times and measure performance and efficiency. In this presentation, the performance of the LTA-SOFC on JP-8 in single cell and stack configurations will be presented. In addition, solid fuel performance on internally gasified coal, direct coal on liquid tin and direct gasified bio-mass (bio-char, switch grass and willow/poplar, etc.) will be introduced. Finally, an update of the tin anode contamination testing will be presented illustrating the ability of the LTA-SOFC system to operate in the presence of significant concentrations of fuel-borne contaminants such as sulfur and vanadium.

4:20 PM

(ICACC-S3-007-2011) Low Cost Process for SOFC Components (Invited)

M. Han*, Z. Liu, Z. Lei, S. Song, China University of Mining and Technology, Beijing, China

Solid oxide fuel cell (SOFC) develops very quickly now, but the cost is one of the bottleneck for its commercial. Lowering the manufacturing cost of SOFC components is one of the best ways for it. Therefore, the low temperature sintering and co-firing process of components are great importance. By controlling the sintering schedule, the submicron yttria stabilized zirconia (YSZ) electrolyte with high ionic conductivity can be densely sintered at 1200~1250 oC. With Co2O3 and Li2O as the sintering additive, the gadolinia doped ceria (GDC) can be densely sintered at 950 and 800 oC, respectively. Based on the results, traditional NiO-YSZ anode-supported and LSM-YSZ cathode-supported half cell with YSZ electrolyte dense film, the novel porous NiO-YSZ(GDC) anode/dense YSZ(GDC) electrolyte/porous YSZ(GDC) matrix tri-layer or porous YSZ(GDC)/dense YSZ(GDC)/porous YSZ(GDC) trilayers were fabricated at low temperature of 1200~1250 oC. The SOFCs exhibited high performance at intermediate temperature. Furthermore, the low sintering methods show great potential prospect for metal-supported SOFCs, ceramic interconnects and protective coatings of alloy interconnects.

4:50 PM

(ICACC-S3-008-2011) Advanced Manufacturing Technology for Solid Oxide Fuel Cells

N. H. Menzler*, W. Schafbauer, R. Mücke, R. Kauert, O. Büchler, H. Buchkremer, D. Stöver, Forschungszentrum Jülich, Germany

SOFCs suffer entering market due to firstly the manufacturing costs of the components and secondly from degradation rates. FZ Jülich has been working on SOFC for approx. 20 y. The focus of the last years was the development of high-power density cells, reduced degradation of SOFC stacks and the introduction of industrial-applicable manufacturing technologies. Typical ASCs were manufactured by tape-casting the support and screen printing of the functional layers. At IEF-1 a new manufacturing technology was introduced. The complete half cell was tape cast, but in reverse order. This means that firstly the electrolyte is cast, then the anode is cast on the electrolyte, dried and afterwards the substrate is cast on the double layer system. The half cell is then cut in green state and sintered. By adapting carefully the powders used for the functional layers and the substrate also the "ironing step" can be omitted. Thus the complete cell is producible by casting the electrolyte, the anode and the substrate on each other, cutting, sintering to electrolyte gastightness and afterwards cathode coating by screen printing followed by a final sintering step. Manufacturing of such cells for single cell and stack testing revealed appropriate electrochemical results. Due to relatively thick electrolyte and anode (~ 20µm each) the power densities are reduced by approx. 10-20% in comparison to state-of-the-art ASCs.

5:10 PM

(ICACC-S3-009-2011) Reactive magnetron sputtering of dense electrolyte layers for intermediate temperature SOFC application

R. Nédélec*, S. Uhlenbruck, D. Sebold, V. Haanappel, H. Buchkremer, D. Stöver, Forschungszentrum Jülich GmbH, Germany

The efforts to increase the performance, longevity and reliability of solid oxide fuel cells (SOFC) have led to a stepwise reduction of the operating temperature to the intermediate temperature range of 600 to 800°C. In order to compensate the associated decrease in performance, which is amongst others due to the reduced oxygen conductivity of the 8YSZ electrolyte, efforts are being made to considerably reduce the electrolyte's thickness well below 1 µm. Previous results by Wanzenberg et al. have shown that bias-assisted reactive DC magnetron sputtering was capable of depositing dense and gastight layers around 5 to 10 µm thickness. In the present work this technology was further optimised to deposit ~1 µm thin layers of fully yttria stabilised zirconia (8YSZ) of comparable quality on warm-pressed ceramic anode substrates for solid oxide fuel cells (SOFC). These substrates comprise an anode functional layer deposited by vacuum slip casting. The morphology as well as the gastightness of the electrolyte layers were studied in dependency of the applied bias power. The analysis of the results showed a net amelioration of the properties of the 8YSZ layer with increasing bias power. Finally, SOFCs were evaluated with respect to their electrochemical performance.

5:30 PM

(ICACC-S3-010-2011) Characteristics of Thin Films for SOFC Prepared by Aerosol Deposition Method

D. Park*, J. Choi, Korea Institute of Materials Science, Republic of Korea; B. Seong, RIST, Republic of Korea; J. Choi, B. Hahn, J. Ryu, W. Yoon, J. Kim, Korea Institute of Materials Science, Republic of Korea

Aerosol deposition (AD) has been known as a novel method for making dense ceramic films at room temperature. It has many advantages including a high deposition rate, easy control of chemical composition of the film, a quite strong adhesion/cohesion between the film and a substrate. One of the biggest merits of AD is that dense ceramic films can be made at room temperature without any further heat treatment for densification. During "conventional fabrication" of SOFC, the components were exposed to a high temperature for sintering, and that often caused degradation of the cell performance. AD has been used for depositing dense LSM, LSCF and LNO films on a ferritic stainless steel for oxidation protection. Since AD produced dense ceramic films, it was used for making other elements of SOFC cells. In this presentation, the microstructure and performance of ceramic films prepared by AD are introduced.

S4: Armor Ceramics

Phenomenology and Mechanics of Ceramics Subjected to Ballistic Impact I

Room: Coquina Salon D
Session Chair: Jeffrey Swab, US Army Research Lab

1:30 PM

(ICACC-S4-001-2011) Nonlinear Granular Protectors (Invited)

C. Daraio*, California Institute of Technology, USA

We study the nonlinear dynamic response of ordered granular crystals to understand how stress waves propagate in highly nonlinear, heterogeneous media. Building from well-studied local phenomena, including the nonlinear Hertzian contact interaction between spheres, we create complex global systems based on geometrically ordered granular particles to achieve unprecedented mechanical properties such as anomalous reflections of compressive waves and tunable acoustic band gaps. The presence of a strong nonlinearity allows us to design new composite materials capable of trapping impulsive energy and vibrations, bending and redirecting stresses and dispersing shock energy. The work is primarily experimental and includes elements of theory and numerical calculations for validation and design. The ultimate goal is to create solid protective systems with tunable dynamic responses that exhibit resonances, dispersion and localization phenomena, acoustic band gaps, and compact discrete waves.

2:00 PM

(ICACC-S4-002-2011) Influence of scale and confinement on the transition from interface defeat to penetration (Invited)

P. Lundberg*, R. Renstrom, O. Andersson, Swedish Defence Research Agency, FOI, Sweden

A large number of interface defeat experiments in thick ceramic targets have been published by various researchers. Unconfined as well as confined and pre-stressed targets in various test scales have been used. An observation is that confinement and pre-stress seems to become less important as the impact test scale becomes smaller. A small scale unconfined target can show similar response as a heavily confined large scale target. A hypothesis is that this behaviour is related to the formation of a cone shaped crack close to the impact zone. Since the crack resistance of the ceramic material increases with decreasing scale, in contrast to the otherwise scale-invariant elastic stress field, the extension of the cone crack to a critical size will occur at higher impact velocities as the scale decreases. A confinement will suppress the growth of the cone crack since the radial compressive stress decreases the driving stress. In order to get more data on the influence of scale and confinement on the transition from interface defeat to penetration, a set of impact experiments in different scales and with different confinement thicknesses have been performed. The experimental procedures are presented and the results are compared to a model for the influence of scale, radial prestress and fracture toughness on the cone crack growth during interface defeat.

2:30 PM

(ICACC-S4-003-2011) 2011 Overview of the Development of Ceramic Armor Technology: Past, Present and the Future

W. A. Gooch*, US Army Research Laboratory, USA

The development and fielding of ceramic armor technology has accelerated with the requirements to provide high ballistic performance using lightweight technology for a wide range of military platforms and applications. This overview paper will expand on presentations given at the 2001 PAC RIM IV Conference in Hawaii and the 2006 30th International Conference on Advanced Ceramics at Coco Beach, examining the history of the development of ceramic armor technology from the past to the present with an emphasis on the primary evolution and developments that advanced the technology. The last portion of the paper will discuss the future direction of this technology, particularly the design issues for emerging applications as seen by the author over the last 40 years.

3:10 PM

(ICACC-S4-004-2011) Characterization of Subsurface Damage Zone in SiC and Si_3N_4 Ceramics with Static and Dynamic Indentation (Invited)

J. Kim, Research Institute of Industrial Science & Technology (RIST), Republic of Korea; D. Kim*, KAIST, Republic of Korea

Silicon carbide (SiC) and Silicon nitride (Si_3N_4) are the most successful engineering ceramics, owing to a favorable combination of properties, including high strength, hardness, and freacture toughness and low thermal expansion coefficient. However, the impact damage behavior of SiC and Si_3N_4 ceramics has not been widely characterized. In this work, 'static' sphere indentation and 'dynamic' explosive indentation were conducted to characterize the impact damage behavior of SiC and Si_3N_4 ceramics with various microstructures and sintering additives. In SiC, the effect of rare-earth oxides, the typical sintering additives, on subsurface damage upon static and dynamic indentation was studied. In Si_3N_4, 3 grades with different grain size and shapes (fine-equiaxed, medium and coarse-elongated) were prepared. In order to observe the subsurface damage zone, a bonded-interface technique was adopted. Subsurface evolution of the specimen was then characterized extensively using optical microscopy, SEM, and TEM. In case of static indentation, examination of subsurface damage reveals the competition between brittle and ductile damage modes. Dynamic indentation, however, induces a massive subsurface yield zone that contains extensive micro-faults. It is suggested that the grain boundary phase plays an important role in dynamic fracture as well as in static fracture behavior of ceramics.

3:40 PM

(ICACC-S4-005-2011) Windows for spacecraft and military vehicles (Invited)

D. A. Shockey*, SRI international, USA

Windows for spacecraft and military vehicles have similar requirements in that both must provide visual access to surroundings and both must resist catastrophic failure from impacting projectiles. But whereas a ground vehicle window must resist penetration by relatively massive, slow moving projectiles designed to penetrate, windows on a space vehicle must resist small cracks produced by tiny

particles impacting at hypervelocities. Thus window materials are selected and configured differently to achieve window integrity. This talk contrasts and compares ground and space windows and discusses measures taken to succeed in their respective and very different threat environments. Underlying these measures is the common need to understand the mechanisms and evolution of impact damage.

4:10 PM

(ICACC-S4-006-2011) Impact Strength of Glass for Armor Applications (Invited)

X. Nie, H. Park, W. W. Chen*, Purdue University, USA

Glass is widely used for transparent armor applications due to its high strength and low cost. Efficient designs of armor structures with glass require accurate description of the mechanical behavior of glass under impact loading conditions. In this presentation, the strengths of two common glasses, borosilicate and soda lime, are experimentally examined over wide ranges of loading rates, stress states, surface conditions and temperatures. The loading rates were varied from 0.7 MPa/s to 4×10^6 MPa/s. The stress states include uniaxial compression, compression/shear, four-point bending and equibiaxial bending. The surface conditions were controlled through mechanical polishing and chemical etching. The temperatures were varied from room temperature to near melting temperature. For material properties, quasi-static experiments were performed with a servohydraulic machine, whereas the dynamic experiments were conducted with modified Kolsky bars. Furthermore, the interaction of a dynamic crack with an interface in the glass was imaged and analyzed.

4:40 PM

(ICACC-S4-007-2011) Post-mortem analysis of fragments from SiC ceramics after ballistic test

S. Ghosh*, H. Wu, Loughborough University, United Kingdom

Armour ceramics could fail during ballistic impact through severe fragmentations. Most impact energy is likely absorbed through cracking in multi scales and ductile deformation. By analyzing the footprints of features of fracture and ductile deformation, it is possible to reconstruct the order of events and processes involved in failure of armour ceramics. SiC ceramics are widely used as shielding part of armours, but there is yet no widely agreed consent on factors/mechanisms that govern their ballistic resistance. In this study, Hexology SA SiC was shattered under very high strain rate ballistic impact, and electronic microscopy techniques, including cross-sectional TEM, were used to identify, analyse and measure any possible microstructure features brought by SiC fragments with different sizes. It was found that the primary mode of fracture was transgranular, but a rather complex cleavage path was developed in micro-scale with the accompany of ductile deformation in much finer scale. Other fracture modes were also noticed and examined. The extracted information opens a possibility of reconstructing the failure of SiC ceramics during ballistic impact with an understanding about the mechanisms.

5:00 PM

(ICACC-S4-008-2011) Spall Strengths of Two Silicon Nitrides

D. Casem*, D. Dandekar, US Army Research Laboratory, USA; V. Prakash, Y. Motoyashiki, Case Western Reserve University, USA; E. Sato, Japan Aerospace Exploration Agency, Japan

Silicon nitride (Si3N4) due to its mechanical properties, especially strength, toughness, wear resistance, excellent corrosion resistance, and exceptional thermal shock behavior has found applications in diverse industries such as aerospace, automotive, electronic, metal and mineral processing, machining, petrochemical etc. In this paper, we present results of shock wave experiments performed to determine the effect of compressive shock duration on the variation in the magnitudes of spall strengths of two varieties of silicon nitrides, SN282 commercially marketed by Kyocera and AS800 produced by Honeywell. The main difference between these two materials is the additives used in producing these two materials, i.e., Lutetia in SN282 and Lanthena in AS800. Two extreme compressive durations selected for these experiments were 0.18 and 0.9 microseconds. The magnitudes of shock induced stress deformed silicon nitrides elastically only or both elastically and inelastically. Thus the history of compressive pulse could be related to the trend in the generation of defects during the compression and release under shock induced wave propagations influencing the spall strengths in these two silicon nitrides.

5:20 PM

(ICACC-S4-009-2011) Deformation and fracture processes in alumina samples indented at high and low strain rates

C. J. Dancer*, H. M. Curtis, S. Bennett, S. Falco, C. R. Siviour, N. Petrinic, R. I. Todd, University of Oxford, United Kingdom

Conclusions from impact tests on alumina for armour ceramics can be limited by complete destruction of the specimen in high velocity impacts or by the use of a limited range of materials. In this work alumina discs with varying glass content, purity, density and grain size were impacted by sharp tungsten carbide projectiles accelerated to sub-ballistic speeds low enough to avoid complete destruction of the specimen. Material response during impact was recorded using high speed photography and modelled using finite elements. Similar tests were carried out under quasi-static conditions using the same projectiles. Post-test characterisation included optical profilometry, scanning electron microscopy and Cr^{3+} fluorescence mapping of the residual stress and plastic deformation in the impacted region. The microstructures and properties of the alumina samples were characterised by standard methods, including dynamic compression testing. Microsections across impact sites showed features characteristic of quasi-static indentations. Considerable plastic deformation and residual stress were evident in the fluorescence maps. There were clear differences in the nature and extent of damage between the different ceramics used and comparison of the materials, their characteristics and the modelling results was used to develop an improved understanding of the impact resistance of alumina-based ceramics.

5:40 PM

(ICACC-S4-010-2011) Damage Propagation Due to Interacting Vickers Indentations on the Basal (c) and Pyramidal (a) Planes of Single Crystal Sapphire: Implications to Multi Hit Resistance

E. J. Haney, G. Subhash*, University of Florida, USA

Induced cracking due to interacting Vickers indentations on EFG sapphire along the c and the a crystallographic axes is investigated. A damage threshold map is proposed describing the minimum radial separation without crack interaction between two sequential indentation sites. The results indicate a damage threshold map with two fold symmetry for indentations on the a-plane and 3 fold symmetry for indentations on the c-plane. Among the planes investigated, a-plane indentation sites demonstrated the highest interaction sensitivity when aligned with the m-axis and the lowest interaction sensitivity when aligned with the c-axis. The c-plane indentation interaction was highest when aligned in the a-axis direction while lowest when aligned in the m-axis direction. The modes and severity of damage induced by interacting crack systems will be discussed along with the implications to resistance to multi hit capability and residual interface defeat capacity at various relative orientations are discussed. Finally, numerical analysis is employed to rationalize the observed crack interactions.

S8: 5th International Symposium on Advanced Processing and Manufacturing Technologies for Structural and Multifunctional Materials and Systems (APMT) in honor of Professor Katsutoshi Komeya

In Honor of Professor Komeya

Room: Coquina Salon B
Session Chairs: Hasan Mandal, Anadolu University; Makio Naito, Osaka University

1:30 PM

(ICACC-S8-001-2011) Half Century Research Life on Nitride Ceramics (Invited)

K. Komeya*, Yokohama National University, Japan

The Author belonged to Toshiba Corp. (1962-88) and Yokohama National University (1989-present). He started research on nitride ceramics in Toshiba R&D Center, Japan, in 1963. In his half century research life on nitride ceramics, especially silicon nitride (Si_3N_4) and aluminum nitride (AlN), he has experienced four categories such as (1) seeds innovation, (2) development of high reliable nitride ceramics, (3) applications development, and (4) fundamental studies based on manufacturing and powder processing. In the meanwhile, he was involved with government projects, Fine Ceramics and Synergy Ceramics, and ISO Standardization of fine ceramics. He has made contributions to several world's first innovations on the both nitrides, among which the discovering rare earth compounds as excellent sintering aids is the most valuable seeds innovation. Since then, Y_2O_3 doped Si_3N_4 and AlN have been recognized as standard materials in both ceramics and have been employed in practical applications worldwide, which especially involved AlN as heat sink substrate and Si_3N_4 as wear resistant parts such as bearing balls. In this presentation, the author will introduce the above important activities in the (1) to (4) categories. In particular, seeds innovation and applications development, some of which have been achieved by the fruit of "SERENDIPITY", will be focused.

2:00 PM

(ICACC-S8-002-2011) Interfacial Adsorption Behavior of Rare Earths in Si3N4 Ceramics and The Impact on Microstructure Evolution (Invited)

P. Becher*, Oak Ridge National Laboratory, USA

Anisotropic grain growth can be used to generate a self-reinforced microstructure in ceramics that can significantly diminish the effects of brittle behavior. Anisotropic grain growth in Si3N4 ceramics containing rare earth oxides is known to vary with the size of the RE ion. Theoretical studies first predicted that there would be differences in the preference for each RE to segregate to the high nitrogen β-Si3N4 grain surfaces (e.g., La) versus to the high oxygen multigrain pockets (e.g., Lu), which was confirmed experimentally. The predicted specific adsorption sites on the prismatic grain surfaces for each RE were confirmed by a series of atomic-resolution STEM studies. Further STEM observations supported the predicted stability of the RE attachment. These findings revealed that both the α to β transformation and the growth rates normal to the prismatic plane, which are both attachment limited, decreased as the extent of RE adsorption increased. The observed differences in RE adsorption behavior remains the same regardless of other additives. The rare earth effect on both the transformation and grain growth anisotropy also are similar except where SiO2 is added. In this case, an extremely viscous liquid phase is formed during densification that leads to diffusion- as well as attachment-, limited transformation and grain growth processes.

2:20 PM

(ICACC-S8-003-2011) Novel Synthetic Routes of Ceria Porous Spheres for Catalytic Application (Invited)

J. Hojo*, M. Inada, N. Enomoto, Kyushu University, Japan

CeO_2 has been studied as automobile catalyst because of its oxygen absorption and release ability. However, the oxygen storage capacity (OSC) is limited owing to lattice distortion caused by oxygen release. To relax the lattice distortion, ZrO_2 is added to CeO_2. In such a catalytic application, the homogeneous solid solution is required as well as porous structure with large specific surface area. The authors have tried two processes to synthesize porous particles of CeO_2-ZrO_2 solid solution. One was a spray pyrolysis method using aqueous solutions of metal nitrates. The spherical hollow particles with a size of about 500nm were prepared by decomposition of sprayed droplets. The addition of citric acid as chelating agent and the low pyrolysis temperature were effective to yield the porous and homogeneous solid solution. The specific surface area was maximally $40m^2/g$, and the OSC reached $650x10^{-6}$mol-O_2/g at 50mol% ZrO_2. Another process was a microwave-emulsion method, in which water micelles including inorganic salts were dispersed in n-hexane including organic emulsifier, and selectively heated under microwave irradiation. CeO_2-ZrO_2 porous spheres were also formed with large surface areas. The particle morphology and oxygen storage property are compared between the two processes on the basis of formation mechanisms.

2:40 PM

(ICACC-S8-004-2011) Comparison of Microwave and Conventionally Sintered Yttria Doped Zirconia Ceramics and Hydroxyapatite-Zirconia nanocomposites (Invited)

S. Hampshire*, C. J. Reidy, D. Curran, T. J. Fleming, University of Limerick, Ireland; M. R. Towler, Alfred University, USA

Comparisons of microwave and conventional sintering of zirconia and hydroxyapatite (HA) – zirconia bodies were investigated in order to understand how microwave energy may affect the physical and mechanical properties of the materials for use in biomedical applications. Powder compacts of commercial nano-sized ZrO2, with 2 to 5 mol% Y2O3, and mixtures of laboratory synthesised nano-sized HA with 0–5 wt% zirconia were microwave and conventionally sintered at temperatures up to 1450°C for the zirconia and 1200°C for the composites with the same heating profile and a 1h hold time. Microwave sintering improves physical and mechanical properties of Y2O3–doped ZrO2 ceramics compared with conventional sintering. Compositions containing 2 mol% Y2O3 exhibit the greatest improvement due to retention of tetragonal ZrO2, with higher relative density, 22% increase in Young's modulus, 77% increase in microhardness and a 165% increase in biaxial flexural strength compared with conventional sintering. Significant grain growth occurred in microwave sintered samples which is thought to be related to enhanced diffusional effects during microwave sintering. Comparisons of microwave and conventionally sintered HA-ZrO2 nanocomposites will also be presented.

3:20 PM

(ICACC-S8-005-2011) Soft Processing for Ceramics: Single-Step Fabrication of Nano-Structured Oxide Ceramics (Particles, Films, Integrated Layers and Patterns) from Solution without Firing (Invited)

M. Yoshimura*, Tokyo Institute of Technology, Japan

Based upon an innovative concept and technology, "Soft Processing" or "Soft Solution Processing," which aims low energetic (=environmentally benign) fabrication of shaped, sized, located, and oriented ceramic materials in/from solutions. We have developed the Direct Patterning of CdS, PbS, and CaWO4 on papers by inkjet reaction method, where the chemical driving force of the reaction, A+B=AB, can be utilized not only for synthesis but also for crystallization and/or consolidation of the compound AB. Further-

more, we have succeeded to fabricate BaTiO3 patterns on Ti by a laser beam scanning and carbon patterns on Si by a needle electrode scanning directly in solutions. Recent success in TiO2 and CeO2 patterns by Ink-jet deposition, where nano-particles are nucleated and grown successively on the surface of substrate thus become dense even below 300[l#8451#l], will be demonstrated. Transparent films of several hundred nm thick can be obtained by 20 times of ink-jet scanning during 15-30 min. We have proposed a new strategy:" Growing Integration Layer[GIL] method", which can provide well-adhered integrated/graded layers: Titanate/TiOx/Ti or Titanate/TiOx/Ti-alloys and/or metallic glass(es) at RT-150 C in a solution. This [GIL] strategy can be applied for many areas of functional ceramics. In addition, our recent results on mono-dispersed nano-particles of CeO2, (Hf,Eu)O2-x,Fe3O4,etc. will be shown.

3:40 PM

(ICACC-S8-006-2011) Parameters Affecting Grain Boundary Chemistry of SiAlON Ceramics (Invited)

H. Mandal*, Anadolu University, Turkey; N. Calis Acikbas, MDA Advanced Ceramics, Turkey; F. Kara, A. Kara, S. Turan, H. Yurdakul, Anadolu University, Turkey; B. Bitterlich, CeramTec AG, Germany

It is well known that β-SiAlON is a strong engineering ceramic with good oxidation and creep resistance up to 1300°C. α-SiAlON has excellent hardness, but slightly worse strength, toughness and oxidation resistance than β-SiAlON. It is possible to obtain composite materials, consisting of both α and β-SiAlON, whose properties can be optimized by controlling the ratio of α and β-SiAlON. The properties of a silicon nitride based materials are strongly affected by the amount and crystallinity of the grain boundary phase, as well. For the wear behavior in machining applications the grade of crystallinity and the type of crystalline phases are critical factors. In this study, α-β SiAlON compositions were designed with different type of cations and at different molar ratios. The effect of Y, Ce, Sm, Er, Yb and Ca and mixtures of them on the composition, the type of intergranular phase (amorphous or crystalline), the development of the resultant microstructures following gas pressure sintering and further heat treatment under different conditions will be presented. The influence of the intergranular phase chemistry and microstructure especially on the machining behavior will also be discussed.

4:00 PM

(ICACC-S8-007-2011) Surface Modification of Powder for Sintering by Rotary Chemical Vapor Deposition (Invited)

T. Goto*, IMR Tohoku University, Japan

A small amount of additives is often significantly effective for sintering of some ceramic powders, typically BN and Si3N4. Since the additives would yield second phases which may degrade intrinsic nature of the ceramic materials particularly at high temperature, the minimal amount of additives should uniformly be mixed with the source powders. A mechanical mixing is common, whereas the surface modification of powders could be more effective to enhance the densification. We have constructed a rotary CVD (RCVD) setup to prepare nanoparticles or thin film on powders to modify the surface. Ni nanoparticles were precipitated on hBN, cBN, TiN and Al2O3 powders using nickelocene as a precursor. Carbon nanotubes (CNT) were prepared on cBN powder by self-catalytic reaction, while no CNT formation was observed on other powders. hBN with Ni was densified to 97.3 % by SPS sintering at 2273 K. CNT on the cBN powder was eliminated by adding oxygen in the precursors during the CVD process. A few mass % Ni was precipitated on cBN powder, and Al2O3-cBN-Ni was SPSed at 1473 K. Al2O3-cBN-Ni composites with a density of 99% were obtained. Ni nanoparticles were also prepared on mesoporous silica powder as a catalyst. Amorphous SiO2 thin films were prepared on cBN powder by using TEOS, and dense SiO2-cBN-Ni composites were obtained.

4:20 PM

(ICACC-S8-008-2011) Corrosion of silicon nitride based ceramics under sub-critical conditions in aqueous sodium chloride solution (Invited)

P. Sajgalik*, Institute of Inorganic Chemistry SAS, Slovakia; D. Galusková, Vitrum Lasugaricio - Joint Glass Centre, Slovakia

The results presented in this paper compare the behaviour of silicon nitride prepared with the addition of yttria as sintering additive, and of a sialon ceramic in contact with an aqueous solution of sodium chloride at temperature lower or equal to 290°C. Both studied ceramics dissolved by preferential attack of Si-N bonds in the matrix accompanied by the release of ammonia and formation of protective, mostly oxide layer of corrosion products at the surface. Increase of dissolution rate of sialon in aqueous sodium chloride solution at 290°C was observed in comparison to dissolution in de-ionised water, achieving the value 0.027 mol.m-2.h-1. Penetration of chloride anions through protective layer of corrosion products is proposed to contribute to destruction of the passivation layer and renewal of the exposure of vulnerable material surface to corrosion medium.

4:40 PM

(ICACC-S8-009-2011) Recent Developments in High Thermal Conductivity Silicon Nitride Ceramics (Invited)

K. Hirao*, Y. Zhou, H. Hyuga, National Institute of Advanced Industrial Science & Technology (AIST), Japan; D. Kusano, Japan Fine Ceramics Co., Ltd., Japan

Power supply and packing density of power modules are increasing more and more as their application field expands, in particular in the automobile industry. In order to guarantee the stable operation of the power module, heat release technology in the module becomes of great importance. So far AlN has been used as a substrate for power devices. However, due to its poor mechanical properties, the electricity industry is eager to seek alternative materials. Because of this situation, silicon nitrides are receiving a lot of attention. In this presentation, recent developments of high thermal conductivity silicon nitride ceramics are reviewed and processing strategy for harmonizing their thermal and mechanical properties as well as for reducing processing costs will be discussed.

5:00 PM

(ICACC-S8-010-2011) Manufacturing and Mechanical Behaviour of MMCs Produced by Liquid Metal Infiltration of Freeze-Casted Ceramic Performs (Invited)

M. J. Hoffmann*, T. Waschkies, R. Oberacker, KIT, Germany

Applications of light metal castings can be substantially enhanced by local strengthening of highly loaded zones with ceramic performs. In the present paper we discuss the role of metal-ceramic interfaces for manufacturing and mechanical properties of appropriate composites based on an aluminium-silicon alloy reinforced with alumina. The MMC was prepared by liquid metal infiltration of alumina performs with unidirectionally aligned pore channels which were produced by freeze-casting of water based alumina suspensions. Pores in the perform are formed by replica of the former ice crystals. It will be shown that the size and structure of the pore channels of the green perform depend on the water/ice-alumina interface energy and the particle mobility. The sintered performs with dense lamellae, separated by pore channels were subsequently infiltrated with liquid metal by squeeze- and die-casting. It will be shown that the properties of the final composites strongly depend on the interfacial strength between the solidified metal and the ceramic. Furthermore, we modified the interfacial strength by coating of the perform with Ni, Cu, and Ag prior to infiltration. Characterization of the mechanical properties indicates a strong dependency on the nature of the interface.

5:20 PM

(ICACC-S8-011-2011) ZrB_2-based Ultra High Temperature Ceramics (UHTCs) by Arc Melting Process (Invited)

Y. Seong, S. Lee, D. Kim*, KAIST, Republic of Korea

Interest in ZrB_2-based ultra high temperature ceramics (UHTCs) has increased significantly in recent years because of thermal protection systems for hypersonic aerospace vehicles and reusable atmospheric re-entry vehicles. Because of its strong covalent bonding and its low self-diffusion coefficient, ZrB_2-based ceramics have typically been densified at high temperature (> 1900 ^oC). A melt-solidification process, however, is another simple route for developing high performance materials. We have prepared several eutectic boride-carbide composites by arc melting process. Arc melted ZrB_2-SiC composite showed round ZrB_2 boride and lamellar structure with ZrB_2 and SiC which is different from conventional microstructure of ZrB_2-SiC. Moreover, the elongated mixed boride phase with lamellar structure was observed by addition of HfB_2 and TaB_2.The lamellar structures were advantageous for oxidation resistance at 1500 ^oC especially low oxygen partial pressure. In this study, the effect of microstructure and interconnectivity of SiC on the mechanical properties and oxidation behavior will be discussed and compared with conventional particulate transition metal borides-SiC composites. The mechanisms of the structure evolution during oxidation in oxyacetylene flame were also analyzed.

5:40 PM

(ICACC-S8-012-2011) Smart Powder Processing for Energy and Environments (Invited)

M. Naito*, H. Abe, A. Kondo, Osaka University, Japan

Smart powder processing stands for novel powder processing techniques that create advanced materials with minimal energy consumption and environmental impacts. Particle bonding technology is a typical smart powder processing technique to make advanced composites. In this paper, its application examples for energy and environments will be explained. This processing also leads to the achievement of minimizing energy consumption and environmental impacts when producing advanced materials. By making use of the particle bonding principle, a new one-pot processing method to synthesize nanoparticles without applying extra heat was developed. Furthermore, by carefully controlling the bonding between different kinds of materials in the composite particles, effective separation of elemental components can be achieved. It leads to the development of a novel technique for recycling advanced composite materials and turns them to high-functional applications. In this paper, these approaches will also be introduced.

S9: Porous Ceramics: Novel Developments and Applications

Processing Methods for Porous Ceramics I

Room: Coquina Salon H
Session Chair: Paolo Colombo, Università di Padova

1:30 PM

(ICACC-S9-001-2011) Porous and Nanostructured Nitrides and Carbides (Invited)

S. Kaskel*, TU Dresden, Germany

The design of new materials with well defined pore size and high accessible surface area plays a key role for the development of new catalysts as well as gas storage systems. By using molecular precursors and organic templates even non-oxide ceramics such as Si3N4 or GaN can be produced in a highly porous form with accessible surface areas up to 1000 m2g-1 and well defined pore size. They are efficient super-base catalysts. High temperature materials such as SiC can be produced as ordered mesoporous materials. Porous SiC materials made from polymer precursors are promising supports in automotive soot filters to enhance combustion in regeneration cycles. The precursor method also allows to use ordered mesoporous oxides as molds for polymer casting. The result is a highly ordered mesoporous SiC ceramic (OM-SiC) with specific surface areas up to 800 m2g-1. Such OM-SiC materials may be converted into pure carbon by chlorination. In this case, additional microporosity is generated resulting in surface areas as high as 2900 m2g-1. Such materials are interesting candidates for gas storage and in electrochemical supercapacitors. Transition metal nitrides such as VN or TiN can be produced in a nanoparticular form by using molecular precursors. A cost-efficient method for the synthesis of VN with high catalytic activity in propane dehydrogenation is the nitridation of oxide foams.

2:00 PM

(ICACC-S9-002-2011) From porous ceramics to mesoporous hollow microcapsules: an insight into the world of particle stabilization

U. T. Gonzenbach*, F. Krauss Juillerat, P. N. Sturzenegger, B. S. Seeber, M. Mücklich, L. J. Gauckler, ETH Zürich, Switzerland

Liquid foams are technically important soft matter and play an important role as intermediate structures in the fabrication of porous ceramics. Their thermodynamically unstable nature is a critical issue that can be drastically improved using particles as foam stabilizers. Already at the beginning of the 20th century, Ramsden and Pickering observed the ability of fine particles to stabilize oil-water interfaces1, 2. For efficient emulsion and foam stabilization, the particle surface energy needs to be tailored in order to promote particle attachment to the liquid-liquid or liquid-gas interface, but also to avoid particle agglomeration in the bulk. In-situ hydrophobization3-6 is a powerful method to deliberately control the wettability of colloidal particles of all kind through adsorption of short-chain amphiphilic molecules in order to enable the formation of stable wet foams and emulsions. This presentation gives an overview over our activities in the field of particle-stabilized ceramic foams and emulsion. The method is described in detail with a focus on the processing of wet foams into highly porous ceramics and their outstanding mechanical and microstructural properties. Additionally, the fabrication of hollow microcapsules with mesoporous particle shells and extraordinary mechanical properties is outlined using the same approach. Potential applications of this technology range from thermal insulation and bone graft materials to microcapsules for encapsulation and release of various compounds.

2:20 PM

(ICACC-S9-003-2011) The fabrication and characterization of porous sintered reaction-bonded silicon nitrides with wide pore channels

Y. Park*, J. Lee, H. Yoon, I. Song, Korea Institute of Materials Science, Republic of Korea

Porous sintered reaction-bonded silicon nitride ceramics (SRBSNs) with wide pore channels were fabricated by using presintered Si-additive mixture granules. By increasing the granule strength through presintering of the weak as-spray-dried granules, the conventional uniaxial pressing was employed to shape the green compact retaining the spherical morphology of granules. The formation of both intergranular pore channels (>10μm) and intragranular pore channels (<1μm) lead to high porosity (≥50%) without blending of pore former. Both the widest pore channel and the highest permeability were measured for the specimen by using dm(mean granule size)=76.5μm granule. The interlocking grain structure at the surface of granules evolved with increase in the post-sintering temperature. Further, despite the decreased pore surface area with increased post-sintering temperature, the size of wide pore channel remained constant.

2:40 PM

(ICACC-S9-004-2011) Influence of sintering conditions on the microstructure and properties of particle-stabilized porous ceramics

B. S. Seeber*, U. T. Gonzenbach, B. Hartmeier, U. Ebneter, L. J. Gauckler, ETH Zürich, Switzerland

Sintering is a crucial step in the fabrication process of porous ceramics as it determines not only the final density, but also the microstructure of the struts, in particular the grain size and its distribution. In turn, these microstructural properties directly influence the thermal and mechanical properties of the final product and it is therefore most important to have a good control of the sintering process. Here, we present the influence of sintering conditions on the sintering characteristics and microstructural properties of dense and porous alumina. The dense samples were prepared by powder pressing, whereas the porous samples were produced via direct foaming of in-situ hydrophobized alumina particles. Analysis of microstructural features such as final density, grain size and grain size distribution in dense samples allows for an optimization of the sintering process towards lower firing temperature, shorter sintering cycles, higher density and smaller grain size. In addition, the sintering characteristics in dense and porous samples are compared and the influence of sintering optimization on the mechanical properties of porous alumina is shown.

Processing Methods for Porous Ceramics II

Room: Coquina Salon H
Session Chair: Dilip Chatterjee, Oxane Materials

3:20 PM

(ICACC-S9-005-2011) Precursors-derived microporous ceramic membranes for gas separation (Invited)

Y. Iwamoto*, Nagoya Institute of Technology, Japan

This paper describes recent progress in the development of precursors-derived microporous ceramic membranes for gas separation. Microstructure and gas transport property of the ceramic membranes are briefly described. Then, high-temperature hydrogen permselectivity and hydrothermal stability of the amorphous silica-based membranes are discussed from a viewpoint of application to membrane reactors for developing novel highly efficient hydrogen production, storage and transportation systems. Novel transition metal-doped amorphous silica-based membranes with unique high-temperature gas permeation behaviors, polymer-derived amorphous Si-(B)-C-N membranes having enhanced thermal and chemical stability, and amorphous silica-based inorganic/organic hybrid membranes for CO2 separations will be also discussed from a view point to develop novel ceramic membranes for gas separation.

3:50 PM

(ICACC-S9-006-2011) Porous 3D ceramic structures formed using a modified weaving technique

S. Matthews*, J. Matthews, SCF Processing Ltd, Ireland

Over the past 18 months a new technique to manufacture 3D ceramic structures has been under development at SCF Processing. The technique combines extrusion, supercritical fluids and weaving techniques, and has resulted in manufacture of carbon, silicon carbide and alumina 3D structures. The key to the technology development has been the ceramic fiber formulation and the manufacturing process. This paper will highlight the most recent developments, namely the development of the fiber formulation for long term flexibilty, controlled fiber porosity and the scaling up of the weaving technique. A number of case studies will also highlight the broad range of end-user applications that can benefit from this technique.

4:10 PM

(ICACC-S9-007-2011) Structure and Properties of Sintered Kaolinite-Silica Nanocomposites

J. Walz*, W. Li, K. Lu, Virginia Tech, USA

This talk will focus on the structure and properties and sintered silica-kaolinite composites produced by freeze-casting. Addition of salt to an aqueous dispersion of kaolinite platelets and silica nanoparticles induces a gel transition in which the silica nanoparticles form a bonded, connected structure. Freeze-drying this gel yields a porous composite with pore sizes ranging from tens of nanometers to tens of microns. The presence of the kaolinite not only alters the microstructure of the materials, it also greatly enhances the strength. Recent work, which will be discussed in this talk, has focused on the structure and properties of the ceramic composite produced by sintering. It is found that the porous morphology is maintained, even though the specific surface area of the material is reduced. The effects of heating rate and duration on densification and pore evolution will be presented. In addition, the effects of kaolinite on both stucture and properties will be evaluated by probing the interaction between the kaolinite platelets and silica nanoparticles.

4:30 PM

(ICACC-S9-008-2011) Fabrication of ceramic/metal functionally graded composite using a novel combination of freeze casting and electrophoretic deposition and vacuum casting

A. Preiss*, B. Su, University of Bristol, United Kingdom; S. Collins, P. Ellison, Corin Ltd., United Kingdom

In this project a novel functionally graded composite (FGC), in which the ceramic and metal phases are interpenetrating each other and are independently continuous in three dimensions, has been developed for use in hip resurfacing arthroplasty. First, functionally graded ZTA ceramics have been fabricated from aqueous suspension with an open porous and aligned lamellae structure on one side and a dense layer on the other side without the presence of an interface. A novel combination of two processes has been merged to achieve such graded structures, i.e. unidirectional freeze casting and electrophoretic deposition (EPD). A custom-designed apparatus has been built in which a controlled double side cooling has been realized in conjunction with the possibility to introduce an electric field over the ceramic slurry prior to the freezing process. It was shown that thicknesses up to 500μm could be achieved. Using temperatures between -1 and -25°C the channel width changed from 220 to 40μm, respectively. The sintered ceramic is characterised with specific properties in order to infiltrate a second metallic phase into it. With this novel combination of freeze casting and EPD, tailored lamellae spacing was achievable and using vacuum casting molten metal could be infiltrated into the ceramic lamellae pores.

4:50 PM

(ICACC-S9-009-2011) Porous SiC - reticulated ceramic from wood charcoal

L. M. Manocha, S. Manocha*, H. Patel, Sardar Patel University, India

Development of Bio-SiC materials with tailor made microstructure and properties using natural biopolymeric cellulose template are of great current interest. Porous β-SiC ceramic has been fabricated by different methods using wood charcoal infiltrated with silicon sol as well as single step method by using pine wood powder. Pine wood charcoal impregnated with resin and subsequent carbothermal reduction process at 16500C in inert Ar atmosphere produced light weight biomorphic β-SiC ceramic with good mechanical properties and porosities. The highly anisotropic cellulose structure of pine wood generates novel cellulose ceramics with a meso and macro structure pseudomorphous to the initial porous tissue skeleton. Microstructural observation and phase identification of resulting wood ceramics have been performed by scanning electron microscopy (SEM) and X-ray diffraction (XRD), respectively. Weight loss during

heating of wood and phenolic resin in N2 atmosphere was investigated by thermo gravimetric analysis. (TGA) Experimental results showed that porous β-SiC possessed topologically homogenous pore structure. This provides a low-cost and ecofriendly route to advanced ceramic materials, with near-net shape potential. Detailed microstructure features of the carbothermal reduction product obtained will be presented.

5:10 PM

(ICACC-S9-010-2011) Fabrication of beta-cristobalite porous material from diatomite with some impurities

O. San*, C. -. Özgür, Dumlupinar University, Turkey

The room temperature stabilized beta-cristobalite ceramic has great potential to use in production of engineering ceramic materials due to its high resistance to thermal shock and low expansion coefficient with high chemical resistance and low density. The material was investigated from the mixture of purified diatomite doped with alumina and calcium ions obtained from nitrates. The diatomite purification was achieved by hot acid leaching for 12 h and obtained relatively high grade of silica powder (96 wt.% SiO2). The materials showed quartz, feldspar and alpha-cristobalite as impurity phases. The beta-phase composition was designed as Si1−xAlxCax/2O2 where x = 0.5. The powder was uniaxially pressed at 15 kPa, and later sintered at 1000°C for 24 h and at 1300°C for one minute. The material sintered at low temperature has promising engineering properties: the thermal expansion is almost linearly and found the thermal expansion coefficient as 11.8×10−6 C−1. High temperature sintering leads to cristobalite crystallization and thus the thermal stability of product sample was significantly decreased.

5:30 PM

(ICACC-S9-011-2011) Water contact angle measures for glassy membrane filters

O. San*, Dumlupinar University, Turkey; C. Karaguzel, Dumlupinar Univ, Turkey; R. Goren, Dumlupinar University, Turkey

Contact angle measurement of porous ceramics is impossible where the water drop immediately absorbed by the filter pores. The dynamic wicking approach is potential technique for the contact angle measurement of the capillary materials. In this study, different microstructures of glassy membrane filters were prepared and determined the water contact angle by thin layer wicking approach. The success of wicking results was examined. The glassy filters were shaped by two techniques (slip casting and pressing) and sintered the samples at different temperatures. Results indicated that both the shaping technique and sintering temperature produced different microstructure and the contact angles obtained by the wicking approach were consistent the hydrophilic nature of the filter materials. The low temperature sintering did not produce well enough glassy dispersion and the high temperature leads to crystallization. The best glassy filter was obtained at the moderate temperatures: the sintering temperature being at 900°C and 1000°C for the material shaped by pressing and slip casting, respectively. At these temperatures, the glassy pore wall microstructure could be obtained. The wicking results correlated the hydrophilic nature of the filters in which the measured water contact angle was at and lower than 11.

5:50 PM

(ICACC-S9-012-2011) Transformations and Micro-Mechanical Instability Behavior in Zirconia-based Porous Ceramic

S. Kulkov*, S. Buyakova, Institute of Strength Physics and Material Sciences RAS and Tomsk State University, Russian Federation

In this work, we have studied the effect of pore morphology on the mechanical behavior of partially stabilized zirconia. The increasing volume of porosity between 2 and 60% decreases tetragonal phase content almost by 2 times. Ceramic with the porosity more than 20% has the complex stress-strain behavior. The exponents k measured from the slopes of the linear segments in stress-strain curves in log-log coordinates are plotted against porosity were shown that the data points for k are well fitted by three straight lines; there exists some critical porosity value at which the deformation of the porous material radically changes: the second exponent of the power function (much larger than that in the initial state) appears. So, the material was split into two subsystems, which deform in different ways under stressing. In this ceramics during sintering were formed rod-like structures with their micro-mechanical instability and considerable macro-deformation as structural elements, which may be realized in the elastic area. It has been found out also the correlation between the sizes of crystallites, fractal dimension, and porosity, which associated with porous structure and the porosity of 20%, corresponds to the first percolation threshold.

S11: Advanced Sensor Technology, Developments and Applications

Advanced Sensor Technology

Room: Coquina Salon C
Session Chair: Linan An, University of Central Florida

1:30 PM

(ICACC-S11-001-2011) Electrochemical sensing of dopamine over polyindole- composite Electrode (Invited)

P. C. Pandey, S. Kumari*, A. P. Mishra, Banaras Hindu University, Institute of Technology, India

Electrochemical sensing of dopamine (DA) on silicate-modified electrodes is reported. The ormosils (organically modified silicates) film were prepared from alkoxysilane precursors namely 3-aminopropyltrimethoxysilne and epoxy cyclohexyltrimethoxysilane along with processable carboxylic acid substituted polyindole at position 5 and 6-of indole ring together potassium ferricyanide followed by manipulation of the matrix with silver and gold nanoparticles (AgNps, AuNps.The electrochemical performances of these PMEs have been studied on electrochemical sensing of dopamine with following remarkable findings : (i) Both PI5CA and PI6CA introduced selectivity in electrochemical sensing of dopamine, (ii) Both polymers showed analogous sensitivity on dopamine sensing, (iii) both polymers are susceptible to enhancement in sensitivity when hydrophobic organic redox mediators are coupled along with modified electrode matrix involving Nafion™, (iv) Both polymers are compatible for fabricating ORMOSIL matrix having option for further enhancement in sensitivity of dopamine analysis, (v) the presence of gold and silver nanoparticles within ormosil matrix along with PI5CA/PI6CA caused > 100 fold increase in sensitivity of dopamine sensing with lowest detection limit to the order of 100 nM. The results based on electrochemical measurements, UV-VIS spectroscopy will be described.

2:00 PM

(ICACC-S11-002-2011) Polyaniline-TCNQ nanocomposite, Application in Electrocatalysis of acetylthiocholine, (Invited)

P. C. Pandey*, S. Kumari, Banaras Hindu University, Institute of Technology, India

Electropolymerization of aniline is studied within the nano-structured domains of organically modified silicate (ORMOSIL). The ormosil matrix has been modified by tetracyanoquinodimethane (TCNQ) to introduce redox activity within nanostructured network. TCNQ-encapsulated ormosil has been found to catalyze the electropolymerization of aniline within nanostructured network of ORMOSIL as compared to the control in absence of TCNQ. Palladium has also been introduced within the nano-structured network of ORMOSIL and used for the electropolymerization of aniline. The presence of palladium has again facilitated the polymerization process. The new composite material has shown efficient bioelectrocatalysis for electrochemical biosensors design. The bioelectrocatalysis of ascorbic acid and acetylthiocholine has

been studied. The results based on electrochemical measurements will be discussed.

2:30 PM

(ICACC-S11-003-2011) Recent Advances on Wireless Passive High-Temperature Sensors for Harsh Environments (Invited)

X. Gong*, L. An, C. Xu, University of Central Florida, USA

This paper will present the recent advances on wireless passive high-temperatures sensors for high environments such as combustion turbines. Specifically, two types of wireless passive high-temperature MEMS sensors are investigated: one is a temperature sensor, and the other is a pressure sensor. The temperature sensor is based on a dielectric resonator whose resonant frequency is determined by the temperature-dependent dielectric constant of polymer derived ceramics (PDCs). The pressure sensor is based on an evanescent-mode cavity resonator whose resonant frequency is controlled by the pressure-dependent gap inside the resonator. The design, simulation, and fabrication of these sensors will be presented. Also the measurement setup to characterize the PDC material properties at high-temperatures and measurement results will be presented.

3:20 PM

(ICACC-S11-004-2011) Polymer derived SiCN pressure sensors

Y. Wang*, Northwestern Polytechnical University, China; L. An, Advanced Materials Processing and Analysis Center, USA

Polymer-derived ceramics are a new class of materials synthesized by thermal decomposition of polymer precursors. Previous studies have shown that the materials exhibit excellent thermo-mechanical properties and can be stable at temperatures up to 2000oC. Furthermore, polymer derived ceramics have excellent oxidation and corrosion resistance in the air or combustion environments, which renders them as potential components applied in gas turbine or other harsh environments. Knowing the environments in combustion chamber is critical to burn the fuel more efficiently. Pressure is one of the key parameters. We studied the possibility of polymer derived SiCN ceramics as high temperature sensors. The piezoresistance properties of SiCN ceramics treated at different temperatures are studied. The mechanism for the piezoresistance of SiCN ceramics is discussed. The feasibility of SiCN as high temperature sensors is presented at the final.

3:40 PM

(ICACC-S11-005-2011) Nano-Calorimeter Platform for Explosives Sensing

S. Kang, N. Niedbalski, M. R. Lane, D. Banerjee*, Texas A&M University, USA

The aim of this study is to develop a robust field deployable portable nano-calorimeter sensor for detection of explosive vapors, typically emanating from Improvised Explosives Devices. The microcantilever sensors are composed of two layers: 400 nm Au film on a 600 nm Si_3N_4 substrate. The microcantilever bends in response to induced thermal stresses arising from temperature changes and the dissimilar Thermal Coefficients of Expansion (bimetallic actuator). The differences in bending response of the sensor arrays to adsorption and combustion reactions (catalyzed by the gold surface) are reported in this study. Different combustible materials were tested for detection by the sensor arrays - including alcohol, acetone, ammonium nitrate, and TNT. Numerical models were developed to predict the bending response of the microcantilevers in different environmental conditions. Joule-heating in the resistive heating element (Au) was coupled with the gaseous combustion at the heated surface to obtain the temperature profile and therefore the deflection of a microcantilever by calculating the thermo-mechanical stress-strain relationships. The sensitivity of the threshold current of the sensor that is used for the specific detection and identification of individual explosives samples - is predicted to depend on the reaction rates and the vapor pressure.

4:00 PM

(ICACC-S11-006-2011) Thick Films for Piezoelectric Sensor

D. Park*, J. Ryu, W. Yoon, J. Choi, B. Hahn, J. Kim, J. Choi, B. Lee, Korea Institute of Materials Science, Republic of Korea

PZT thick films were prepared by Aerosol deposition (AD) in order to investigate the effect of its thickness on the electrical properties and charge generation upon exposure to a vibrating force. Since the film was delaminated during post-deposition heat treatment at 973 K, controlled porosity was introduced in the film for relaxation of the residual stress between the film and the substrate. As the film thickness increased up to 30 micrometer, the electrical properties including dielectric constant and piezoelectric constants were improved. The amount of charge was also increased according to the film thickness. In spite of exhibiting similar piezoelectric constants, the 30 micrometer thick film exhibited much larger charge generation than the 15 micrometer thick film, suggesting a strong effect of the film thickness on the performance of piezoelectric sensor.

4:20 PM

(ICACC-S11-007-2011) High Temperature Stability of Thin Film Thermocouples and Strain Gauges in the System In-O-N

O. J. Gregory, M. Amani*, University of Rhode Island, USA

Ceramic thin film thermocouples and strain gauges are being developed for use at temperatures in the range of 500 to 1500°C. These ceramic films were prepared by reactively sputtering In2O3 in nitrogen rich plasmas. Scanning electron microscopy of the nitrogen processed films after thermal cycling at temperatures above 1200°C revealed a partially sintered microstructure consisting of nanoparticles with isolated pores. A nitride rich shell forms around the nanoparticles during deposition, which prevents oxygen diffusion into the bulk ceramic. This combined with the extremely sluggish sintering kinetics associated with nitride ceramics, improved the high temperature electrical stability of the ceramic. By controlling the nitrogen content in the plasma during deposition, reproducible thermoelectric and piezoresistive properties were realized at high temperature. Specifically, sensors with large and stable Seebeck coefficients and gauge factors were fabricated from optimized partial pressures of argon and nitrogen during sputtering and by post deposition annealing.

4:40 PM

(ICACC-S11-008-2011) Development of Sensor Materials for On-line Process Monitoring

J. Jue*, S. Herrmann, S. Herbst, S. Li, Idaho National Laboratory, USA; S. Gopalan, Boston University, USA

A solid state sensor-based process monitoring technology is under development at the Idaho National Laboratory. The materials used in these sensors need to withstand highly radioactive and corrosive environments. Finding suitable electrolyte materials which conducting tri-valance ions is the key to the success of this sensor development effort. Several tri-valance ion conducting electrolyte materials which might be used for such applications were evaluated. A few types of the materials were selected and subjected to further development. By using rare earth as a surrogate for actinide elements, methods were successfully developed to fabricate dense ceramic electrolyte materials. Applying similar methods to synthesize actinide bearing ceramic electrolyte materials is also making progress. In parallel, a computer modeling on ionic selectivity has been initiated. An update on this electrolyte material development effort will be presented.

S14: Advanced Materials and Technologies for Rechargeable Batteries

Advanced Materials for Lithium-ion Batteries

Room: Coquina Salon F
Session Chairs: Ilias Belharouak, Argonne National Lab; Shirley Meng, University of California, San Diego

1:30 PM

(ICACC-S14-001-2011) Present Status of the Lithium-Ion Cell Manufacturing in the U.S (Invited)

R. J. Brodd*, Kentucky Argonne Battery Manufacturing Research and Development Center, USA

Electrochemical R&D in the US has benefitted greatly from the interest in electric and hybrid vehicles for transportation. The American Recovery and Reinvestment Act of 2009 provided funding for the construction of lithium ion (Li-Ion) battery production facilities in the U.S. The construction of battery production facilities will create over 5 major battery assembly operations as well and reestablish the active infrastructure for the production of materials and processes to support the battery industry in the U.S. In addition, The Advanced Research Projects – Energy, (ARPA-E) provided funding to foster research and development of transformational energy-related technologies. ARPA-E is designed to fund the development of an immature technology that has promise to make a large impact to ensure that the United States maintains a technological lead in developing and deploying advanced energy technologies. A third major program funds the sustaining R&D activity in support of the development of electric and hybrid vehicles as well as electrochemical energy storage. All together, these programs established funding of well over $2 billion. The status of these programs will be reviewed. Key Words: lithium ion, electric vehicles, energy storage

2:00 PM

(ICACC-S14-002-2011) Synchrotron imaging of the lithium battery electrodes during their functioning (Invited)

G. Ouvrard*, M. Zerrouki, B. Lestriez, P. Soudan, Institut des Materiaux Jean Rouxel, France; C. Masquelier, S. Hamelet, M. Morcrette, J. Lesage, Laboratoire de Réactivité et de Chimie des Solides, France; S. Belin, A. Flank, Synchrotron Soleil, France

In order to better understand the functioning of lithium battery materials, it is of primary importance to characterize the structural and electronic changes induced by the battery cycling. In a specially designed in situ electrochemical cell, we have used the intense X-ray flux delivered by the synchrotron source Soleil, to perform fast (few seconds) X-ray diffraction (XRD) and X-ray absorption (XAS) experiments. We have especially characterized the changes occurring in the positive electrode material LiFePO4. By a combination of the two techniques and different beam lines we have been able to quantify these changes at different time and space scale. In the two phase process, corresponding to the coexistence of LiFePO4 and FePO4, we put in evidence a delay in the phase transformation in both charge and discharge of the battery. This is very clear in XRD and XAS experiments, and depends on the regime, the particle size, the electrode formulation and the pressure applied on the electrodes. In using XAS experiments, by a true mapping of the electrodes with a probe size of 7x7 μm2, we have demonstrated that this delay corresponds to a large inhomogeneity in the electrode transformation: if some parts are delayed, some others are in advance. In using these fast synchrotron techniques, it is now possible to check the true behaviour of battery electrodes.

2:30 PM

(ICACC-S14-003-2011) Advanced High Capacity Materials for Automotive Lithium-Ion Battery Applications (Invited)

K. Amine*, Argonne National Lab, USA

Research groups have been inventing and developing novel cathode materials whose main characteristic is to store more and more electricity per mass and volume. Lithium and manganese enriched materials have been reported to deliver more than 200 mAh.g-1 specific capacity. These materials attracted significant attention because they also exhibit much improved thermal stability. Of these materials, Li1+tNixMnyO2 ($x<0.5$, $x + y = 1$, $0<t<0.65$) were found to deliver high reversible capacity while being structurally stable upon charging to 4.6 V. These properties, in addition to being cobalt-free, make these materials excellent candidates to surmount the energy density shortfall of current lithium-ion batteries and to meet the lower cost requirement targeted by the automotive industry.

3:20 PM

(ICACC-S14-004-2011) Advanced positive electrode materials for Li-ion batteries: overlithiated layered oxides and Tavorite-type phosphates (Invited)

C. Laurence*, J. Bains, ICMCB-CNRS and IPB-ENSCBP, France; N. Marx, ICMCB-CNRS, France; D. Carlier, ICMCB-CNRS and IPB-ENSCBP, France; L. Bourgeois, Université de Bordeaux-ISM and IPB-ENSCBP, France; A. Wattiaux, ICMCB-CNRS, France; C. Delmas, ICMCB-CNRS and IPB-ENSCBP, France

The Li1+x(Ni1/2-yMn1/2-yCo2y)1-xO2 – type system is one class of materials, with olivines, that was shown to be a good alternative to LiCoO2. It has the advantage to deliver a higher energy density with higher thermal stability in the charged state. Impact of the synthesis conditions, composition, cation distribution and microstructure on its cycling performance and thermal stability will be discussed, especially in the case of an aluminum substitution for cobalt. It will be shown that excellent thermal stability with promising electrochemical performances (both in capacity and power) was achieved for optimized substituted Li1+x(Ni1/2-yMn1/2-yCo2y)1-xO2 materials. Very recently a few groups focused also their interest on Tavorite-type materials AMPO4X (A = Li or H; M = Fe, V or Ti and X = OH or F). In our group, interesting results were obtained for LiFePO4(OH) and for the new phase HFePO4OH (FePO4.H2O). Fine structural characterization of these two phases was achieved combining diffraction and theoretical (GGA+U) calculations, as well as Mössbauer and vibrational spectroscopies. For the first time, lithium intercalation was shown to occur in LiFePO4(OH)and in FePO4.H2O. A comparison of these results with those obtained for instance for the recently reported new phase LiFePO4F will be given.

3:50 PM

(ICACC-S14-005-2011) Probing nano-scale structural and electronic properties of lithium electrodes using electron microscopy and EELS (Invited)

F. Wang, M. Moreno, L. Wu, Y. Zhu, V. Volkov, J. Graetz*, Brookhaven National Laboratory, USA

Batteries are complex and dynamic devices that rely on a series of intricate mechanisms, involving ion transport, charge compensation, structural changes, the formation of metastable phases and thermodynamic instabilities. The relentless push to increase the electrode energy and power density will continue to lead to less stable materials and more complex reactions. The development of safer lithium batteries requires a better understanding of the physical and chemical processes that occur during cycling. However, high-resolution chemical and structural mapping and the ability to identify and characterize nanoscale inhomogeneities in lithium electrodes remains a challenge. Transmission electron microscopy (TEM), diffraction and electron energy-loss spectroscopy were used to investigate the (de)lithiation reactions in a variety of electrode materials (e.g., Li-C, Li-Si, Li-FeF2, Li-Li4Ti5O12). The sample preparation and experimental conditions were optimized to mitigate radiation damage and plural scattering. High-resolution chemical and structural mapping, combined with analysis of the ionization edge fine structure, provides direct information on lithium transport, charge compensation, phase distribution and the local chemical and structural changes that occur

during cycling. Opportunities for time-resolved nanoelectrochemistry in the TEM will also be discussed.

4:20 PM

(ICACC-S14-006-2011) Structural characteristics and electrochemical performance of layered "Li-excess" Oxide Electrode materials Li[Li1/3-2x/3NixMn2/3-x/3]O2 (x=1/3, 1/4 and 1/5)

C. R. Fell*, University of Florida, USA; Y. S. Meng, K. Carroll, University of California San Diego, USA

The lithium-excess layered oxide compounds Li[NixLi1/3-2x/3Mn2/3-x/3]O2 ($0 < x < 1/2$) are of great interests as a new generation of positive electrode materials for high energy density lithium-ion batteries. Following lithium deintercalation and the associated oxidation of Ni2+ to Ni4+, lithium may continue to be extracted from this material despite the fact that all the manganese and nickel ions are in their fully charged (+4) oxidation state. Relations between synthesis conditions, detailed crystal structures and electrochemical properties of the layered "lithium-excess" oxide compounds were studied by XRD, neutron diffraction, XPS, HRTEM, combined with electrochemical property measurements. Li[NixLi1/3-2x/3Mn2/3-x/3]O2 (x=1/3, 1/4, 1/5) were synthesized from mixed nickel-manganese hydroxide precursors and prepared by the co-precipitation method. The prepared materials were electrochemically tested in 2016 type coin cells between 2.0 and 4.8 V for 1 and 10 cycles. Our results suggest that the first cycle irreversible capacity is possibly affected by the surface characteristics of the pristine materials, which is strongly influenced by precursor chemistry. X-ray diffraction data of electrochemically cycled electrode materials show an expanded c/a lattice ratio and peculiar cation migration.

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(ICACC-S14-007-2011) Graphene -$LiFePO_4$ Nanocomposite Cathode For Lithium Ion Batteries

A. Kumar*, C. Venkateswara Rao, R. Thomas, Institute for Functional Nanomaterials, University of Puerto Rico, USA; M. S. Tomar, University of Puerto Rico, USA; Y. Ishikawab, R. S. Katiyar, Institute for Functional Nanomaterials, University of Puerto Rico, USA

The cost effectiveness, environmental benevolently, and thermal stability have made Lithium iron phosphate ($LiFePO_4$) as one of the most attractive cathode materials for rechargeable Li-ion batteries. $LiFePO_4$ exhibiting theoretical capacity of ~170 mAh/g and a flat charge/discharge profile at ~ 3.4 V Li^{1+}/Li. However, slow diffusivity of Li^{1+}/ in $LiFePO_4$ ($D_{Li} \sim 10^{-14} - 10^{-16}$ cm^2/s) compared to the widely used layered $LiCoO_2$ ($D_{Li} \sim 10^{-12} - 10^{-13}$ cm^2/s) allowed only 60% of the capacity to be tapped in the early work. The control on the particle size in the nano-regime along with conductive carbon coating found beneficial to increase capacity and rate capability of $LiFePO_4$ cathode materials. In this study, we have studied the effect of Graphene coating on $LiFePO_4$ to improve the rate-capability. X-ray diffraction (XRD), scanning electron microscopy (SEM) and electrochemical properties were investigated systematically. The XRD pattern demonstrated that an olivine phase of Graphene coating $LiFePO_4$ and the structure was indexed to the orthorhombic Pnma space group. The SEM image revealed that the particles were agglomerated and the particle sizes were almost homogeneously distributed. The cyclic voltammetry (CV) and galvanostatic charge and discharge test showed the 15% Graphene coating $LiFePO_4$ has higher electrochemical reactivity than 5% Graphene coating $LiFePO_4$.

5:00 PM

(ICACC-S14-008-2011) Lithium storage in graphene nanoribbons

V. Barone*, B. Fahlman, A. Antic, T. Bhardwaj, C. Uthaisar, Central Michigan University, USA

I will discuss the rich variety of electronic and adsorption properties displayed by different types of graphenes and their potential as Li storage materials. Strips of graphene can be produced in a controllable manner by unzipping carbon nanotubes and their electronic and adsorption properties strongly depend on the nature of the edges. Based in our combined first-principles calculations and electrochemical experiments, I will discuss their energy density capacity with respect to graphite and other graphitic materials.

5:20 PM

(ICACC-S14-009-2011) Nanostructured electrodes for high power lithium-ion batteries

J. Schorr, S. Sengupta*, R. Revur, MetaMateria Technologies, USA

Lithium ion cells represent the essential building blocks for a wide range of batteries used in consumer electronics and military applications, as well as in next generation hybrid electric vehicles. Many of the new applications for lithium ion batteries require high energy and power densities, quick recharging time, and safe operation at different ambient temperatures. Nanostructured electrodes offer a tremendous potential for developing high power density lithium ion batteries with high rate capabilities. MetaMateria is developing nanomaterials (electrodes) for both thin film and bulk batteries. Both approaches start with colloidal dispersion of nanoparticles which can be either coated or electrospun to produce fibers. Nanostructuctured anodes (Sn/CNT and Li4Ti3O12) and Nanostructured cathodes (LiCoO2, LiMn2O4 and other related materials) are being developed. A high rate charging and discharging capability was observed in batteries fabricated from coatings and fibers (Coin cells) and will be described.

Pacific Rim Engineering Ceramics Summit

Pacific Rim Engineering Ceramics Summit I

Room: Ponce de Leon
Session Chairs: Yu Zhou, Harbin Institute of Technology; Mrityunjay Singh, Ohio Aerospace Institute

1:30 PM

(ICACC-PACRIM-001-2011) Need for Green Materials Selection and Manufacturing Education and Research (Invited)

R. D. Sisson*, Worcester Polytechnic Institute, USA

In materials science and engineering undergraduate and graduate programs the relationships among processing – structure – properties – performance have been the guiding principle for the curriculum. In more recent years society and regulators have emphasized environmental, health and safety issues associated with materials selection and processing operations. In this paper the need for incorporating "green materials selection and manufacturing" principles into the curriculum including course, project and thesis work will presented. Our students need to understand the impact of the selection of toxic or energy intensive materials. The importance of developing new materials and processes to reduce environmental, health and safety impacts as well as the carbon footprint will be emphasized. In addition, the importance of incorporating these issues into multidisciplinary design projects to help the students learn will be discussed.

2:00 PM

(ICACC-PACRIM-002-2011) Ceramics Researches and Education in P.R. China (Invited)

Y. Zhou*, D. Jia, Z. Yang, Harbin Institute of Technology, China

The current expansion of ceramics science and engineering in both higher education and researches is improving very quickly in China. This paper presents the history, current situation, and future development of the ceramics research and education in China. The achievements of the researches and education on ceramics over the past 90 years were introduced. Some prospects related to the ceramics researches and education, such as, institutes and universities, higher education system, quantity and quality of faculties, current status of students, national investments for scientific researches, applications

of scientific researches and technological achievements, international cooperation, and industrial output, et al. were also introduced. Finally, some suggestions for the future development of ceramics in China were presented.

2:30 PM

(ICACC-PACRIM-003-2011) Current Status and Future Challenges of Multifunctional coatings for energy and environmental systems in Taiwan (Invited)

J. Huang*, C. Fan, J. Song, M. Wu, National Cheng Kung University, Taiwan

The current energy import volume is about 95% in Taiwan. The major resources with high levels carbon emission are about 83.25% and low levels or without carbon emission are only 16.75% of the total energy. A national energy policy has been developed to increase the percentage of energy with low levels of carbon emission to ≥ 55% in 2025. Now, the researchers in Taiwan have put many efforts for finding new technologies to achieve clean energy. The multifunctional coatings technology definitely plays an extremely important role in the government energy policies. There are three major research trends of multifunctional coatings in Taiwan such as, Energy conversion coatings, Nanostructured coatings and Optoelectronic coatings. In the Industry, there exist three energy sectors such as, Solar energy, Fuel cell and LED technologies. Taiwan PV industry supplies the world market with 12% of solar cells (globally ranked 4th). The current progress of thin film-solid oxide fuel cells (TF-SOFCs) in Taiwan is the planer type cells. Light Emitting Diode (LED) that lies on low power consumption, energy efficiency, longevity, durability, small size and quick reaction time. This report will give the brief description about the above front areas of research with special emphasis on multifunctional coating and their future challenges by taking environmental aspects into consideration.

3:20 PM

(ICACC-PACRIM-004-2011) Current Status of Research & Technology Development in the Areas of Ceramics, CMCs and Ceramic Coatings (Invited)

G. Sundararajan*, Y. R. Mahajan, Int. Adv. Res. Centre for Powder Metallurgy & New Materials (ARCI), India

The Indian research activity in the areas of ceramics, ceramic coatings and ceramic matrix composites (CMC) has accelerated in the last decade with more and more institutions embarking on research in this area. The presentation will start with the identification of industry and other segments in India having the potential to utilize ceramics, ceramic coatings and CMCs. The second part of the presentation will be devoted to the review of current R&D work in ceramics, ceramic coatings and CMC being carried out in various universities, R&D laboratories and industrial R&D centres. Next, the technology development and demonstration activities being carried out at various R&D centres will be presented. The future directions for research and technology development in the area will be the subject of the concluding part of the presentation.

3:50 PM

(ICACC-PACRIM-005-2011) Research Status of Carbon/carbon Composites in China (Invited)

H. Li*, S. Zhang, Q. Fu, K. Li, Northwestern Polytechnical University, China

Carbon/carbon (C/C) composites are the leading candidates for high temperature structural components in aeronautics and astronautics fields. Within the last few years, investigation on densification, interface modification, anti-oxidation and property has been developed in China. Some new techniques, including super high pressure impregnation and carbonization, thermal gradient self-heated CVI, microware assisted CVI, and forced pressure-pulsed CVI, have been invented. Some potential precursors of pyrolytic carbon, such as ethanol, n-propanol, n-butyl alcohol and toluene, have also been applied for densifying C/C composites. To improve the toughness of C/C composites, some techniques including bromine intercalation in graphite microcrystal, toughening by carbon nanotube have been used to modify the interface between carbon fiber and carbon matrix. To protect C/C composites against oxidation, some novel coating systems were developed, such as the multi-phase inlay ceramics, whisker-toughed ceramics and gradient coatings. Simultaneity, some new techniques were explored to obtain more perfect coatings. Additionally, matrix modification technique has developed obviously. High temperature mechanical properties, fatigue strengthening behavior, ablation performances, friction and wear behavior of C/C composites have been attracted much attention, on which some interesting results were produced.

4:20 PM

(ICACC-PACRIM-006-2011) Photocatalytic Fibers with High Quantum Efficiency (Invited)

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

The polycarbosilane can be converted into silicon carbide or silica by firing in inert gas atmosphere or in air, respectively. Making the best use of this basic property of the polycarbosilane, we synthesized unique photocatalytic fibers composed of silica-based core structure and surface gradient composition of titania crystals. That is to say, the concentration of surface titania crystals increases from inside to outside of the fiber. This structure was created using the polycarbosilane containing a selected low-molecular-mass additive (Ti(OC4H9)4), which can be into titania by firing in air. After melt-spinning, heat treatment of the spun fiber leads to controlled phase separation of the additive; subsequent calcination stabilizes the compositionally changed surface region, generating a functional surface. Accordingly, this fiber solved the conventional problems regarding peering of the titania coating layer, and also achieved high strength. Furthermore, we developed a water-purifier using this fiber, which was designed for obtaining effective contact with organic pollutants. The first system was very simple with a module composed of the cone-shaped felt material and UV lamp. Any bacteria and organic chemicals were effectively decomposed into CO2 and H2O using the above purifier. We designed several types of water purifier for obtaining further decomposition ability of organic pollutants with very high energy-efficiency.

4:50 PM

(ICACC-PACRIM-007-2011) Development of Silicon carbide Fibers in Korea: One-pot Process for Aluminum Doping of Polycarbosilane in the Presence of Solid Acid Catalyst and Low Temperature Halide Gas Curing Process (Invited)

D. G. Shin, K. Y. Cho, Seoul National University of Technology, Republic of Korea; E. B. Park, Korea Institute of Ceramic Engineering and Technology, Republic of Korea; Y. H. Kim, J. S. Hong, H. R. Lim, Y. R. Cho, M. S. Kang, D. Riu*, Seoul National University of Technology, Republic of Korea

We have been fabricating aluminum modified polycarbosilanes (Al-PCS) through one-pot doping process. One-pot means that the precursor polymers, i.e, polydimethylsilanes(PDMS) are just mixed with doping compounds (i. e. aluminumacetylacetonate) at room temperature, and are thermally treated in the presence of solid acid catalyst such as ZSM-5 and gamma-alumina. The thermolysis and polymerization are conducted via two steps of temperatures at 350°C and 400°C for different time periods. During the first step of thermolysis at 350°C, most of aluminum are inserted into the backbones of PCS. The role of the solid acid catalyst on the rearrangement reaction of the PDMS into PCS is still not clear, however, the presence of the catalyst is an essential part for the successful fabrication of Al-PCS at a lower temperature. An additional 400°C treatment was applied to the oligomer PCS in order to further polymerize and to adjust the molecular weight of the PCS.

5:20 PM

(ICACC-PACRIM-008-2011) Silicon Nitride Ceramics for Turbine Engine Applications (Invited)

H. Lin*, Oak Ridge National Laboratory, USA

Since the 1970s several research programs sponsored by U.S. Department of Energy were initiated aiming to develop silicon nitride ceramic components for stationary and mobile gas turbine engines. The main driving force behind the silicon nitride ceramic development was the potential of ceramic gas turbine engines running at very high temperatures and air/fuel pressures compared to conventional metallic engines, thus enabling higher engine thermal efficiency, lower engine weight, and reduced fuel consumption and exhaust emission. The demands of these higher temperature hot-section components require materials with high-temperature mechanical strength, creep, thermal shock, and resistance to oxidation and wear with high reliability. As a result, silicon nitride ceramics have been researched intensively to develop hot section engine components with required long-term reliability and durability performance. The various ceramic engine programs have only partially succeeded due to continued limitations of some material mechanical properties (i.e., fracture toughness, and material recession issue in the gas turbine environments). This paper will provide an overview of silicon nitride gas turbine engine programs and discuss lessons and issues learned. Also, the current status and future prospects of the use of silicon nitride ceramics for turbine engine applications and the critical challenges forward will be presented and discussed. Research sponsored by Korea Institute of Materials Science under DOE Work-for-Others project NFE-10-02614 administered by UT-Battelle, LLC under DOE contract DE-AC05-00OR22725

Tuesday, January 25, 2011

S1: Mechanical Behavior and Performance of Ceramics & Composites

Reliability and Life Prediction Methodologies

Room: Coquina Salon A
Session Chair: Jonathan Salem, NASA Glenn Research Center

8:00 AM

(ICACC-S1-013-2011) Orbiter Window Hypervelocity Impact Strength Evaluation (Invited)

L. Estes*, NASA/JSC, USA

When the Space Shuttle Orbiter incurs damage on its windowpane during flight from particles traveling at hypervelocity speeds, it produces a distinctive damage that reduces the overall strength of the pane. This damage has the potential to increase the risk associated with a safe return to Earth. Engineers at Boeing and NASA/JSC are called to Mission Control to evaluate the damage and provide an assessment on the risk to the crew. Historically, damages like these were categorized as "accepted risk" associated with manned spaceflight, and as long as the glass was intact, engineers gave a "go ahead" for entry for the Orbiter. Since the Columbia accident, managers have given more scrutiny to these assessments, and this has caused the Orbiter window engineers to capitalize on new methods of assessments for these damages. This presentation will describe the original methodology that was used to asses the damages, and introduce a philosophy new to the Shuttle program for assessing structural damage, reliability/risk-based engineering. The presentation will also present a new, recently adopted method for assessing the damage and providing management with a reasonable assessment on the realities of the risk to the crew and vehicle for return.

8:30 AM

(ICACC-S1-014-2011) Use of Modern Statistical Techniques in the Prediction of Brittle Failure

S. Freiman*, Freiman Consulting, USA; J. Fong, NIST, USA

Designing ceramic components for safe operation over long periods of time involves issues of both the statistical nature of their fracture and the fact that most ceramics undergo slow crack growth in moisture containing environments. As a further complication, stresses can arise in components, not just due to mechanical loads, but also because of thermal gradients, phase transformations, or the presence of electric fields. This paper outlines the fracture mechanics expressions, experimental procedures, and statistical techniques needed to determine the mechanical reliability of brittle materials. As an example, data taken from a previous publication1 describing design procedures for all-glass aircraft windows is presented, but now makes use of more modern statistical techniques to determine the overall uncertainty in lifetime prediction for the windows. A more detailed description of the statistical procedures is being prepared for publication.

8:50 AM

(ICACC-S1-015-2011) Unit Sphere Stochastic-Strength Failure Criterion For Anisotropic Brittle Materials

N. N. Nemeth*, NASA Glenn Research Center, USA

Models that predict the failure probability of ceramic components in multiaxial stress states have been developed by authors such as Batdorf (1974, 1978), Evans (1978), and Matsuo (1981). These models assume that the strength-controlling flaws are randomly oriented non-interacting planar microcracks of specified geometry but of variable size. Fracture mechanics relationships for mixed-mode (modes I, II, and III) crack growth combined with the weakest-link theory and integration over the surface area of a unit radius sphere representing all possible orientations of microcracks, are used to determine component probability of failure. This methodology has been extended for anisotropic brittle materials and builds upon work done by Batdorf (1973) and Buch (1977). Two scenarios are considered: (1) flaw orientation anisotropy whereby a pre-existing microcrack has a higher likelihood of being oriented in one direction over another direction, and (2) K_{Ic} orientation anisotropy whereby the level of fracture toughness for Mode I crack propagation, K_{Ic}, changes with regard to the orientation of the microstructure. This methodology is demonstrated for transversely isotropic strength response. Possible applications include describing the strength response of mildly anisotropic materials such as graphite, or use as a failure criterion inside micromechanics software codes for composite material constituents.

9:10 AM

(ICACC-S1-016-2011) Deformation and strength evaluation of SiC/SiC composites using Distributed-Micro-Crack Model

H. Baba*, IHI Corporation, Japan; A. Suzuki, Oita University, Japan

Toughness property of SiC/SiC composites is generally higher than that of monolithic ceramics in elevated temperature. Therefore, they have been expected to apply as structural components/parts operated in elevated temperature. However, number of practical application cases of SiC/SiC composites has not been increasing due to their complex mechanism of deformation and difficulties fracture strength prediction. To overcoming these problems, Distributed-Micro-Crack Model has been applied to evaluate deformation and fracture strength of SiC/SiC composites. In this analysis, development of damage in SiC/SiC composites is assumed as micro crack propagations distributed in components. The results are shown that Distributed-Micro-Crack Model can predict deformation property and fracture strength of SiC/SiC composites.

9:50 AM

(ICACC-S1-017-2011) Fatigue threshold R-curves for fatigue reliability predictions in grain bridging ceramics

S. Gallops*, J. J. Kruzic, Oregon State University, USA; T. Fett, University of Karlsruhe, Germany

The purpose of this presentation is to explore a new methodology to make fatigue reliability predictions for grain bridging ceramics. Fatigue thresholds were measured as a function of crack extension using compact tension specimens for two microstructures (fine and coarse) of a 99.5 % pure polycrystalline alumina in order to develop fatigue threshold R-curves. The coarse microstructure was also tested in dry nitrogen to probe the effects of increasing the intrinsic grain boundary toughness. Bridging stress distributions were calculated from the R-curves, which allows R-curves to be calculated for other geometries using weight functions. Fatigue endurance strength predictions were made as a function of initial semi-elliptical surface flaw size using both the measured R-curve for the compact tension specimen and a calculated R-curve for a semi-elliptical surface crack. To verify the predictions, semi-elliptical surface cracks were induced in bend beams with a Knoop indenter, and the samples were polished until both the indent and residual stress field were removed. The indent load and polishing procedure were varied to induce a range of initial crack sizes. The beams were then fatigued in four-point bending at loads above and below the predicted endurance strengths to evaluate the accuracy of the predictions.

10:10 AM

(ICACC-S1-018-2011) High Reliability Alumina-Silicon Carbide Laminated Composites

F. De Genua, V. M. Sglavo*, University of Trento - Italy, Italy

High mechanical reliability and surface damage insensitivity can be obtained in ceramics through laminated structures able to develop, upon processing, a specific residual stress profile with a maximum compression at a proper depth from the surface. Following this approach, low-density laminates in the alumina/silicon carbide system were designed and fabricated by thermo-compressing tape cast layers, the obtained laminate being consolidated by pressureless sintering or Spark Plasma Sintering (SPS). Mechanical characterization was carried out by using the ring-on-ring loading configuration; fracture behaviour was analyzed both on as produced and pre-indented samples and specific observations were performed to point out the stable growth of surface cracks. The reliability was evaluated in terms of Weibull modulus or minimum threshold strength. The mechanical performances were analyzed in terms of the consolidation process and correlated to the composition and architecture of the laminates.

Nondestructive Evaluation

Room: Coquina Salon A
Session Chair: Jiangang Sun, Argonne National Laboratory

10:50 AM

(ICACC-S1-019-2011) Nondestructive Evaluation of Ceramic Materials by Thermal Tomography

J. Sun*, Argonne National Laboratory, USA

Infrared thermal imaging has been widely used for nondestructive evaluation of ceramic matrix composites (CMC) and thermal barrier coatings (TBC) that are developed/used for high-temperature turbine engine applications. Current thermal imaging methods may measure the gross thermal property or detect flaws within the ceramic materials. They however are not well suited to determine the property and flaw distributions within the volume. Recently a thermal tomography method was developed that can resolve the volume distribution of material composition and flaws within the ceramic material. It utilizes the one-sided flash thermal-imaging data to construct three-dimensional images of material's thermal effusivity within the entire material volume. This paper presents typical experimental results for three-dimensional volumetric imaging of CMC and TBC components. The capabilities and limitations of this method in terms of inspection requirement, detection sensitivity and spatial resolution will also be discussed.

11:10 AM

(ICACC-S1-020-2011) Identification of damage modes in ceramic matrix composites by acoustic emission

N. Godin, M. R'Mili, P. Reynaud, G. Fantozzi, J. Lamon*, MATEIS-INSA de Lyon, France

The damage of composite materials is a key point for the control of durability. A big issue is therefore a sound identification of the damage mechanisms and their kinetics with a view to predicting the remaining lifetime of the structures. For that purpose, acoustic emission (AE) is an interesting and powerful tool for detection of active damage mechanisms and monitoring of their evolution. AE is a transient wave resulting from the sudden release of stored energy during a damage process. Damage of fiber reinforced ceramic matrix composites involves several phenomena at various length scales including matrix cracking, fiber debonding, fiber failures. The objective of the present paper is to propose a quantitative approach to damage identification based on signal analysis by pattern recognition. An unsupervised classification method was used to differentiate the signals generated during reference fatigue tests performed on C/SiC samples at high temperature. Each class of signals was then associated to relevant damage mode: collective or individual fibre failures, matrix cracking, fibre / matrix debonding. The library of signals was then used to identify the damage mode generated during fatigue tests performed at different temperatures. For this purpose a supervised classification method was required. Promising results were obtained. Application to lifetime prediction is discussed.

11:30 AM

(ICACC-S1-021-2011) Comparison of Synchrotron Radiation X-ray tomography with novel Lab based CTs in 3D microstructures and porosity characterization

S. H. Lau*, L. Hunter, T. Fong, J. Gelb, A. Gu, W. Yun, Xradia Inc., USA

Characterization of 3D microstructures, porosity, voids, defects within materials and in situ testing are routinely been carried out at Synchrotron Radiation facilities at high resolution with submicron and nanotomography systems using both hard and soft x-ray energies. In comparison, the spatial resolution of typical lab based microCT and nanoCT systems are limited by x-ray source spot size, sample dimension and sample working distance. It is difficult to achieve submicron resolution in 3D for the majority of samples. We describe a suite of novel lab based x-ray computed tomography system which overcome the resolution and contrast limitation of conventional microCT and nanoCTs. The novel MicroXCT has continuously variable resolution ranging from 50 microns to 500 nm, while the novel nanoXCT through its x-ray optics achieves 50 nm resolution. Both systems have the ability to employ phase contrast which significantly increases imaging contrast for soft materials and detect small density difference between material phases, microcracks and voids. Comparison of data from the novel CTs with synchrotron based micro and nanotomography and SEM demonstrates that for several materials tested: ceramics, coatings, composite materials, semiconductor, geomaterials, polymeric membranes and biological tissue,- the novel lab systems achieve comparable results..

11:50 AM

(ICACC-S1-022-2011) An Indentation Based Non-Destructive Evaluation Technique for Thermal Barrier Coating Spallation Prediction

J. M. Tannenbaum*, K. Lee, B. S. Kang, West Virginia University, USA; M. Alvin, National Energy Technology Laboratory, USA

A load-based micro-indentation method for NDE of TBCs exposed to thermal loads has been developed. TBC thermal cyclic exposure tests were performed where after a defined thermal cycling period, surface stiffness response was measured to assess damage accumula-

tion and identify macroscopic debonding failure sites. Microstructural analyses were conducted correlating YSZ adherence to TGO/BC and evidence of internal crack formations with the measured surface stiffness responses. Finite element analyses indicate that high YSZ/BC interfacial rumpling leads to the development of both in-plane and out-of-plane residual stresses upon cooling. Additional rumpling of this interface as a result of non-uniform oxide growth leads to enhanced residual stresses. Average stress levels within the TBC have been found to decrease with accumulated thermal exposure, yet the variance of these values was found to increase primarily due to enhanced residual stress variation across the coupon which can be identified by our micro-indentation technique. As a result, areas producing relative increases in surface stiffness response enable early detection of initial TBC spallation locations. In addition, finite element analyses of YSZ/TGO/BC interfacial stresses generated upon cooling provide an explanation for the experimentally observed micro-cracking and failure patterns.

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

Thermal Barrier Coatings II

Room: Coquina Salon G
Session Chairs: Robert Vassen, IEF-1; Bryan Harder, Northwestern University

8:00 AM

(ICACC-S2-013-2011) Damage development characterisation in thermal barrier coatings (Invited)

H. Brodin*, Siemens Industrial Turbomachinery AB, Sweden; S. Sjöström, S. Johansson, Linköping University, Sweden

Thermal barrier coating (TBC) degradation and coating failure has been investigated for different coating systems, where bond coat (BC) composition and top coat (TC) thickness has been in focus. Influence on TBC degradation of thermal loading is studied on cross-sections of coating systems exposed to high temperature under cyclic and monotonic conditions. Also non-destructive testing with acoustic emission monitoring has been used in order to understand TBC damage development. From the experimental work information is retrieved on how oxidation and cyclic temperature loading influences delamination at the TC/BC interface. The development of delamination cracks into local spallation of the TC is also considered. Furthermore, TC degradation is evaluated since the TC microstructure will change during thermal exposure. As a consequence of TC microcracking or sintering, the stiffness will be affected and, hence, the stress state at the ceramic metal interface will be changed. Results from testing are supported by a fracture mechanical analysis of corresponding cases with finite element modelling of cracks present in a TBC system. Furthermore, experimental and fracture mechanical data are compared to a previously developed fatigue life model in order to improve the model range of validity in terms of variations in coating systems. The general correlation between experimental and modelling results is also addressed.

8:30 AM

(ICACC-S2-014-2011) Effects of ageing on mechanical properties and damage behavior of EB-PVD thermal barrier coating systems (Invited)

M. Bartsch*, L. Chernova, N. Dzodzovic, German Aerospace Center (DLR), Germany; M. T. Hernandez, A. M. Karlsson, University of Delaware, USA; N. Zotov, G. Eggeler, Ruhr-Universität Bochum, Germany

Multilayered materials subjected to high temperatures exhibit time and temperature dependent microstructure evolution, which alter the mechanical properties of the respective components and consequently the damage behavior of the layered structure. The here presented investigation was motivated by the observation that in complex thermal mechanical fatigue tests pre aged and as coated specimens of a thermal barrier coating (TBC) system showed completely different damage behaviour. The pre aged specimens displayed perpendicular to the mechanical fatigue load cracks in the thermally grown oxide (TGO) between ceramic top coat and underlying metallic bond coat. The cracks started in the TGO, propagated into top coat and bond coat, entailing a scenario of local oxidation and crack kinking at the bond coat, and finally spallation of the ceramic coating. In contrast, the as coated TBC-system did not show crack formation even after a higher number of test cycles. In order to explain the effect of ageing on the crack initiation, changes of the TBC microstructure and related mechanical properties have been investigated experimentally (scanning electron microscopy, nanoindentation) and by means of finite element analyses. The investigations suggest that only in the aged TBC system tensile stresses can accumulate in the TGO, which are sufficient to initiate the observed cracks.

9:00 AM

(ICACC-S2-015-2011) Stress evolution and microstructure relationship in plasma-sprayed ceramic coatings

K. Shinoda*, J. Colmenares-Angulo, G. Dwivedi, T. Nakamura, C. A. Johnson, S. Sampath, Stony Brook University, USA

The stress evolution during plasma spraying plays an important role in the development of coating microstructures including vertical crack formation in thermal barrier coatings. In addition to processing parameters such as the local deposition temperature and in-flight particle states, thermo-mechanical properties of the coating materials can affect the stress evolution. In this study, we utilize a novel in situ curvature monitoring system to investigate how the stress state can be different among various industrial ceramic materials and how the stress state can affect the coating microstructure. Various industrial ceramics including yttria-stabilized zirconia and gadolinium zirconate as well as titania and alumina were plasma-sprayed onto metal beams. The stress evolution during the coating deposition was monitored via curvature change of the beams with the deposition temperature measured as well. The stress evolution during the deposition (named the evolving stress) tended to be proportional to the in-plane modulus of the coating, suggesting a constant elastic residual strain in the coating. Those strain values were dependent on the sprayed materials; titania tended to show higher strains than zirconia-base materials, while alumina lower ones. Above a certain deposition temperature, the stress was not accumulated during the deposition, and vertical cracks were observed in such a coating.

9:20 AM

(ICACC-S2-016-2011) Characteristic Micro-scale Damage Evolution Behavior in EB-PVD TBC System under Out-of-phase Thermo-mechanical Fatigue Tests

R. Kitazawa*, Y. Kagawa, The University of Tokyo, Japan

Out-of-phase thermo-mechanical fatigue (TMF) tests of EB-PVD Y_2O_3-ZrO_2 thermal barrier coating system (8wt% Y_2O_3-ZrO_2/CoNiCrAlY/IN-738 substrate) were done under strain-controlled mode. During hot time, surface temperature of the TBC layer was kept at 1150 ^{o}C and the substrate was kept at 1000 ^{o}C, i.e., temperature gradient of 150 ^{o}C was achieved during the test. At the same time, during hot time, a uni-axial compressive strain was simultaneously applied to the specimen. Under out-of-phase tests, applied stress at a minimum temperature shifted from compression to tension after ~10^3 applied cycles, which depends on the applied strain level. After selected applied cycles, tests were interrupted and the specimen was carefully observed. Anisotropic thermally grown oxide layer (TGO) growth behavior, measurement of stress distribution in the TGO layer was done using luminescence spectroscopy. Discussions were made on the effects of applied strain/strain on the micro-scale damage evolution of the TBC system under out-of-phase TMF tests.

10:00 AM

(ICACC-S2-017-2011) The Effect of a Thermal Gradient on the Performance of CMAS Infiltrated TBCs

R. Jackson*, E. M. Zaleski, E. Veron-Tocquet, C. G. Levi, University of California, Santa Barbara, USA

Calcium magnesium alumino-silicate (CMAS) deposits on thermal barrier coatings (TBCs) melt above ~1200°C, whereupon they infiltrate and crystallize within the pores of the structure, stiffening the penetrated layer and leading to a loss of strain tolerance. This loss of compliance can lead to coating delamination when the strains generated during thermal cycling produce sufficiently high stresses in the affected coating. To determine the thermal conditions under which TBC delamination will occur, a novel laser thermal gradient test (LGT) was developed that allows control of the thermal gradient across the TBC as well as the thermal history. Both 7YSZ and gadolinium zirconate TBCs, with and without CMAS deposits, were subjected to the LGT. Subsequent microstructural analysis was performed to determine where delaminations occurred, which was used in combination with the specimen's thermal history to assess current delamination models.

10:20 AM

(ICACC-S2-018-2011) Variation of creep properties and interfacial roughness in thermal barrier coating systems

P. Seiler*, TU Braunschweig, Germany; M. Schweda, IEF-2, Germany; M. Bäker, J. Rösler, TU Braunschweig, Germany; T. Beck, IEF-2, Germany

Typical thermal barrier coating systems are used at high temperature in gas turbines. They protect the nickel-based components and consist of the bond-coat (BC) the thermal barrier coating (TBC) and a thermally grown oxide (TGO) between the BC and TBC. The coatings fail in service because of different failure mechanisms which are not fully understood, yet. A simplified coating system is introduced which consists of a MCrAlY bond-coat material as the substrate, an artificial TGO, and a TBC on top. Hence, the influence of the nickel-based substrate can be neglected, which reduces the influencing parameters. The failure mechanism can be analysed by varying the creep properties of the bond-coat material (fast creeping Fecralloy and slow creeping ODS strengthened MA956). The influence of the interfacial roughness can be examined in the system by sandblasting with different powders and a micro-cutting process. The influence of creep in the TGO can be determined by applying different layers of aluminium oxide on top of the bond-coat material. PVD is used to apply a fine grained and fast creeping TGO, on the other hand a coarse grained TGO is generated by a heat treatment. It is shown that a fast creeping bond-coat and a fast creeping TGO benefit the lifetime of the coating system. Different FEM calculations and crack propagation simulations of the coatings support this assumption.

10:40 AM

(ICACC-S2-019-2011) Investigation into delamination of air plasma sprayed thermal barrier coatings after thermal treatments

A. Shinmi*, X. Zhao, P. Xiao, University of Manchester, United Kingdom; N. Markocsan, P. Nylen, University West, Sweden

The delamination behaviour of air plasma sprayed (APS) calcia stabilised zirconia thermal barrier coatings after annealing at 1050 degree for various time were investigated. A modified 4-point bending technique was employed to evaluate the interfacial fracture toughness. In all conditions, the delamination occurred primarily within the top coat, just several micrometers above the thermally grown oxide layer. When the coating delaminates, the energy release rate increases first to the maximum after 10h annealing, and then gradually decreases with further annealing. The reasons for phenomenon were further discussed and related to the phase transformation and sintering occurring during the annealing.

11:00 AM

(ICACC-S2-020-2011) Microstructure and thermal cycling lifetime of plasma sprayed Lanthanum-Lithium-hexaaluminate for use in thermal barrier coatings

D. E. Mack*, A. Guignard, G. Mauer, Forschungszentrum Jülich GmbH, Germany; N. Melendez, University of Alberta, Canada; D. Sebold, R. Vassen, D. Stöver, Forschungszentrum Jülich GmbH, Germany

Some materials of aluminate type with relative low thermal expansion coefficients have been discussed for TBC application since some years. One example of those is $LaLiAl_{11}O_{18.5}$ which belongs to the group of hexaaluminate compositions owing magnetoplumbite structure. This hexaaluminate tends to be in a partly amorphous state when deposited by means of thermal spraying. Re-crystallization takes place at elevated temperatures and segmentation cracks can form which induce increased strain tolerance. Thermal gradient cycling tests and SEM inspections indicate that the incorporation of small particles into the coating which are incompletely molten may play an important role to the mechanical stability and thermal cycling lifetime. In this study the role of grain size and plasma spraying parameters on the microstructure evolution after heat treatment has been studied e.g. by means of DPV measurements, XRD and materialographic analysis. Those results will be also discussed in respect of the lifetime of double layered TBCs utilizing $LaLiAl_{11}O_{18.5}$ as a topcoat onto a standard YSZ layer in thermal gradient tests.

S3: 8th International Symposium on Solid Oxide Fuel Cells (SOFC): Materials, Science and Technology

Electrodes I

Room: Coquina Salon E
Session Chairs: Meilin Liu, Georgia Tech; Mihails Kusnezoff, Fraunhofer IKTS

8:00 AM

(ICACC-S3-011-2011) Electrochemical phenomena in MEA electrodes (Invited)

M. Kusnezoff*, N. Trofimenko, S. Mosch, A. Michaelis, Fraunhofer Institute for Ceramic Technologies and Systems, Germany

The numerous measurements of I-V-characteristics and impedance spectra on symmetrical cells and MEAs with various types of electrodes have been carried out at different temperatures using various gas compositions to characterize the performance of the electrolyte supported cells (ESC). The tests have been performed in ceramic housing in absence of any contamination sources resulting from experimental setup. The cathodic and anodic reaction steps have been investigated as a function of fuel composition. It was found that the cathode polarization can be described by three processes: (i) oxygen adsorption on the cathode surface, (ii) oxygen diffusion to the three phase boundary followed by electrochemical reaction and (iii) oxygen transfer into electrolyte. In the MEA impedance spectra mainly the processes (i) and (ii) were observed. For LSCF based cathodes mainly the impact of oxygen adsorption on the total polarization resistance was reduced. In the anode the number of observed processes depends strongly on the art of the used anode and on the fuel humidification level. The Ni/YSZ anodes have mainly two arcs in impedance spectra connected with (i) hydrogen adsorption on Ni surface and (ii) diffusion of adsorbed species and formation of water. In the ceria based anodes the additional electrochemical reaction on ceria has been seen. With both anodes the ASR below 0.2 Ωcm2 @ 850°C for 10Sc1CeSZ based ESCs is achieved.

8:30 AM

(ICACC-S3-012-2011) Doped CeO_2 and $LaFeO_3$ Composite Oxide Anode for Direct Hydrocarbon type SOFCs (Invited)

T. Ishihara*, T. Shin, S. Ida, Kyushu University, Japan

Until now, mixture of Ni and ion-conducting oxides such as Y_2O_3-ZrO_2 or Gd-CeO_2, is usually used as an anode for SOFCs. In this study, we demonstrated that the relatively high power density could be achieved by using oxide composite of $Ce_{0.6}Mn_{0.3}Fe_{0.1}O_2$-$La_{0.6}Sr_{0.4}Fe_{0.9}Mn_{0.1}O_3$ for oxidation tolerant and direct hydrocarbon type SOFCs. Application of oxide composite anode for direct hydrocarbon type fuel cell was studied. Comparing with the power density of the cell using H_2, not only power density but also open circuit potential decreased when CH_4 was used for fuel. This suggests that Ce(Mn,Fe)O_2-La(Sr)Fe(Mn)O_3 exhibits low activity to electrochemical oxidation of CH_4. On the other hand, power density is much improved by using C_2H_6 and further improved by C_3H_8 or C_4H_{10}. In particular, when C_3H_8 or C_4H_{10} is used for fuel, theoretical open circuit potential was observed and the maximum power density was achieved at 1.0W/cm^2 at 1073K, which is almost double higher than that of H_2 fuel. Over 100h, stable power density was exhibited.

9:00 AM

(ICACC-S3-013-2011) Effect of Microstructural Evolution of Anodes with Various Pore Formers on Electrochemical Performance of SOFC

A. Sarikaya*, F. Dogan, Missouri University of Science and Technology, USA

Microstructural evolution of anode materials, particularly the pore-size and its distribution play a critical role in the development of anode supported solid oxide fuel cells (SOFC). Various pore formers (polystyrene, polymethyl methacrylate, graphite and sucrose) were evaluated to optimize the anode microstructure for improved electrochemical performance of the fuel cells composed of NiO-YSZ (Y-stabilized ZrO_2) anode, YSZ electrolyte and YSZ-LSM (lanthanum-strontium manganese) cathode materials. NiO-YSZ anode was prepared by using of 30 vol% pore forming powders which were characterized with respect to their particle size and surface area. Microstructural development of the cells, particularly the anode, was investigated by SEM and porosimetry techniques before/after reduction of NiO to Ni and electrochemical measurements. The relationship between the anode pore structure and electrochemical properties of the cells will be presented. This study allowed describing the pore former – microstructure – performance relations.

9:20 AM

(ICACC-S3-014-2011) A-site Doping of Double Perovskites in SOFC's

C. P. Kuhnell*, T. G. Howell, T. J. Bocock, M. A. Rottmayer, T. L. Reitz, AFRL/RZPS, USA

SOFCs have sparked interest due to their potential for high energy conversion efficiencies and fuel flexibility. One limitation restricting proliferation of SOFCs for many applications includes their limited compatibility with sulfur-containing fuels. The use of reformation technology has been a viable option for fuel cells, but the reformate may still contain as much as 140 ppm sulfur for logistic fuels. Advanced materials including double perovskites (A2BB'O6) have demonstrated exceptional sulfur tolerance when compared to traditional Ni-based anodes but are limited by their conductivity. Double perovskites including Sr2MgMoO6 have been synthesized and evaluated electrochemically using a lanthanum-doped ceria buffer layer to prevent lanthanum diffusion from the Lanthanum-doped Gallate electrolyte. Doping of the A-site with La will help prevent La diffusion, remove additional resistance from LDC, and show the true sulfur tolerance of the material. The objective of this work is to determine the optimum level of La doping to maximize conductivity and sulfur tolerance without an LDC layer. Synthesis of doped-Sr2MgMoO6 will be discussed in detail as well as characterization of the crystal structure and conductivity performed by XRD and EIS, respectively. A thorough discussion on the complete cell testing will be presented utilizing LSGM-supported cells with Pt or LSCF as cathode in 140 ppm H2S/H2 at 650C, 700C, 750C, and 800C.

10:00 AM

(ICACC-S3-016-2011) Microanalyses of Surfaces and Interfaces in Catalyst-Infiltrated LSCF Cathodes (Invited)

W. Qin, M. Liu, M. Lynch, J. Choi, M. Liu*, Georgia Institute of Technology, USA

Recent studies have shown that the stability and performance of a porous LSCF cathode may be enhanced by infiltration of a thin-film catalyst coating such as LSM and SDC. However, the mechanism of the observed enhancement is still unknown. This presentation will highlight our recent findings in microanalyses of the structure, composition, and morphology of LSM and LSCF surfaces as well as the LSM/LSCF interfaces in LSM-infiltrated LSCF cathodes. Microanalyses reveal that a thin (~ 50 nm) LSM film is relatively stable on the surface of an LSCF substrate after annealing at 850C for 900 hours, although the regularity of atom arrangement in the outer layer of the film was reduced from long to short range order. The inner layer of the LSM film and the underlying LSCF maintain their respective crystal structures and their structural coherence. For an LSM-infiltrated porous LSCF cathode, an amorphous layer (~2 to 20 nm) was formed on the surface of LSCF grains. DES analysis of the amorphous layer suggest that it contains La, Sr, Co, Fe, and Mn; this surface LSCFM layer may have enhanced oxygen ion conductivity due to the disorder the high concentration of defects. Also, there was no evidence that Sr has enriched near LSCF surfaces. Thus, the resulting coating of LSCFM not only promotes facile transport of oxygen ions to the underlying LSCF but also inhibits formation of Sr-oxide on the LSCF surfaces.

10:30 AM

(ICACC-S3-017-2011) PrBa0.5Sr0.5Co2O5+δ layered perovskite cathode for intermediate temperature solid oxide fuel cells

X. Xue*, H. Ding, University of South Carolina, USA

Layered perovskite oxides have ordered A-cations localizing oxygen vacancies, and may potentially improve oxygen ion diffusivity and surface exchange coefficient. The A-site-ordered layered perovskite PrBa0.5Sr0.5Co2O5+δ (PBSC) was evaluated as new cathode material for intermediate temperature solid oxide fuel cells (IT-SOFCs). The material was characterized using electrochemical impedance spectroscopy in a symmetrical cell system (PBSC/Ce0.9Sm0.1O1.9 (SDC) /PBSC), exhibiting excellent performance in the intermediate temperature range of 500-700C. An area-specific-resistance (ASR) of 0.23 Ω cm2 was achieved at 650Cfor cathode polarization. The low activation energy (Ea) 124 kJ mol-1 is comparable to that of La0.8Sr0.2CoO3-δ. A laboratory-scaled SDC-based tri-layer cell of Ni-SDC/ SDC/ PBSC was tested in intermediate temperature conditions of 550 to 700C. A maximum power density of 1045 mW cm-2 was achieved at 700C. The interfacial polarization resistance is as low as 0.285, 0.145, 0.09 and 0.05 Ωcm2 at 550, 600, 650 and 700C, respectively. Layered perovskite PBSC shows promising performance as cathode material for IT-SOFCs.

10:50 AM

(ICACC-S3-018-2011) Development of Low Thermal Expansion $Ca_2Fe_2O_5$ Cathode Materials for Solid Oxide Fuel Cells

S. Lee*, D. Kim, D. Kim, KAIST, Republic of Korea

A cobalt-free $Ca_2Fe_2O_5$ oxide with alternating perovskite layers of corner-sharing FeO_6 octahedra and layers of FeO_4 tetrahedra have been synthesized and investigated as a potential cathode material for solid oxide fuel cells (SOFCs). Our preliminary electrochemical testes show a rather high area specific resistance (1.03 Ωcm^2 at 700 °C) for

~20 μm thick layers with GDC electrolyte. The electrochemical performances are improved in the composite with 30 wt % GDC (CG30-70, 0.31 Ωcm^2 at 700 °C). In addition, thermal expansion coefficient (TEC) values of CG30-70 specimen demonstrated $12.9x10^{-6}$ $°C^{-1}$ in the range of 25-900 °C, which provides good thermal expansion compatibility with the GDC electrolyte. The long-term thermal stability and thermal cycle tests of the CG30-70 cathode were carried out. The stable ARS values were observed during both the long-term thermal stability test and the thermal cycle test. An electrolyte supported (300-μm-thick) single-cell configuration of CG30-70/CGO/Ni-CGO delivered a maximum power density of 563 $mWcm^{-2}$ at 800 °C. The unique composite composition of CG30-70 demonstrates improved electrochemical performance and good thermal stability for IT-SOFCs.

11:10 AM

(ICACC-S3-019-2011) The Effect of A-site Stoichiometry on LSCF Cathode Performance and Stability

J. Hardy, J. W. Templeton*, Z. Lu, J. W. Stevenson, Pacific Northwest National Laboratory, USA

Anode-supported SOFCs were prepared and tested identically except for variations in the A-site stoichiometry of the LSCF cathode. A commercial supplier provided LSCF powders that were stoichiometric [La0.6Sr0.4Co0.2Fe0.8O3-δ], A-site deficient [(La0.6Sr0.4)1-xCo0.2Fe0.8O3-δ], and Sr-deficient [La0.6Sr0.4-xCo0.2Fe0.8O3-δ], in which the imposed defiency on the A-site (x) was 0.02, 0.05, and 0.1 in the non-stoichiometric cases. Multiple long-term (1,000 hour) tests were run using each LSCF cathode composition. The performance and stability of the cells will be discussed.

S4: Armor Ceramics

Phenomenology and Mechanics of Ceramics Subjected to Ballistic Impact II

Room: Coquina Salon D
Session Chair: David Stepp, Army Research Office

8:00 AM

(ICACC-S4-011-2011) Depth-of-Penetration Experiments on Transparent Materials

S. Bless*, The University of Texas at Austin, USA

Transparent armor for protection from warhead fragments is a growing priority in the research community. Depth-of-penetration experiments have been adapted for this application. The substrate, against which armor performance is measured, was made from polycarbonate. Projectiles were .30-caliber steel fragment-simulating projectiles (FSP). The materials tested were soda-lime glass (SLG), borosilicate glass (BSG), layered soda-lime glass, stacked bars of soda-lime glass, glass ceramic (GC), spinel, and for reference a glass-reinforced plastic. BSG is found to be better than SLG. Layering SLG always decreases its efficiency. The more advanced materials, GC and spinel, do not provide improvements for FSP protection. These data will be compared with performance against bullets, and interpretation of these results will be in terms of relative compressive and tensile strengths of materials.

8:20 AM

(ICACC-S4-012-2011) Constitutive Response of Intact and Pre-Damaged Soda-Lime Glass

C. E. Anderson*, S. Chocron, A. E. Nicholls, K. A. Dannemann, Southwest Research Institute, USA

Characterization experiments for intact and damaged soda-lime glass as a function of confinement pressure are described. The results are interpreted in terms of two pressure-dependent constitutive models—Drucker-Prager and Mohr-Coulomb—and then compared to the response of a borosilicate glass. An observation is that the slopes of the two models appear to be independent of the degree of damage (intact, predamaged and severely damaged specimens), but the zero-pressure intercept decreases with increasing damage. It is also observed that there is a maximum strength for the damaged glass, i.e., there is a cap on the strength. The characterization results are also compared to the response of flyer-plate impact experiments.

8:40 AM

(ICACC-S4-013-2011) Analysis of the fragmentation of spinel under ballistic impact

E. Strassburger*, M. Hunzinger, Fraunhofer EMI, Germany; P. Patel, J. W. McCauley, U.S. Army Research Laboratory, USA

The fragmentation of two types of spinel with average grain sizes 0.6 μm and 1.6 μm at impact of 7.62 mm AP projectiles was analyzed. The spinel specimens of 6 mm thickness were glued to an aluminum backing and impacted at two different velocities, 850 m/s and 1100 m/s. The targets were integrated in a target box, which allowed for an almost complete recovery and analysis of the ceramic fragments. Different types of high-speed cameras were applied in order to visualize the different phases of fragment formation and ejection. A laser light-sheet illumination technique was applied in combination with high-speed cameras in order to determine size and speed of ceramic fragments during projectile penetration. The application of the visualization techniques allowed the analysis of the dynamics of the fragment formation and interaction with the projectile.

9:00 AM

(ICACC-S4-014-2011) Effect of Acoustic Impedance Mismatch on Fragmentation in Bilayers

E. A. Gamble*, B. G. Compton, F. W. Zok, University of California, Santa Barbara, USA

Dynamic impact tests on Al2O3 - transparent material bilayers were performed to determine the effect of acoustic impedance mismatch on ceramic fragmentation in bilayer systems. Spherical and blunt cylindrical projectiles were used to vary the character and magnitude of the pressure pulse imparted to the system. PMMA and glass back plates allowed assessment of impedance mismatch conditions. The back face was monitored during testing to directly observe spall and fracture behavior. The impact velocity, and consequent elastic wave, required to cause spall was determined for each sample configuration.

9:20 AM

(ICACC-S4-015-2011) Elastic-Plastic Indentation Response of Two Transparent Fine-Grained Polycrystalline Spinels

A. M. Muller*, D. J. Green, The Pennsylvania State University, USA

Indentation of a surface with a hard sphere, known as Hertzian indentation, can be used to statically generate loading conditions resembling the early stages of a ballistic impact event. In addition, the cracking morphologies observed during indentation show similarities, particularly with the formation of cone cracks at the impact site. Failure processes involved in a ballistic impact often entail the production of an inelastic zone that expands and stresses the surrounding elastic material below the impact site. The deformation mechanisms involved in the formation of this inelastic zone are not well understood. Consequently, the transition and interactions between the elastic, inelastic and fracture zones are of great interest especially since they are easily studied by simply choosing the appropriate radius indenter. The emphasis of this study has been on the characterization of plastic deformation during indentation and the transition from elastic to inelastic deformation. In particular, the aim was to study the indentation stress-strain behavior obtained from the analysis of the load–displacement curves of two transparent fine-grained polycrystalline spinels (MgAl2O4) with different grain sizes. Additionally, hardness data from in-situ tests and traditional hardness measurements, such as Vicker's, Knoop and Meyer's, were compared.

S4: Armor Ceramics

High-Rate Real-Time Characterization

Room: Coquina Salon D
Session Chair: David Stepp, Army Research Office

10:00 AM

(ICACC-S4-016-2011) Use of Real-Time X-ray Diffraction Measurements to Examine Shocked Solids at the Microscopic Level (Invited)

Y. M. Gupta*, Washington State University, USA

Dynamic loading experiments (shock wave and shockless compression) are uniquely suited to examine material response at high stresses (10-100 GPa and beyond) and high loading rates (105/s and higher). Additionally, the macroscopic condition of uniaxial strain is exactly satisfied in these experiments. The very short loading times (ps-ns time scales) associated with these experiments provide the opportunity to probe, in real time, material changes (phase transitions, inelastic deformation) as they occur. However, mechanistic understanding of material phenomena has been limited due to the difficulty in obtaining in-situ, microscopic data in real time. This talk will summarize recent experimental developments and results related to real-time, x-ray diffraction measurements in single event experiments. Having successfully demonstrated the use of a synchrotron facility to probe the shocked state on nanosecond time scales, planning is underway to develop a sector dedicated to x-ray diffraction and imaging measurements under dynamic loading at the Advanced Photon Source (at the Argonne National Laboratory). A progress report regarding this proposed first-of-a-kind experimental facility and the scientific payoff from such a capability will be presented.

10:30 AM

(ICACC-S4-017-2011) The strength and failure of ceramics at very high strain rates

G. Hu*, J. Kimberley, K. Ramesh, Johns Hopkins Uni., USA; J. McCauley, Army Research Laboratory, USA

There is very limited experimental work on the strength and the dynamic failure of ceramics at very high strain rates (~10e4 1/s), or equivalently at very high stress rates, even though the behavior of ceramics under these conditions is critical in a variety of impact applications. In previous work, a modified compression Kolsky bar has been used to determine the dynamic compressive strength of aluminum nitride (AlN), at stress rates of approximately 150 MPa/μs. The current work involves the characterization of the mechanical properties of AlN within the very high stress rate range (500~1,000 MPa/μs) using the Desktop Kolsky Bar (DKB) and taking advantage of the benefits of miniaturization. Simultaneously, we use very-high-speed photography to visualize the dynamic failure process. A very strong influence of the loading rate on the compressive strength under uniaxial stress conditions continues to be observed at these very high strain rates. A recently developed scaling model based upon interacting micro-cracks is used to understand the loading rate sensitivity.

10:50 AM

(ICACC-S4-018-2011) The Influence of Temperature and Confinement Pressure on Dynamic Response of Damaged Borosilicate Glass

X. Nie*, W. Chen, Purdue University, USA

Comminution and pulverization of glass is frequently encountered in the process of projectile penetration on vehicle and building glass windows. During such events, the glass material in front of the penetrator nose will be severely damaged and counteract with further penetration, for which both high confinement pressures and high temperatures are expected to take place, and subsequently influence the dynamic mechanical response of damaged glass. The purpose of this study is to investigate such influences on a damaged borosilicate glass with a modified high temperature Kolsky bar setup. Intact glass samples were confined by metal sleeves and loaded to fracture by the primary incident pulse. A secondary incident pulse arrived several hundred microseconds later and continued to load on the damaged glass samples under different confinement levels. Non-contact heating technique was also used to investigate the possible temperature effects. The results showed that under dynamic loading conditions, the shear strength of damaged glass increases linearly with confinement pressures, while the temperature itself did not show any noticeable effect on the shear strength.

11:10 AM

(ICACC-S4-019-2011) Comparison of Damage Propagation Due to High Velocity Ball Impact on Unstrengthened and Chemically Strengthened Glasses

G. Subhash*, University of Florida, USA

Lithium aluminosilicate glass rods were surface strengthened using a patented ion-exchange process which resulted in surface residual stress up to 1 GPa. These rods were impacted with steel balls at 330 m/s. The damage propagation was observed using a high-speed camera in normal light, shadow light and photoelasticity. It was observed that in the unstrengthened glass damage initiates and propagates for a short distance at a maximum velocity of shear wave and then stops. On the contrary, in the strengthened glass the damage propagates at a shear wave velocity for the entire length of the rod and forms needle like damage fragments. Interestingly, the damage propagates along the periphery of the rod and leaves behind small lobes of undamaged glass in the center. The results indicate that the extremely high surface residual stresses caused by the impregnation of foreign atoms during ion implantation allow the stress wave to propagate at a faster rate along the boundary of the rod. As the damage progresses, the stress is released simultaneously in the surrounding regions and promotes further damage with in the glass. This process allows the damage front to sustain its velocity until the entire rod is fully consumed. The insights gained from the three video modes as well as the implications of this damage mode in armor applications will be presented.

11:30 AM

(ICACC-S4-020-2011) The strain-rate dependence of the hardness of AlN doped SiC

L. J. Vandeperre*, N. Ur-rehman, Imperial College London, United Kingdom; P. Brown, Defence Science and Technology Laboratory, United Kingdom

Tailored nanoindentation experiments were used to determine the strain rate dependence of the hardness of AlN doped SiC produced by spark plasma sintering. It is shown that in the nano-indentation regime, where cracking is limited, the hardness of SiC reduces by 0.8 GPa per decade reduction in strain rate. This measured variation in hardness is consistent with estimates for the strain rate dependence of the lattice resistance (Peierls stress) of SiC. These experiments therefore open up the possibility to determine real constitutive equations for plasticity in SiC and other ceramics.

11:50 AM

(ICACC-S4-021-2011) The Effect of Interfacial Toughness on Energy Absorption during Ballistic Impact of Ceramic-Composite Bi-layers

E. K. Oberg*, T. W. Clyne, University of Cambridge, United Kingdom; H. Specht, TenCate Advanced Armour, Denmark

A small gas gun has been used to measure the energy absorption during ballistic impact of bi-layered specimens comprising alumina front plate and carbon composite laminate back plates. A projectile steel ball of 8mm diameter was used and the impact velocity ranged to

about 250ms-1. Energy absorption was monitored via incident and emergent projectile velocities, measured with light gates and electromagnetic induction gates. The ceramic layer thickness was 2 mm and the composite back-plate was varied down to that of a single ply. Specimens were produced by hot pressing of ceramic plates with composite pre-preg sheets. The toughness of the interface between front and back plate was varied via the hot pressing conditions and characterised using the 4-point bend delimitation test. Results show that the interfacial toughness is sensitive to the processing conditions. Ballistic tests were carried out and it is shown that the interfacial toughness can have a significant effect on the crack propagation pattern and on the absorbed energy. An electrical technique was developed to monitor certain crack characteristics, which involves printed circuits on the front alumina plate, allowing the velocities of radial cracks to be measured. It is concluded that the interfacial bond strength is an important parameter in such ballistic protection systems.

S7: 5th International Symposium on Nanostructured Materials and Nanotechnology: Development and Applications

Nanostructured Membranes, Thin Films, Functional Coatings

Room: Coquina Salon C
Session Chairs: Suprakas Sinha Ray, Council for Scientific and Industrial Research; Sanjay Mathur, University of Cologne

8:00 AM

(ICACC-S7-001-2011) Thin Film Ferrites by ALD for Solar Thermal Water Splitting Redox Cycles

J. R. Scheffe, University of Colorado, USA; A. H. McDaniel, M. D. Allendorf, E. N. Coker, Sandia National Laboratories, USA; A. W. Weimer*, University of Colorado, USA

Iron oxide (γ-Fe2O3) and cobalt ferrite (CoxFe3-xO4) thin films have been synthesized via atomic layer deposition (ALD) on high surface area (50 m2/g) m-ZrO2 supports. After deposition of iron oxide and cobalt oxide multilayers at 450 oC, the resulting films are shown to be crystalline consisting of the spinel phase as verified by high resolution transmission electron spectroscopy and Raman spectroscopy. Fe2O3 samples reduced to metallic Fe without CO2 and rapidly deactivated, but when reduced to Fe2+ with the addition of CO2, cycling behavior was improved. Cobalt ferrite samples were successfully cycled without any signs of deactivation, and about four times more H2 was produced because it was reduced to metallic Co and Fe rather than Fe2+. Cobalt ferrites deposited on Al2O3 substrates are capable of being thermally reduced at lower temperatures than bulk CoxFe3-xO4 (200oC-300oC lower) due to a reaction between the ferrite and substrate to form FeAl2O4 (hercynite). Significant quantities of H2 are produced at thermal reduction temperatures of only 1200 oC, whereas, CoxFe3-xO4 produced little or no H2 until thermal reduction temperatures of 1400 oC. CoxFe3-xO4/Al2O3 was capable of being cycled at 1200 oC reduction/ 1000 oC oxidation with no obvious deactivation. Free energy minimization calculations also show that no apparent deactivating slag phase is present up to 1600oC.

8:20 AM

(ICACC-S7-002-2011) Dye Sensitized Solar Cells Employing Nb-doped TiO_2/Al-doped ZnO Transparent Conducting Multilayer Films

J. Noh*, H. Han, S. Lee, D. Kim, J. Park, S. Park, K. Hong, Seoul National University, Republic of Korea

We present the dye sensitized solar cell (DSSC) employing the thermally and chemically stable Nb-doped TiO_2 (NTO)/Al-doped ZnO (AZO) multilayer transparent conducting oxide (TCO) thin film. The NTO over-layer successfully functioned as an oxygen blocking layer during inevitable air-annealing within the fabrication of DSSC and thereby rather enhancing the conductivity of the multilayer TCO after the air-annealing at 450 °C. In addition, the NTO over-layer inhibited Zn^{2+}-dye aggregates from forming at surface of the AZO. Therefore, the NTO over-layer materialized AZO to used as TCO in DSSCs. The DSSC employing the multilayer TCO showed twice enhanced photon to electron conversion efficiency of 3.8 % compared to 1.9 % of that employing the AZO single layer. In this work, cell performance of the DSSC employing the NTO/AZO multilayer TCO and charge transport properties at NTO/AZO interface were characterized by electrochemical impedance spectroscopy (EIS) and photocurrent-voltage measurement, suggesting that the NTO/AZO is a promising TCO for large scaled DSSC in the commercial aspect.

8:40 AM

(ICACC-S7-003-2011) Doped TiO2-Nanotubular Sensor Electrodes for Gas Sensing Applications

B. Saruhan-Brings*, Y. Gönüllü, A. Yüce, G. C. Mondragon Rodriguez, German Aerospace Center, Germany

Relying on its unique properties, titanium dioxide is employed in a versatility of applications, gas sensing being one of them. Low temperature synthesis of doped TiO2-coatings and their nano-structuring enhance these properties. It is reported that the use of one-dimensional (1-D) nanostructures instead of nano-crystalline films yields more than 2-fold increase in efficiency by improving the sensing properties. Nano-tubular sensing electrodes improve sensing performance due to high surface to volume ratio and thus enabling strong interaction between the surrounding gas and the sensing material. This work reports the synthesis of coatings having TiO2-nanotubes by AAO-templated and non-templated anodic oxidation method. Using these coatings gas sensor devices was fabricated and their sensing properties were analyzed towards reducing and oxidizing gases. Long-term stability of the nano-structures was investigated to determine the life-time of sensors. Additionally trivalent additive doped TiO2 nanotubes were synthesized by AAO-templated sol-gel method and phase sequences with composition and temperature were analysed. Sensor properties obtained with various compositions and synthesis methods were compared.

9:00 AM

(ICACC-S7-004-2011) Nanostructured Gas Separation Membranes

R. Prasad*, M. Bazarjani, A. Gurlo, R. Riedel, Technische Universitaet Darmstadt, Germany

Tunable synthesis of materials with desired porosity has received considerable attention in the last decades due to their application as hydrogen storage materials, molecular sieves and catalysts. In the present work we address two applications of nanoporous ceramic materials, i.e. (i) as hydrogen purification membranes and (ii) as filters /protection coatings chemiresistors for CO /H2 sensing in extremely harsh conditions. The hydrogen and carbon monoxide separation is an important step in the hydrogen production process. If H2 can be selectively removed from the product side during hydrogen production in membrane reactors, then it would be possible to achieve complete CO conversion in a single-step under high temperature conditions. Due to the several drawbacks of the state-of-the-art membrane materials, there is a continuous need in the development of novel ceramic materials with desired porosity and stability. Promising candidates are silicon-based polymer-derived ceramics (PDCs), e.g. polysilazane-derived ternary Si-C-N- and quarternary Si-C-N-(O) / Si-B-C-N systems with excellent thermal and chemical stability.

9:20 AM

(ICACC-S7-005-2011) Rare Earth Scandates and Interlanthanide Oxides for DRAM Capacitor Applications

S. P. Pavunny, R. Thomas*, R. S. Katiyar, University of Puerto Rico, USA

In the integrated circuit, insulating layers have attracted much attention for the active and passive devices. Dynamic random access mem-

ory technology evolved through SiO_2, SiO_2/Si_3N_4, Si_3N_4, Al_2O_3, Ta_2O_5 material systems. In 2005 DRAM entered the sub-100 nm node and now slowly moves from MIS to MIM capacitors with focus on the design and new high-k dielectric materials. Since 2001 many linear dielectric materials have been investigated like ZrO_2, HfO_2, and Pr_2O_5 for this purpose with HfO_2 offering most robust capacitance performance. Recent reports on the scandate for gate-oxide applications in active devices showed encouraging results in terms of high dielectric constant and structural stability. Here we consider one scandate and an interlanthanide oxide for DRAM application. $DyScO_3$ and $LaGdO_3$ thin films were grown on $Pt/TiO_2/SiO_2/Si(100)$ substrates. In the case of $DyScO_3$ films, the dielectric constant of the films was ~21. Electrical properties are promising: $DyScO_3$ film reached an equivalent oxide thickness (EOT) of ~1.9nm and the dielectric breakdown field of ~2.3MV/cm. In the case of $LaGdO_3$ the dielectric constant was ~25 and the loss tangent was ~0.001. All the encouraging properties of these materials; negligible frequency, bias voltage and temperature dependence of the electrical properties are of importance for the DRAM application.

10:00 AM

(ICACC-S7-006-2011) Mechanical Properties and Microstructure Evaluation of Spark Plasma Sintered Al_2O_3-ZrO_2-TiCN Nanocomposites (Invited)

G. Sundararajan*, D. Chakravarty, Int. Adv. Res. Centre for Powder Metallurgy & New Materials (ARCI), India

The primary objective of the presentation is to illustrate the influence of addition of nanocrystalline zirconia and TiCN to ultrafine alumina in terms of the resulting mechanical properties (hardness, toughness and flexural strength) and the microstructures. As a first step, the addition of nanocrystalline zirconia to nanocrystalline alumina was varied over a range and the optimum zirconia content was established on the basis of the mechanical properties. To these optimized Al_2O_3-ZrO_2 composition, TiCN was added in different weight percentages and the effect of such additions of mechanical properties of Al_2O_3-ZrO_2-TiCN composite was evaluated. In all the above cases, sintering was carried using spark plasma sintering (SPS) facility. Addition of nanocrystalline zirconia to alumina led to improvement in both hardness (~24 GPA) and toughness (5.5 – 6.0 MPa √m). However addition of TiCN led to reduction in both hardness (20 GPa) and toughness (4.0 - 4.5 MPa.√m). The above results will be presented in detail and also reasons for the observed mechanical behavior and microstructure will be explained on the basis of detailed TEM studies.

10:30 AM

(ICACC-S7-008-2011) The Effect of Synthesis Parameters on the size of Carbon Spheres Produced by Chemical Vapour Deposition without a Catalyst

I. Sibiya*, S. K. Pillai, Council for Scientific and Industrial Research, South Africa; S. D. Mhlanga, University of the Witwatersrand, South Africa; S. Sinha Ray, Council for Scientific and Industrial Research, South Africa

A chemical vapour deposition method is used to prepare carbon spheres (CSs) from Acetylene without any catalyst. The size, quality and quantity of these spheres are then controlled by changing the composition of flow rate, temperature and synthesis time. These CSs have been systematically studied by scanning electron microscopy (SEM), transmission electron microscopy (TEM), thermogravimetric analysis (TGA) and X-ray diffraction (XRD). SEM studies reveal how the sizes of the spheres vary with varying conditions, while TEM reveals how graphitic spheres of smooth surface with varying diameter and rough surface with uniform diameter vary with conditions as well. The higher the temperature and flow rate of the carbon source the bigger the spheres and the higher the production rate, while the shorter the time of flushing the synthesis gas the smaller the size of spheres. TGA and XRD analysis of carbon, hydrogen and nitrogen reveal a higher amount of carbon in the spheres.

10:50 AM

(ICACC-S7-009-2011) Effects of 120 MeV Ag9+ and 100 MeV Si8+ ions irradiation on Photoelectrochemical Properties of Nanocrystalline Strontium Titanate Thin Films

J. Shrivastava, S. Upadhyay, N. Singh, V. Sharma, P. Kumar, V. R. Satsangi, R. Shrivastav, S. Dass*, Dayalbagh Educational Institute, India

Solar energy driven water splitting combines several attractive features for energy utilization. Hydrogen generated from water using solar energy, is a leading candidate for renewable and environmentally safe energy carrier. Photoelectrochemical water splitting has attracted attention as one of the ideal hydrogen production processes. In search for efficient photocatalysts for water splitting, the effect of various nanostructured mixed oxides are being investigated on account of stability and photocorrosion resistance offered by them. Among them, SrTiO3 appears to be an interesting candidate due to its good thermal & chemical stability. In the present study, thin films of nanostructured SrTiO3 were prepared on ITO coated glass substrate by sol-gel spin coating. X-ray diffraction, X-ray photoelectron spectroscopy, UV-Vis absorption spectroscopy, atomic force microscopy and scanning electron microscopic techniques were used to study the effect of 120 MeV Ag9+ and 100 MeV Si8+ ions irradiation on the photoelectrochemical behaviour of nanocrystalline SrTiO3 thin films. The films were irradiated at six different fluences i.e. 1×1011, 2×1011, 5×1011, 3×1012, 1×1013 and 2×1013 ions cm−2. The X-ray diffraction profiles of ST samples represent no change in the perovskite cubic structure upon irradiation of the samples.

11:10 AM

(ICACC-S7-010-2011) Wear properties of nano-composite MoN-5, 10, 20 at. % Cu coatings deposited by reactive magnetron sputtering with single alloying target

K. Moon*, H. Lee, D. Jung, S. Shin, Korea Institute of Industrial Technology, Republic of Korea

In this study, to reduce energy consumption and wear problems of engine parts, it has been tried to deposit the MoN-Cu thin coatings showing high hardness and low friction at low and high temperatures. This kind of nano-composite coating is generally made by various processes using multiple targets such as Mo and Cu. However, during the deposition with multiple targets, it is not easy to control the exact composition, homogeneous deposition of large scale specimens. Also it is very difficult to add the third elements to the coating. So, in this study, it has been tried to make the single Mo-Cu alloying targets with the composition which showing the best friction coefficient and surface hardness. For this, it has been reviewed the properties of MoN-Cu coating with various composition that were prepared by unbalanced magnetron sputtering using multiple targets. Single alloying targets with the composition showing the best properties were prepared by powder metallurgy methods such as mechanical alloying and spark plasma sintering. Also, 10, 20, 30 at. % Cu added Mo-Cu targets and third elements added Mo-Cu-X (X= Co, Cr, Ag) were also prepared. The nano-composite MoN-Cu-X coating prepared using the alloying targets will be compared with the films from the multiple targets.

S8: 5th International Symposium on Advanced Processing and Manufacturing Technologies for Structural and Multifunctional Materials and Systems (APMT) in honor of Professor Katsutoshi Komeya

Novel Forming and Sintering I

Room: Coquina Salon B
Session Chairs: Rainer Gadow, IFKB University of Stuttgart; Eugene Medvedovski, Umicore Indium Products

8:00 AM

(ICACC-S8-013-2011) Ceramic injection molding of alumina-silicon carbide nanocomposites (Invited)

R. Gadow*, F. Kern, IFKB University of Stuttgart, Germany

Alumina-SiC nanocomposites have attracted the interest of material scientists due to their excellent mechanical and thermomechanical properties. Compared to alumina they offer higher strength, toughness and reliability. The high creep resistence of alumina-SiC makes it attractive for high temperature structural applications. Commercial applications however require performing and reliable manufacturing technologies. Ceramic injection molding (CIM) was chosen for the production of small and complex shaped components with narrow dimensional tolerances used in engineering applications. In this study the complete process cycle of thermoplastic injection molding was studied with the aim to evaluate its suitability for industrial production of alumina-SiC nanocomposites. Compounding of the feedstocks, forming by CIM and the subsequent thermal treatment – debinding and pressureless sintering were investigated. Intermediate and final products were characterized with respect microstructure and mechanical properties.

8:30 AM

(ICACC-S8-014-2011) Tunable Thermoreversible Gels for Casting Processes (Invited)

K. T. Faber*, N. O. Shanti, M. E. Seitz, Northwestern University, USA

Thermoreversible triblock copolymer gels provide an attractive vehicle for the casting of ceramic materials. By tuning the triblock architecture (block length and endblock fraction) and chemistry, it is possible to adjust the rheological and green body properties of the slurries and the cast body, respectively. This design flexibility broadens the types of casting for which the triblock gels are suited. We describe examples of gelcasting of porous alumina where the ideal triblock copolymer has a relatively short midblock and a nearly equivalent midblock/endblock ratio. Thermoreversible gels for tape casting will also be demonstrated for laminate solid oxide fuel cells. Here, triblock copolymers should have low total molecular weight with short end blocks.

9:00 AM

(ICACC-S8-015-2011) Injection Molding Alumina Suspension Gels at Room Temperature

V. L. Wiesner*, J. P. Youngblood, R. W. Trice, Purdue University, USA

Injection molding a ceramic suspension gel (CeraSGel) at room temperature is proposed to develop a novel, low-cost and energy efficient processing method capable of forming ceramic parts with complex geometries. Fabricating an alumina CeraSGel involves dispersing alumina powder in water by ball milling with ammonium polyacrylate Darvan 821A dispersant. Polyvinylpyrrolidone (PVP), which is a water-soluble polymer, is added to increase suspension viscosity through gel formation. The gel-like mixture has been observed to behave like a yield-pseudoplastic fluid at room temperature. Increasing the shear rate applied to the suspension during the injection molding operation decreases viscosity. Thus, controlling the rate at which the gel is fed into a mold allows the suspension to flow at a lower viscosity, while maintaining a high enough consistency to retain its initial shape. After drying, binder burnout, and sintering, bulk density was measured using the Archimedes technique. Samples were observed to reach 98% theoretical density. The strength of the formed part will be measured using the C-ring test per ASTM C 1323-96. Parallel plate rheometry will be used to characterize CeraSGel rheological behavior, and scanning electron microscopy will be used to analyze the microstructure of sintered samples.

9:20 AM

(ICACC-S8-016-2011) The Mechanisms and Kinetics of AlN Powder Hydrolysis

A. Kocjan*, A. Dakskobler, K. Krnel, T. Kosmac, Jozef Stefan Institute, Slovenia

We have conducted extensive research in order to better understand and control the process of AlN powder hydrolysis. The reaction of AlN powder with water in diluted aqueous suspensions in the temperature range 22–90 °C was studied in detail. The pH and the temperature variation of a 3 wt. % AlN powder suspension at 22 °C, 50 °C and 90 °C were monitored. TG and TEM analyses were employed to study the temperature-dependent course of the hydrolysis and the reaction kinetics, which was described by an unreacted-core model. The hydrolysis exhibits three interdependent steps, i.e., the induction period, the first and the second stage of hydrolysis. The hydrolysis of the AlN powder is a reaction-controlled process in the temperature range 22-70 °C, for which the activation energy was calculated. At 90 °C the diffusion of OH- ions through the product layer determines the rate of hydrolysis. A mechanistic model was proposed for the hydrolysis in the temperature range 22-90 °C with the use of SEM and XRD techniques. The thorough analysis of the temperature dependence of the course of the hydrolysis and the reaction kinetics, along with a mechanistic model set up for the hydrolysis reactions, gives a unique perspective on the hydrolysis, in a form that has not been presented in the literature so far.

10:00 AM

(ICACC-S8-017-2011) Large Size Structural Ceramic Manufacturing by the Shaping of Thixotropic Slurries

E. Medvedovski*, Umicore Thin Film Products, USA

Manufacturing of large-sized structural ceramics is quite challenging, especially, if the ceramic components are designated for wear-, corrosion- and thermal shock-resistance applications. In many cases, monolithic complicated shapes, such as cones, cyclones, elbows and other components with sufficient wall thickness (up to 3-5") are required in industry. The shaping from thixotropic slurries contained particles of various sizes allows processing complicated large-sized (up to 1 m diameter and height) components for structural applications. This technology is versatile, and it does not require expensive and complicated equipment. As example, silicon carbide-based ceramics obtained by the proposed technology are demonstrated.

10:20 AM

(ICACC-S8-018-2011) A Forming Technique to Produce Spherical Ceramic Beads Using Alginic Acid, Sodium Alginate and Ammonium Alginate

C. J. Espinoza*, T. Wei, B. Cho, W. M. Kriven, University of Illinois at Urbana Champaign, USA

The purpose of this study was to investigate a novel forming method to produce spherical ceramic beads by the sol-gel method using alginic acid, sodium alginate and ammonium alginate. The process involves preparing the slurry formulation and the gelling solution. The preparation of the slurry formulation includes mixing oxides, distilled water, dispersant and alginate solution with respect to the ceramic powders. The gelling solution was composed of CaCl2 with a thin layer of ethanol and petroleum solvent to retain the spherical shape. The gelling solution was prepared by mixing CaCl2 with distilled water. The ceramic droplets passed through the immiscible lay-

ers into an aqueous gelling solution and they are converted into rigid beads. It was found the alginic acid produces spherical beads with wrinkles, tails and dimples. However, when the viscosity of the alginates was tested in a slurry with 50 to 70 wt% alumina concentration with everything else being constant, spherical beads without deformations resulted. Results showed that higher alumina ratio leads to shorter gellation time but requires a higher concentration of petroleum solvent to help to retain spherical shape. The method could obtain a density greater than 98% theoretical density and it could be tailored to produce any ceramic beads useful such as catalyst supports and grinding media.

10:40 AM

(ICACC-S8-019-2011) The Effect of Texturing Techniques on the Permeability and Permittivity spectra of Sintered Single Phase Ba3Co2Fe24O41 (Co2Z) Hexaferrite Ceramics for magneto-dielectric antenna applications

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

Among the technological advances in antenna technology leading to improved WiMax and GPS functionality is that of magneto-dielectric antennas. For applications in the 100 MHz-1GHz range, hexagonal ferrites are among the most promising materials. This range is too high in frequency to be served by conventional oxide spinel materials and too low in frequency to be suitable for dielectric antennas. Hexagonal ferrites have the advantage in that, with suitable texturing, the magnetic permeability can be made to be equivalent to the permittivity, therefore leading to a perfect impedance match to free space and zero reflection over the air-ceramic interface. Additionally, high miniaturization factors are possible since the size scales as the square root of the product of the permittivity and permeability. Currently, the state-of the-art material is known as Co2Z with the formula (Ba3Co2Fe24O41) and an unaligned permeability of 8-10. With various magnetic texturing techniques, this permeability can be increased to near 30 making this material suitable for these applications.

11:00 AM

(ICACC-S8-020-2011) Oriented alumina ceramics prepared from colloidal processing in magnetic field

S. Tanaka*, R. Furushima, Z. Kato, K. Uematsu, Nagaoka University of Technology, Japan

The crystallographic orientation of ceramics is an attractive method for improving functional property. The crystal oriented ceramics is prepared from colloidal processing in the magnetic field and subsequent sintering. The objective of this study is to show influence of particle size, dispersion state and sintering processing on the textured microstructures. Alumina particles with 0.5-1.3 μm were used. Dispersed slurry was prepared by ball milling. Each slurry was dried in high magnetic field at room temperature. Then, they were sintered. The particle dispersion was characterized by microscopy and rheology measurement. The orientation degree of the green compact and sintered ceramics was evaluated by the XRD measurements. Textured structure in ceramics was observed by the SEM. The degree of orientation of compacts made from particles 1.3 μm was the highest among several conditions. Characteristics of slurry showed that the particle-particle interaction cause the orientation degree lower. However, the degree of orientation of the green compacts with smaller particles increased drastically by densification and grain growth during sintering processing.

11:20 AM

(ICACC-S8-021-2011) Servo Motor Drive Press for Uniaxial Compacting

W. Schuebl*, H. Schmidt, Dorst Technologies, Germany

Dorst Technologies has introduced a major innovation to the uniaxial compacting process with a new drive principle for powder presses. The highly dynamic and electrically efficient servo drives allow the programming of individually well defined press movements and speeds throughout the compacting cycle, the availability of the full torque load from the start of the cycle delivers unrestricted press forces when needed, and the integral closed loop control ability of servo drives allows the operation of the press by attaining a predetermined position or force within very tight and steadily repeatable tolerance windows. Compared to the traditional principles of mechanical and hydraulic drives the servo motors offer through their inherent electrical efficiency a significant potential for the reduction of primary energy consumption. By buffering the DC power supply to the servo drives in an energy warehouse the connected load for a press with nominal pressing force of 150 KN is reduced to only 5 kW. From this set of conceptual advantages an entirely new line of axial powder presses utilizing the servo drive principle has been developed. The new press type EP is available as single or multi-platen version for pressing forces ranging from 150 to 1200 kN. The paper discusses the advancements these improvements represent to the compacting process in a production environment.

11:40 AM

(ICACC-S8-022-2011) Preparation of MgSiN2–based Phosphors by Combustion Synthesis

Y. Zhou*, National Institute of Advanced Industrial Science and Technology (AIST), Japan; D. Wakimoto, Nagoya Institute of Technology, Japan; Y. Yoshizawa, K. Hirao, National Institute of Advanced Industrial Science and Technology (AIST), Japan; S. Hashimoto, Y. Iwamoto, Nagoya Institute of Technology, Japan

A combustion synthesis method, also termed self-propagating high-temperature synthesis (SHS), was used to prepared MgSiN2 and the related phosphor powders. By using Si3N4 and Mg as raw powders and selecting appropriate starting compositions and combustion parameters, single phase MgSiN2 was synthesized under an atmosphere of 6 MPa nitrogen gas within only a few minutes. Moreover, by doping Mn2+ and/or Ce3+ ions, a variety of phosphors based on the MgSiN2 host lattice could be prepared by such a highly efficient combustion synthesis method. Phase compositions and particle morphologies of the synthesized powders were characterized and their photoluminescence properties were measured. Effects of the type and amount of the doped activator ions on the photoluminescence properties of the synthesized phosphors were discussed.

S9: Porous Ceramics: Novel Developments and Applications

Structure and Properties of Porous Ceramics I

Room: Coquina Salon H
Session Chair: James Zimmermann, Corning Incorporated

8:00 AM

(ICACC-S9-013-2011) High performance SiC foams: properties and applications (Invited)

A. Ortona*, SUPSI-ICIMSI, Switzerland; S. Gianella, Erbicol SA, Switzerland

Silicon carbide open cell ceramic foams with elevated porosity and macro pores are a crucial components of high energy heat radiation porous burners employed in industrial plants for paper production, moulds heating, painting. Foams geometry, architecture and base materials, have been adapted to several other high temperature applications. SiC foams are under testing in catalysis, heat transfer, concentrated solar absorbers, aeronautics and aerospace. This work presents Si-SiC foams main characteristics as well as an overview of the above-mentioned applications.

8:30 AM

(ICACC-S9-014-2011) Ceramic Foams with Increased Specific Surface Area

M. Fukushima*, Università di Padova, Italy, National Institute of Advanced Industrial Science and Technology (AIST), Japan; P. Colombo, Università di Padova, Italy

Catalyst-Assisted-Pyrolysis of preceramic polymers was used to grow silicon nitride and silicon carbide nanowires on commercially available reticulated open cell foams (SiC and Alumina). Depending on the nature of the coating of preceramic polymer, the type of catalyst (Co or Fe-based) and on the processing conditions (gaseous atmosphere and temperature), 1D nanostructures of different amount, length and size were obtained. This led to an increase of the specific surface area of the cellular ceramic substrates and to a varied nanowire morphology. The main properties of the materials were investigated, including mechanical strength and BET surface area. The proposed method is a simple and effective route to provide 1D nanostructures and high specific surface area to cellular ceramics.

8:50 AM

(ICACC-S9-015-2011) Biomorphic SiC, from Porous to Solid, by Reactive Infiltration

J. Narciso*, N. Rojo-Calderón, Alicante University, Spain

Biomorphic SiC components were manufactured using reactive infiltration. SiC components were fabricated by employing carbon substrates obtained from different precursors. Graphitizable and non-graphitizable carbon precursors were selected, these being petroleum residues and lignocellulosic materials, respectively. The carbon microstructure of each precursor has been also modified by high temperature treatment of the precursor. Chosen the adequate precursor an heat treatment we can obtained different microstructures (from cellular to solid) with a wide range of properties.

9:10 AM

(ICACC-S9-016-2011) Preparation and characterization of in-situ anchored Pt NPs into frameworks of mesoporous silica

H. Lee*, J. Jeong, J. Yoo, S. Lee, Korea Institute of Ceramic Engineering & Technology, Republic of Korea

Platinum nanoparticles (Pt NPs) are attractive for catalyses because of their size effects. To design high-performance and robust catalysts in terms of activity, the stability at high temperatures and the resistance to deactivation is of great importance. Even though engineering metal nanoparticles with different sizes and morphologies is very well established now, it has been difficult to adopt these advances into successful application in catalysis. The main drawback is the possibility of coalescence and sintering of the nanoparticles under harsh catalytic reaction conditions. Here, we present an improved method to synthesize an in-situ anchored Pt NPs into the frameworks of the sulfur-containing mesoporous silica (SMS) through co-condensation of bis[3-(triethoxysily)propyl]tetrasulfide (TESPTS) and tetraethyl orthosilicate (TEOS) in the presence of a triblock copolymer template. Based on the co-condensation of siloxane and organosiloxane precursors, the Pt NPs anchored into the SMS frameworks by strong interaction between the Pt NPs and S moieties of TESPTS, which was verified by XPS, played an important role in the stabilization of Pt NPs against the sintering or coalescence problems. The Pt NPs well dispersed and anchored into the frameworks of the SMS are the main factors leading to the high catalytic activity and enough stable to be recycled multiple times.

9:30 AM

(ICACC-S9-017-2011) Electrical Properties and Evolving Microstructure of Ceramic Powder Compaction

T. Pruyn*, R. Gerhardt, Georgia Institute of Technology, USA

The use of ceramic and glass composites with percolated segregated microstructures have numerous potential applications. In order to understand the influence that percolation will have on these composites, the electrical behavior of the filler was studied. Using a custom made die with an insulating outer sleeve, dc measurements and ac measurements using impedance spectroscopy were made on a variety of ceramic conducting powders as a function of loading and unloading compaction pressure. From the impedance spectroscopy data, two semicircles were observed in the complex impedance plot. One of these semicircles is believed to represent the material property, while the other is likely due to the void space and interfaces. In addition to the impedance, the capacitance, admittance, and permittivity were also determined. Since the volume of void space changes with compaction pressure, the capacitance was found to have non-linear variation with application of pressure.

Structure and Properties of Porous Ceramics II

Room: Coquina Salon H
Session Chair: Irene Peterson, Corning Incorporated

10:10 AM

(ICACC-S9-018-2011) Not all microcracks are born equal: thermal vs mechanical microcracking in porous ceramics (Invited)

G. Bruno*, Corning Incorporated, USA; A. M. Efremov, CSC, Russian Federation

Experimental evidence for a fundamental difference between thermal and mechanical microcracking in porous cellular ceramics will be given. The first is created during cooling from the firing temperature and is due to the high expansion anisotropy at crystal level; the second is created when the porous microcracked body is subjected to an external (compressive) stress and is due to damage to the microstructure. Whereas thermal microcracks are closing fast, the mechanical ones are opening slowly upon compression. Indeed, characteristic times of the two phenomena differ by one order of magnitude. The first phenomenon is reversible, as CTE (coefficient of thermal expansion) and Young's Modulus curves vs Temperature show: upon cycling they superpose almost identically. The second phenomenon is irreversible, as demonstrated by the fact that the Young's modulus changes as a function of applied stress and does not recover upon unloading. As an example of the superposition of the two phenomena, β-eucryptite shows a Young's modulus vs Applied Stress with a maximum at intermediate stress values. This can be explained by the initial closure of thermal microcracks upon external pressure, and the successive opening of new mechanical microcracks. By comparison to FEM simulations of cracks in pore structures, it is believed that mechanical microcracks are larger in size than the thermal microcracks.

10:40 AM

(ICACC-S9-019-2011) 3D Microstructures and Porosity characterization at Multiscale resolution-transitioning from Synchrotron to Laboratory

S. H. Lau*, Xradia Inc., USA; J. McCutcheon, University of Connecticut, USA; A. Gu, L. Hunter, J. Gelb, Xradia Inc., USA

Characterization of 3D microstructures is important in almost all disciplines of science-from biological system to an engineered material.Accurate characterization of micro and nanostructures, its porosity and connectivity is highly critical to predict thermal-mechanical and transport properties of the material.While Non invasive 3D imaging of materials has routinely been reported using synchrotron radiation computed tomography(CT)at the micro and nano-scale resolution, their accessibility is limited to the research community. We describe studies using a suite of novel lab based x-ray CT systems with imaging capabilities across wide lengthscales. Samples with dimensions from several cm to micron size may be imaged non-invasively at varying resolution from tens of microns to sub 50 nm. The high resolution and unique phase contrast features of the novel CT also lend itself to characterization of soft materials, small density differences between material phases, microcracks and voids. Porosity and 3D structural characterization for a variety of materials including

ceramics, composites and polymeric membranes will be discussed, with illustrations from SOFC material, thermal barrier coatings, ceramic foams and water filtration membranes.These Lab based CT images and analysis will be compared with with synchrotron based tomography, SEM and porosimetry measurements.

11:00 AM

(ICACC-S9-020-2011) Alternative Test Coupons for Failure Stress Evaluation of Diesel Particulate Filters

A. Wereszczak*, E. Fox, M. Lance, Oak Ridge National Laboratory, USA

Established mechanical test coupons and methods that are used to evaluate the stress of failure initiation in brittle materials are adapted here to examine failure initiation in diesel particulate filters (DPFs). Custom designed test coupons are harvested out of a DPF to accommodate each test method and to promote a particular orientation of crack initiation with respect to a DPF's four-fold rotational symmetry. Biaxial flexure testing of DPF disks produces a radial tensile stress and a crack whose plane is parallel with the DPF's longitudinal axis. The DPF theta specimen can accomplish the same. The DPF O-ring specimen and its testing produces hoop tension at specific locations at the DPF's original outer diameter (OD) and at the inner diameter of the test coupon, and a crack whose plane is parallel to the DPF's longitudinal axis. The DPF sectored flexural testing produces axial tension at the DPF's OD and a crack whose plane is perpendicular to the DPF's longitudinal axis. These geometries and modes of produced crack initiation are discussed in context to the DPF's rotational symmetry along with the assessments of each specimen's ease of fabrication, testing, failure stress determination, and ultimate viability. Research sponsored by the Propulsion Materials Program, DOE Office of Vehicle Technologies, under contract DE-AC05-00OR22725 with UT-Battelle, LLC.

11:20 AM

(ICACC-S9-021-2011) Elevated Temperature Fracture Toughness Behavior of Porous Ceramic Materials

T. R. Watkins*, A. Shyam, Oak Ridge National Laboratory, USA; R. J. Stafford, Cummins Inc., USA

Fracture toughness measurements of various porous ceramic materials have been performed under ambient conditions to rank their performance in terms of crack propagation resistance in exhaust aftertreatment devices. Since these devices operate at elevated temperatures, additional tests to examine the elevated temperature response have been conducted using the double torsion testing methodology. The double torsion tests were performed on rectangular plate specimens fabricated from walls of honeycomb aftertreatment devices. The room temperature fracture behavior will be compared with elevated temperature fracture behavior of porous cordierite and silicon carbide materials.

11:40 AM

(ICACC-S9-022-2011) Microstructural Simulation of Mechanical Behaviour of porous CMC matrices by means of a parametric Unit Cell Approach

H. Richter*, C. Heinig, M. Bartsch, German Aerospace Center, Germany

Wound highly porous oxide ceramic matrix composites (WHIPOX®), manufactured by German Aerospace Center in Cologne, consist of oxide fibres, embedded in an oxide matrix. WHIPOX® applies the concept of a highly porous matrix to achieve weak fibre-matrix bonding and macroscopic non-brittle, damage tolerant behaviour under mechanical loading. In this class of materials, damage evolution initiates on the microscale in the matrix component, and interacts with damage processes on subsequent length scales in a complex manner. To study the influence of changes in matrix porosity or particle diameter on the microscopic mechanical properties, a unit cell approach has been chosen. Based on comprehensive microstructure analyses, the unit cells are generated parametrically by means of a random sequential addition algorithm that randomly places spherical matrix particles inside a bounding box. This facilitates the numerical simulation of the mechanical behaviour of virtual matrix microstructures under different loading conditions via finite element method. The simulation results are compared with experimental data. To validate the numerical model, mechanical tests on small specimens of porous matrix material and microscopic investigations have been performed.

12:00 PM

(ICACC-S9-023-2011) Cell-size effect in cellular ceramics

T. Fey*, B. Ceron-Nicolat, P. Greil, University of Erlangen, Germany

Polymer derived Si-O-C ceramics with a wide cell range extending from 10 ppi up to 80 ppi which correlates to cell sizes of 50 to 2500 μm were produced from PU-Templates by using slurry-infiltration techniques. Fractional density, permeability, porosity and morphology were analyzed and the mechanical and thermal properties were measured. The relative density varies from 0.16 up to 0.3 with increasing compressive strength from 1.8 MPa up to 3.6 MPa. μCT-measurements were used to generate FE-Meshes from the volume data. Thermal and mechanical loads were applied to simulate stress and strain response as a function of cell size. Furthermore, local failure of the cellular structure was simulated by using fracture criteria implemented in the STAU package extension to the FE-code.

S13: Advanced Ceramics and Composites for Nuclear Fusion Applications

Fuel Ceramics Science and Technology I

Room: Oceanview
Session Chair: Ping Xiao, University of Manchester

8:00 AM

(ICACC-S13-001-2011) Zirconium carbide for gas cooled reactor fuels (Invited)

S. L. Lance*, Y. Katoh, G. Vasudevamurthy, T. Besmann, Oak Ridge National Laboratory, USA

Zirconium carbide has been discussed for use in high temperature gas cooled reactors for decades. The primary application was as direct replacement for the SiC "pressure vessel" of the typical tri-isotropic (TRISO) fuel. The motivation for this replacement was two-fold. Firstly, ZrC offered the possibility of superior high temperature performance and secondly, ZrC had been shown to resist diffusion and external release of certain fission products such as silver. Another potential use and benefit of ZrC is its benefit as an oxygen getter stabilizing the evolving fuel. In this paper, recent work evaluating the performance of ZrC for very high performance "Deep Burn" fuels will be presented. Included in this discussion will be the fundamental properties of ZrC and how they impact high temperature performance of fuels. Additionally, the encouraging performance of this material under high temperature (600-1500°C), high dose (up to 8 dpa) irradiation will be presented.

8:30 AM

(ICACC-S13-003-2011) Multiphase Ceramics for Nuclear Fuel

D. Men, University of California, Irvine, USA; M. K. Patel, Los Alamos National Laboratory, USA; M. L. Mecartney*, University of California, Irvine, USA

Reprocessing of spent nuclear fuels produces high level waste containing minor actinides. In order to reduce the radiotoxicity, one of the methods proposed is the transmutation of minor actinides in existing fats reactor or in and accelerator driven sub-critical system.

This can be done by incorporating them into a matrix which is inert against formation of new actinides. Candidate inert matrix materials should have thermal conductivity higher than UO_2 to avoid central melting, high melting point, good radiation stability, and good solubility for the actinides. In the current work, we propose a three/four-phase ceramics, composting of i) CeO_2/ZrO_2 as a surrogate for UO_2, ii) Al_2O_3 as the heat conducting phase, and iii) $MgAl_2O_4$, MgO or $LaPO_4$ as the radionuclide-bearing phase with good amorphization resistance. Complex oxides with wide ranges of stoichiometry like $MgAl_2O_4$ have a natural tendency to accommodate lattice disorder. $LaPO_4$ can incorporate a wide variety of the radionuclides into its structure and recrystallizes at relatively low temperatures. ZrO_2 is a candidate material for use as an inert matrix for Pu burn-up. Studies of the creep behavior and radiation stability were performed using high temperature deformation and ion beam implantation, along with electron microscopy analysis.

8:50 AM

(ICACC-S13-004-2011) The Influence of Phosphorous on the Growth Morphology of CVD-grown 3C-SiC

I. J. van Rooyen*, National Laser Centre, CSIR, South Africa; J. H. Neethling, Nelson Mandela Metropolitan University, South Africa; A. Henry, E. Janzen, Linkoping University, Sweden

The effect that different Si isotopes may have on the SiC surface morphology during the CVD manufacturing process and after transmutation due to irradiation is of interest as it may influence the interface properties between the SiC grains and SiC-PyC layers of the TRISO coated particles used in HTRs. 30Si transmutes to phosphorous (31P) and other transmutation products during irradiation, which may affect the integrity of the SiC layer. This study describes the work done on unirradiated SiC, but the SiC samples were prepared with varying phosphorous levels to "simulate" the presence of P due to transmutation. Phosphorous-doped 3C-SiC layers were deposited on Si (100) substrates with silane (SiH4) and propane (C3H8) as precursors diluted in hydrogen (H2). Growth procedures were changed to obtain different surface morphologies. Phosphorus doping of the layers was done during epitaxy using tertiary butyl phosphine (TBP) (C4H9PH2) as a donor source, the doping level was varied between 1.1x1015 - 1.2x1019 atom/cm3. The effect of deposition temperature and P-doping level on thirteen samples is critically examined using Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD) and Atomic Force Microscopy (AFM).

9:10 AM

(ICACC-S13-005-2011) Atomistic modeling of Ag diffusion in β-SiC

I. Szlufarska*, D. Morgan, S. Khalil, D. Shrader, University of Wisconsin, USA

Cubic (β) SiC plays an important role in the design of TRISO-coated fuel particles in the High Temperature Gas Cooled Reactors. The primarily role of the SiC layer in TRISO is to prevent metallic fission products (MFPs) from diffusing into the coolant system. However, some of the MFPs (e.g., Ag and Cs) have been shown to diffuse through the coating. In this study we test the hypothesis that diffusion of Ag through SiC grain boundaries (GBs) is the dominant escape mechanism of MFPs. Using atomistic modeling we identified key differences between diffusion of Ag through bulk and through $\sum 3$ GB of SiC. Modeling of diffusion is carried out by direct ab initio calculations of defect formation and migration energies. Realistic GB structures have been prepared using molecular dynamics simulations based on empirical potentials and our recently developed structure optimization scheme. We determined the diffusion mechanisms and rates of the most stable Ag defects in SiC. Our results show that there is strong segregation tendency of Ag to GBs of SiC and that at least for selected GBs the estimated diffusion coefficients in SiC GBs can be as low as those calculated from integral release measurements.

Carbon Materials and Fuel Ceramics

Room: Oceanview
Session Chair: Jochen Linke, Research Center Juelich

10:10 AM

(ICACC-S13-006-2011) Prediction of Structural Graphite Strength Loss Due to Oxidation in the Chemical Environment of High Temperature Gas-Cooled Reactor (HTGR) (Invited)

C. Contescu*, Oak Ridge National Laboratory, USA

Due to high temperatures, the HTGR core is made of graphite, which has a small (but not negligible) reactivity towards oxidizing impurities (oxygen, water). Small concentrations of impurities may enter the He coolant during periodic refueling. In addition, there is the possibility of moisture addition to the primary coolant in steam generator versions of the HTGR. The effect of oxidant additions is to cause a hopefully acceptably small alteration of the basic strength of the graphite structure components during the life time of the reactor. The purpose of this study is to provide the designer with the basic information needed to assure with a sufficiently high level of confidence that the strength loss is acceptably small. This task is complicated by the difficulty in reproducing prototypic conditions in the laboratory, primarily due to the large size of structural components, low levels of oxidants, and long exposure times. Therefore the program includes accelerated corrosion over a range of temperatures and specimen sizes, and measurement of strength loss over this range of conditions. Nevertheless, extrapolation to realistic conditions requires understanding of the strength loss mechanism. Toward this goal, the measurements include determination of the corrosion profile as well as microstructural evaluation of the corroded specimens.

10:40 AM

(ICACC-S13-007-2011) R&D and irradiation plans for new nuclear grade graphites for application to VHTR

K. Takizawa*, K. Kakehashi, T. Fukuda, J. Sumita, Tokai Carbon Co. LTD., Japan; K. Sawa, Japan Atomic Energy Agency, Japan; Y. Katoh, S. L. Lance, Oak Ridge National Laboratory, USA

Fine-grained isotropic graphite shows high strength making it a promising material for the graphite component of High Temperature Gas-cooled Reactor (HTGR) and Very High Temperature Reactor (VHTR). Service life of the graphite component is determined primarily by the residual stress after neutron irradiation in the reactor core. It is expected that development of a new nuclear grade graphite possessing higher strength will contribute toward added design margins and an extension of the service life of components, which likely improve the reactor economy very significantly. Tokai Carbon Co. LTD. has started the development of nuclear grade graphite for the graphite component of VHTR. G347S and G458S grades are fine-grained isotropic graphites having high tensile strength greater than 30MPa. It is planned to carry out the neutron irradiation tests using High Flux Isotope Reactor at Oak Ridge National Laboratory up to the neutron fluence of 30 dpa and the irradiation temperatures of 300-900°C. The dimensional changes, elastic modulus, coefficient of thermal expansion, etc., will be studied. It is also planned to evaluate the non-irradiated mechanical/thermal properties and the irradiation effects in collaboration with Japan Atomic Energy Agency. This paper introduces our technical R&D plan for G347S and G458S. The initial results of the properties and the irradiation test plan are also shown.

11:00 AM

(ICACC-S13-008-2011) Oxidation Behavior and Property Change of Nuclear-Grade C/C Composites

W. Kim*, M. Seo, J. Park, Korea Atomic Energy Research Institute, Republic of Korea; J. Sumita, T. Shibata, K. Sawa, Japan Atomic Energy Agency, Japan

Carbon-carbon (C/C) composites have been widely used for high-temperature structural applications because they possess excellent mechanical properties such as high specific strength and thermal

shock resistance. In the nuclear industry, the composites have been also considered for plasma facing materials in fusion reactors and high-temperature structural parts in gas cooled reactors. In the high-temperature gas cooled reactor, the composites are being considered for the application of various high-temperature structural parts such as control rod components, core restraint belts, tie rods, upper plenum shroud, hot duct insulation cover sheets, and floor blocks. However, the carbon based materials are susceptible to oxidation at temperatures above 400C. Therefore, the oxidation behavior and property degradation at high temperature under impure He or in air in case of accidental air ingress should be evaluated before the deployment of composites. In this study, the oxidation behavior of several nuclear-grade C/C composites was evaluated at various temperatures. Thermal and mechanical properties of the composites were also measured before and after oxidation. The oxidation experiments were performed in range of 500 to 1100C under air or Ar atmosphere. Thermal diffusivity, flexural strength, tensile strength, and interlaminar shear strength of as-received and oxidized specimens were evaluated.

11:20 AM

(ICACC-S13-009-2011) Investigation on Irradiation Effect and Fracture Behavior of C/C Composite for VHTR Application

J. Sumita*, T. Shibata, K. Sawa, Japan Atomic Energy Agency, Japan; I. Fujita, Toyo Tanso Co. LTD., Japan; J. Ohashi, Ibiden Co. LTD., Japan; K. Takizawa, Tokai Carbon Co. LTD., Japan

Since the temperature condition in Very High Temperature Reactor (VHTR), one of the Generation-IV reactor systems, is severe, the application of heat-resistant carbon fiber reinforced carbon matrix composite (C/C composite) for control rod elements is one of the important subjects for the VHTR development. JAEA focuses on the application of two-dimensional (2D-) C/C composites for control rod. The 2D-C/C composite has an anisotropy in properties for parallel and perpendicular to lamina directions. Irradiation effects of the 2D-C/C composite also show anisotropic behavior. It is hence important to consider the anisotropy in control rod design. To investigate the irradiation effects of the 2D-C/C composite on properties, irradiation test and post irradiation examination (PIE) were carried out and the irradiation effects were evaluated for the both directions. Since the C/C composite is composed of fibers and matrix, this geometry should be considered to evaluate the crack propagation in the composite. To assess the fracture behavior with crack propagation, bending test was carried out assuming a crack in the control rod and cracks in specimens were observed. This paper describes the irradiation effects of the 2D-C/C composite based on the PIE results considering the anisotropy. The evaluation results on equivalent fracture toughness and fracture mechanism are also discussed.

11:40 AM

(ICACC-S13-010-2011) High Temperature Strength of Zirconium Carbide Stoichiometric Variants

G. Vasudevamurthy*, Y. Katoh, L. L. Snead, Oak Ridge National Laboratory, USA

Zirconium carbide is a candidate for high temperature fission barrier coatings in advanced nuclear fuels. Attractive properties include high melting temperature, fission product retention capability comparable to silicon carbide, and resistance to corrosion by fission product palladium. High temperature strength of nuclear fuel coatings is a priority where a breach can lead to release of fission products. Currently, little is known about the strength properties of ZrC and the effects of C/Zr ratio on these properties in the proposed operating temperature range of ~300 to 1870K. Fabrication of ZrC coatings often yields a range of stable hyper and hypo stoichiometric compositions. The presence of carbon vacancies or excess carbon is expected to have significant effects on the high temperature mechanical properties. The initial results of characterizing high temperature mechanical strength of zone refined ZrC is presented. These specimens were used in lieu of the prototypical CVD-ZrC due to similarities in compositional purity and relative ease with which specimens could be fabricated in the required geometries for the designed test method. Samples in the hypo and hyper stoichiometric ranges of carbon were tested using three point, truncated disc flexural tests. Results are analyzed using information on the prominent deformation mechanisms prevailing in the relevant temperature and stress regimes.

S14: Advanced Materials and Technologies for Rechargeable Batteries

Diagnostics and Materials Characterization for Lithium-ion Batteries

Room: Coquina Salon F

Session Chairs: Khalil Amine, Argonne National Laboratory; Marca Doeff, Lawrence Berkeley National Lab

8:30 AM

(ICACC-S14-010-2011) Probing the electrochemical processes of Carbon Bismuth Fluorides/Oxyfluorides Nanocomposites as Positive Electrode Materials in Li Ion Batteries via Solid-Sate NMR and Pair Distribution Function Analysis (Invited)

L. Du*, Stony Brook University, USA; K. W. Chapman, Argonne National Laboratory, USA; A. Gmitter, N. Pereira, Rutgers University, USA; P. J. Chupas, Argonne National Laboratory, USA; G. G. Amatucci, Rutgers University, USA; C. P. Grey, Stony Brook University, USA

Carbon metal fluorides/oxyfluorides nanocomposites are potential positive electrode materials in rechargeable Li ion batteries because of their high voltages and high energy densities.[1,2] These materials react via conversion reactions during the electrochemical reaction with Li metal.[3,4] Solid-state NMR spectroscopy and Pair Distribution Function (PDF) analysis techniques have been shown to be an effective method for probing short- and intermediate-range structure, making them an ideal tool for exploring the reaction mechanisms of these nanocomposite materials. In this study, 19F and 7Li MAS NMR techniques were performed to monitor the speciation of bismuth fluorides/oxyfluorides during cycling. The evolution of the degree of disorder and phase transformation of the electrode materials, and the changes in the sizes of the (nano)particles upon cycling were further examined by PDF analysis. Possible electrochemical processes are proposed and a comparison with other conversion systems is made.

9:00 AM

(ICACC-S14-011-2011) Highly reversible Co3O4/graphene hybrid anode for lithium rechargeable batteries

H. Kim*, D. Seo, S. Kim, J. Kim, K. Kang, KAIST, Republic of Korea

Introduction: It is increasingly important to search for reliable energy storage devices that can satisfy ever increasing demand in the fields of electronics, vehicles and so on. Lithium rechargeable batteries that can deliver high energy and power density are one of the most promising candidates. For new applications such as vehicles and large energy storage devices, it is necessary to dramatically increase the capacity. Experiment: Graphite oxide was synthesized by using a modified Hummers method. Then, 0.1 g of the graphite oxide was added to 400 mL of DI water and solution underwent sonication for 90 minutes. 350 mg of cobalt acetate and 400 mL of DI water were added dropwisely to the graphene oxide solution. Finally, 3800 ul of NH4OH and 250 ul of Hydrazine were added to reduce cobalt ions and graphene oxide simultaneously. Results and discussion: By analysis using XRD, Raman, TEM and AFM, we confirmed that extremely small Co3O4 particles are uniformly dispersed on graphene. Due to the unique structure of the hybrid material, excellent electrochemical properties could be achieved. The typical charge/discharge profiles of the hybrid are not significantly altered during cycles, indicating the stability of the composite as anode. The anode can retain a reversible capacity of 778 mAhg-1 with coulombic efficiency of 97% after 42 cycles.

9:20 AM

(ICACC-S14-012-2011) In-situ electrochemical analysis of $LiNi_{0.66}Co_{0.17}Mn_{0.17}O_2$ as a layered cathode material for Lithium-ion batteries

L. C. Torres*, J. J. Saavedra-Arias, University of Puerto Rico, USA; A. Manivannan, US DOE/NETL, USA; R. S. Katiyar, University of Puerto Rico, USA

$LiNi_{0.66}Co_{0.17}Mn_{0.17}O_2$ is a promising layered cathode material for lithium-ion batteries. First principles calculations were made to examine the phase stability and the relative formation energy of different compounds, including $LiNi_{0.66}Co_{0.17}Mn_{0.17}O_2$, the most stable after the delithiaton process. $LiNi_{0.66}Co_{0.17}Mn_{0.17}O_2$ has been synthesized by sol gel and citric acid methods and the formation of single phase of the material was confirmed by XRD after calcination at 850°C for 12 hours. The electrochemical behavior of the half cell has been tested using cyclic voltammetry and charge-discharge analysis using a Solatron battery tester. In-situ electrochemical impedance spectroscopy was performed during charge discharge cycles. Discharge capacities as high as 240 mAh g^{-1} has been observed. The electrochemical performance with respect to the intensity ratio of 003 and 104 XRD peaks for samples annealed at 800°C, 850°C, and 900°C will be discussed.

10:00 AM

(ICACC-S14-013-2011) Evaluation of redox-active organic structures as an alternative to inorganic electrode materials for greener Li-ion batteries (Invited)

P. Poizot*, F. Dolhem, University of Picardie, France

The energy issue constitutes one of the greatest challenges of the 21st century facing mankind. One major goal is to identify secure and sustainable energy supplies whereas reducing carbon dioxide emissions. One technological challenge in this field relies on designing advanced batteries to store more electrical energy while being environment-friendly. Widely used in "nomadic" electronic devices, Li-ion batteries also appear to be an important element to mitigate the CO2 releases i) as a promising power source for advanced electric vehicles and ii) as a potential buffer energy storage system to manage the intermittent renewable energy resources. However, electrode materials are in fact based on the use of inorganic electro-active compounds typically synthesized from high temperature reactions and non-renewable resources. The life cycle analysis of such inorganic-based electrode materials a noticeable CO2 footprint at large scale, which can lessen the benefit of the present Li-ion technology. Alternatively, we have put forward the concept of a greener Li-ion battery thanks to the use of organic active materials (stabilized carbonyl/carboxyl structures) derived from biomass and produced via eco-efficient processes and created a reliable experimental database of model chemical structures in relation with their solid state electrochemical behaviour.

10:30 AM

(ICACC-S14-014-2011) Liquid Silicon-Based Electrolytes for Li-Ion Batteries

Z. Zhang*, Argonne National Laboratory, USA

Silicon-based electrolyte has emerged as a primary candidate for the development of large lithium-ion batteries for electric vehicle (EV) and other systems in which safety is a primary consideration. Comparing to the electrolyte used in the conventional lithium-ion batteries, which are flammable, volatile, and highly reactive organic carbonate solvent, Silicon-based electrolytes are thermally and chemically stable, less flammable and environmental benign. Oligo(ethylene glycol)-functionalized silane (1NM3) was identified as a focus of investigation due to its high conductivity with low viscosity. In this paper, we show the results of a systematic investigation of the 1NM3-based electrolytes, including ionic conductivity, viscosity, and electrochemical window by cyclic voltammetry method and lithium ion cell performance. Lithium-ion cells with LiNi1/3Co1/3Mn 1/3O2 and LiMn2O4 as the positive electrodes and MAG graphite as the negative electrode have shown excellent cycle life both at room temperature and at elevated temperature.

10:50 AM

(ICACC-S14-015-2011) Probing Lithium Insertion and Conversion Reactions in a Titanium Hydroxyfluorides

D. Dambournet*, R. Gerald, Argonne National Laboratory, USA; C. Labrugere, Institut de Chimie de la Matière Condensée de Bordeaux-CNRS, Université Bordeaux 1., France; N. Penin, Institut de Chimie de la Matière Condensée de Bordeaux-CNRS, Université Bordeaux 1., France; I. Belharouak, K. Amine, Argonne National Laboratory, USA; A. Demourgues, Institut de Chimie de la Matière Condensée de Bordeaux-CNRS, Université Bordeaux 1., France; A. Tressaud, Institut de Chimie de la Matière Condensée de Bordeaux-CNRS, Université Bordeaux 1., France

Titanium-based materials have attracted extensive research activity in the field of energy storage due to the abundance of titanium as well as its redox chemistry. Nowdays, only few studies have reported on the conversion reaction involving titanium as the active element. Based on thermodynamic considerations, Li et al [1] have calculated that the theoretical voltage for a conversion reaction of TiO2 was around 0.6V (vs Li0) but experimentally, such a reaction was not observed. Contrarily, TiF3 was shown to undergo a conversion reaction leading to a high practical capacity (500-600 mAh/g). Due to the strong electronegativity of fluoride ions, the active metal can be easily reduced. Searching for new high capacity anode material, this work reports on the electrochemistry of a nanosized titanium-based compound having fluoride and hydroxyl group as anionic environment. [2] The lithium insertion/extraction mechanism was probed by using electrochemical characterizations (galvanostatic measurement and cyclic voltammetry), X-ray diffraction analysis, X-ray photoelectron spectroscopy, and electrochemical impendance spectroscopie. [1] H .Li, P.Balaya and J. Maier, J. Electrochem. Soc., 2004, 151, A1878. [2] A. Demourgues, N. Penin, E. Durand, F. Weill, D. Dambournet, N. Viadere and A. Tressaud. Chem. Mater., 2009, 21 (7), 1275.

11:10 AM

(ICACC-S14-016-2011) Electrochemical Performance of TiO_2 Nanoflakes as an Anode Material for Lithium Ion Batteries

M. Yang*, Y. Lee, University of Florida, USA; Y. S. Meng, University of California San Diego, USA; K. Powers, University of Florida, USA

Anatase TiO_2 is a promising electrode material for Li-ion batteries due to its good Li-storage capacity, safety against overcharging and stable voltage plateau at 1.78V.In addition,it is an non-toxic and cheap material. However, the poor rate capability and cycling performance limit its application. Various nanostructure Titanium oxides have been developed to address these issues. TiO_2 nanoflakes are of great interests because of their larger surface area and pore volume.The TiO_2 nanoflakes have been synthesized through spreading method. For spreading to be possible, the pentane and titanium tetrabutoxide were used as precursors and continuously added to the solution on the surface of flowing water. The supercritical drying process was performed to remove the residual water. The size of the nanoflake is about several micrometers composed of 5nm grains. The thickness of the nanoflakes is about 40nm. In order to understand the relationship between crystal structure, surface area,pore volume and electrochemical properties of nanoflakes, the nanoflakes were studied by BET, X-ray diffraction, scanning electron microscopy(SEM) , and Transmission electron microscopy (TEM). Electrochemical performances were investigated by galvanostatic technique in lithium half-cells. TiO_2 nanoflakes exhibit excellent rate capability and good cycling stability compared to TiO_2 nanoparticles.

11:30 AM

(ICACC-S14-017-2011) Studies of Li-ion Battery Materials Using Synchrotron Methods (Invited)

M. Balasubramanian*, Argonne National Laboratory, USA

Batteries with high energy and power density are needed for a variety of existing and emerging technologies. Lithium-ion batteries have

cornered the lion's share of present day rechargeable batteries for consumer electronics and power tool applications. They are also poised to be used in hybrid and plug-in hybrid vehicles. Knowledge of the redox chemistry and changes in the structure during electrochemical cycling is of paramount importance in designing new battery materials with superior properties. In situ x-ray diffraction and x-ray absorption studies have played a vital role in elucidating the structural and electronic changes that accompany lithiation/delithiation. The advent of third generation synchrotron sources coupled with dedicated and specialized instruments has opened a new window to systematically investigate the structure-property relationship of advanced materials under operating conditions. Using synchrotron based x-ray methods we seek to provide definitive characterization of the redox chemistry of operating batteries, a topic of continuing fundamental and applied interest. In this talk, I will highlight the role played by spectroscopic and novel scattering methods in providing key information on the electronic and atomic structure of energy storage systems under operating conditions.

Pacific Rim Engineering Ceramics Summit

Pacific Rim Engineering Ceramics Summit II

Room: Ponce de Leon
Session Chairs: Tatsuki Ohji, National Institute of Advanced Industrial Science and Technology; Jow-Lay Huang, National Cheng Kung University

8:00 AM

(ICACC-PACRIM-009-2011) R&D Activities on Engineering Ceramics in AIST (Invited)

T. Ohji*, H. Kita, Y. Yoshizawa, K. Hirao, National Institute of Advanced Industrial Science and Technology, Japan

This paper introduces recent research activities on engineering ceramics in AIST Japan. First, emphasis is placed on the importance of tailoring microstructure to obtain good mechanical and physical properties. Next, the paper will deal with our several green manufacturing processes which realize good cost/energy performances and reduce environmental burdens friendliness, including: (1) Correct selection of sintering additives in the cost-effective reaction bonding process has been found to improve substantially the productivity, particularly for large scale components, without sacrificing the properties of sintered bodies. (2) Such reaction bonding process can be also applied into high thermal conductivity ceramic substrates with good mechanical properties and relatively low cost. (3) Combustion synthesis method is cost-effective approach to make high-performance ceramic powder; here an example of fabricating SiAlON phosphor powders will be given. (4) Fabrication of large components is possible through assembling ceramic units/parts into 3D structure. Joining is a key technology for this, and reaction bonding joining is a promising approach due to relatively good mechanical reliability, etc. Finally, the paper introduce several of recently developed novel processing approaches for making macro porous ceramics with critically controlled porosity, sizes and shapes of pores.

8:30 AM

(ICACC-PACRIM-010-2011) Nano-Coating for High-Efficiency Energy Use and Rare-Metal Substitution (Invited)

T. Goto*, IMR Tohoku University, Japan

A national project of "nano-coating" has started in Japan since 2001 for six years, and that project has been partially continued in a "strategic element" project since 2008. The nano-coating aimed to develop high-performance coatings, particularly thermal barrier coating (TBC). Atmospheric plasma spray (APS) and electron-beam physical vapor deposition (EBPVD) have been practically used for yttria stabilized zirconia (YSZ) TBC, and these processes were further developed under the point of nanostructure control. Chemical vapor deposition (CVD) has scarcely been employed in TBC due to slow deposition rate and low deposition efficiency. The present authors have developed laser CVD, and achieved a high deposition rate of 660μm/h for YSZ coating with significantly oriented feather-like columnar microstructure as fabricated by EBPVD. The laser CVD technique has been adopted in the succeeding strategic element project, where the substitution of a rare-metal of W by common metals in WC-Co cutting tools is intended. TiN-Ni cermets can be a candidate substitute, while the top surface of cermets should also be coated by α-Al2O3 as that of WC-Co. However, α-Al2O3 coating on TiN-Ni cermet has not been achieved mainly due to Ni outward diffusion caused by a high deposition temperature. Laser CVD has successfully coated α-Al2O3 on cermets owing to high deposition rate and low deposition temperature.

9:00 AM

(ICACC-PACRIM-011-2011) Introduction of KICET (Korea Institute of Ceramic Engineering & Technology) (Invited)

K. Kim*, KICET, Republic of Korea

KICET(Korea Institute of Ceramic Engineering & Technology), the government-sponsored institute, is committed to offering a vast range of technology support for ceramic industry as the Ceramic Hub of Korea ; R&D of new ceramic materials, testing and evaluation lab services, technology transfer and commercialization, and so on. Since its beginning in 1912 as a division under the Central Testing Laboratory of Korea, KICET has specialized in ceramic and new materials technology. So due to continuous growth, KICET has become one of world-class ceramic institutes which 74 persons with Ph.D work, R&D funds come to more than $35 million in 2009. In addition, KICET is collaborating actively with 22 organizations around 10 countries in joint research and researcher exchange programs. To make the domestic ceramic industry competitive in the future, KICET is conducting research in new ceramics technologies like electronic and bio that can be applied to various convergence-oriented industry sectors, which straddle two or more industries.

9:50 AM

(ICACC-PACRIM-012-2011) Status of Ceramic Components in Korean Semiconductor Industry (Invited)

S. Lee, KICET, Republic of Korea; D. Kim*, KAIST, Republic of Korea

The Korean semiconductor industry has grown rapidly, due to a combination of the Korean government's aggressive promotion policies and large-scale investments by private companies. As a result, Korea's semiconductor industry currently leads the worldwide market in memory semiconductors. As the semiconductor industry continues to develop, the semiconductor equipment industry becomes increasingly important. In addition, the applications of ceramic components for the semiconductor equipment are also increasing. Ceramic components such as quartz, SiC, Al_2O_3 and AlN are widely applied for various rings, wafer boat, susceptor, heater and electro-static chuck, etc. The Korean industry of semiconductor equipment still lags behind its counterparts in other advanced countries such as USA and Japan. The major process equipment for chip manufacturing is being imported from international major equipment suppliers. Recently, domestic Korean equipment manufacturers have been developing by their capabilities and collaboration with several research institutes accompanied by the development in the technology for precision ceramics. Under the circumstance, some equipment manufacturers have successfully developed front-end process equipment. This presentation describes an overview of current status of ceramics components for the application in the semiconductor equipment and its future potential.

10:20 AM

(ICACC-PACRIM-013-2011) Overview of ceramics in energy and related industry in Korea (Invited)

S. Woo*, I. Han, S. Kim, Korea Institute of Energy Research, Republic of Korea

In resent years fossil fuel prices have been volatile. They look set to remaina of high levels compared to the past. A number of factors

contribute to this trend, including rising energy demand, particularly in the developing world, and concerns over the security and availability of oil and gas supplies. Reducing fossil fuel dependency is an important energy policy target in many countries. The energy materials are important fundamental technology all over the industrial field for preparation of fossil fuel depletion and self-sufficiency in energy. Generally, these energy materials are applied at hydrogen energy exchange - storage - utilization, fuel cell, thermo-electric and building materials for securing re-newable energy that does not use fossil fuel. Also energy materials are used at separation membrane and filters for clean environment. This presentation contains the ongoing research trend of ceramic energy materials in Korea that used for severe environmental condition because of its high thermal and chemical resistance.

10:50 AM

(ICACC-PACRIM-014-2011) Seeds Innovation and Applications Development of Silicon Nitride Ceramics (Invited)

K. Komeya*, J. Tatami, Yokohama National University, Japan

The author have investigated both Si_3N_4 and AlN for a long time, and fortunately discovered in the initial stage in Toshiba that rare earth compounds (Y_2O_3 etc.) are excellent sintering aids for the both nitrides. Since then Y_2O_3 doped Si_3N_4 and AlN have gained general acceptance as standard materials and employed in practical applications, in which Si_3N_4 ceramics based on the Y_2O_3 and Al_2O_3 addition have been recognized as the most attractive materials for the wear resistant applications as bearing balls. After that it was found that the addition of TiO_2 to the Si_3N_4-Y_2O_3-Al_2O_3 originated the densification promotion and the improvement of the cyclic fatigue life. In the sintered bodies, TiN grain changed from TiO_2 was located in the grain boundary. Most recently author's group have developed a new Si_3N_4 ceramics designed with nano-sized TiN dispersion, which shows lower damage for mating material in the bearing system. The development of the highly reliable bearing balls using the newly innovated seeds was provided as the collaborative research with the industries under the NEDO contract. The key processing factor is to design and control nano-dispersion of TiN in the sintered bodies. In this paper, research activities for the new wear resistant Si_3N_4 including seeds innovation in the initial stage will be presented.

11:20 AM

(ICACC-PACRIM-015-2011) Development of Supercritical-Property-Ceramics through Interface Engineering (Invited)

H. Kim*, Korea Institute of Materials Science, Republic of Korea

The main target of this program is to develop the engineering ceramic materials with supercritical properties to be used in various industries such as semiconductor, display, machine and automobile, aviation and aerospace, etc. Korean economy is largely dependent on the export of semiconductor, automobile, etc. In order to keep up with the leading position they need to have engineering ceramic materials with supercritical properties. Depending on the megatrend of such industries we defined the technical requirements for such materials. For example the megatrend of semiconductor industry is to decrease the width of circuit, to increase the diameter of wafer, and to level up the purity. In order to meet such megatrend we need to develop engineering ceramic materials with better resistance to high-density plasma, engineering ceramics with higher purity, engineering ceramics with multi functions. Some examples for engineering ceramics with supercritical properties which are being developed will be introduced.

11:50 AM

(ICACC-PACRIM-016-2011) Dye-sensitized Solar Cells Based on Nanocrystalline TiO2 – Recent Progress in Taiwan (Invited)

J. Ting*, National Cheng Kung University, Taiwan

Due to the low-cost and facile fabrication, dye-sensitized solar cells (DSCs) based on nanocrystalline TiO2 have received numerous attentions since its introduction. A typical DSC is composed of a dye-sensitized TiO2 mesoporous photoelectrode on a transparent conducting oxide (TCO) current collector, a Pt coated TCO counter electrode, and I-/I3- redox electrolyte. Conventionally, both the photoelectrode and counter electrodes are rigid. With the increasing need for flexible electronics, the development of flexible DSC (FDSC) has thus occurred. More importantly, large scale roll-to-roll process can be applied for the fabrication of FDSC, making its commercialization more viable. As a result, increasing efforts have been made to investigate the assembly and performance of FDSC. This paper reviews major research activities on FDSC as well as rigid DSC in Taiwan where significant progresses have been made in different aspects of DSC.

S1: Mechanical Behavior and Performance of Ceramics & Composites

Mechanical Behavior of Ceramics and Composites

Room: Coquina Salon A

Session Chairs: Jacques Lamon, CNRS; Dietmar Koch, Univ. of Bremen

1:30 PM

(ICACC-S1-023-2011) Measurement of the Elastic Modulus of CMCs in All Directions (Invited)

G. Morscher*, The University of Akron, USA; M. Singh, Ohio Aerospace Institute, USA

Ceramic matrix composites are highly anisotropic materials with the potential for the elastic properties to vary considerably both in any direction in-plane as well as in the through-thickness direction depending on fiber architecture and composite constituent properties. Accurate measurement of the anisotropic elastic properties is essential in order to accurately model multi-directional elastic behavior of CMCs and ultimately design with CMCs. In this presentation, the in-plane and through-thickness elastic modulus was determined with two different sound techniques for a variety of composites which included SiC fiber-reinforced SiC matrix and C fiber-reinforced C matrix composites with different 2D and 3D architectures. In some cases mechanical modulus was measured to confirm sound measurements. The techniques offer useful and simple approaches to measure elastic modulus in all directions on plates, specimens, and components including those with complex shapes.

2:00 PM

(ICACC-S1-024-2011) Influence of pre-loading on the interlaminar properties of Ceramics Matrix Composites

D. Koch*, T. Krause, K. Rezwan, G. Grathwohl, Univ. of Bremen, Germany

2D reinforced ceramic composites as e.g. C/C represent high strength and enhanced damage tolerance when cracks propagate through the microstructure. Especially between the individual layers which are reinforced with woven long fiber fabrics matrix rich areas exist. It is observed in tensile as well as in compressive loading that at stresses below strength matrix cracks occur within the layers perpendicular to the loading direction. These cracks also propagate and distribute in the interlaminar regions parallel to the loading direction. In order to investigate this effect interrupted tensile and compressive tests are performed up to various stresses and then specimens are tested in transverse tensile mode or compression shear test for investigation of shear in mode I and mode II, respectively. By changing the weaving structure and the matrix porosity the mechanical response of the interlaminar region can be modified. Larger fiber tows in the fabric result in larger bending of the fiber tows and different interlocking of the layers in shear mode. Lower matrix porosity induces higher strength and therefore change of crack propagation. It is obeserved that the mechanical behavior of the interlaminar region differs strongly dependent on the microstructural properties and on the tensile or compressive pre-load. With these results a correlation of mode I and mode II damage will be drawn.

2:20 PM

(ICACC-S1-025-2011) Mechanical properties of two different carbon-carbon composites before and after heat treatment

S. S. Iqbal*, Southern Illinois Univ, Carbondale, USA

Tensile properties of two C/C composites, two-directional (2D) short pitch-based carbon-fiber with charred resin, and three-directional (3D) continuous PAN-based carbon-fiber with CVI carbon matrix, were investigated heat treated materials. The heat treatment was performed at 1800, 2100 and 2400 °C for one hour in inert argon atmosphere. Average tensile strength of 2D-material heat treated at 1800 °C was the highest with material heat treated at 2100 °C exhibiting highest failure strain. Similarly, 3D C/C exhibited a progressive decrease in tensile strength with heat treatment. Tensile strength of 3D C/C heat treated at 2400 °C decreased by 40% as compared to NHT materials. Overall tensile strength of 3D continuous PAN-based C/C was the highest than 2D short pitch-based C/C composites. Polarized light microscopy images showed progressive improvement in the microstructure of C/C composites after increasing heat treatment temperature. Light microscope images of the fractured specimens showed mixed mode of failure for both materials. A fiber bridging is obvious route for extended failure strain and corresponding high tensile strength of the materials. SEM images show sliding of fibers after heat treatment when compared to NHT material. Fibers and carbon matrix morphology indicate a lower frictional force for the release of strain energy after tensile tests.

2:40 PM

(ICACC-S1-026-2011) Creep Behaviour of BSCF Oxygen Transport Membranes

R. W. Steinbrech*, B. Rutkowski, J. Malzbender, B. Huang, Forschungszentrum Jülich GmbH, Germany; R. Kriegel, Fraunhofer IKTS, Institutsteil Hermsdorf, Germany; T. Beck, Forschungszentrum Jülich GmbH, Germany

The prediction of the long term mechanical performance of mixed ion-electron conducting perovskites as membranes in gas separation units requires knowledge of the deformation behaviour at operation temperatures. The creep of Ba0.5Sr0.5Co0.8Fe0.2O3-δ (BSCF) perovskite material was characterized under compressive load using tubular specimens in the temperature range 700 to 950 °C. In addition to the effect of the compressive stress the influence of the oxygen partial pressure and grain size was considered. The BSCF perovskite showed pronounced creep rates (~ 10-9 /s) even under moderate stresses (20 MPa) at 850°C. A transition to enhanced creep rates was observed above 850°C in air. The comprehensive BSCF tests revealed under reduced oxygen partial pressure significantly higher creep rates and a less pronounced transition. Also hysteresis effects could be measured depending on whether the constant stress creep tests were carried out in a sequence of increasing or decreasing temperature. The hysteresis effect appeared to be related to the cubic - hexagonal phase transition of BSCF occurring in this temperature range. Complementary C-ring testing of BSCF specimens revealed additional information on the creep failure mechanism of the perovskite under tensile stresses. Post test SEM and TEM investigations were carried out to gain insight into the microstructural aspects of BSCF creep and associated deformation mechanisms.

3:20 PM

(ICACC-S1-027-2011) Microstructure and creep behavior of intergranular alumina/SiC nanocomposites sintered by SPS

M. Jaafar*, G. Bonnefont, G. Fantozzi, H. Reveron, Insa Lyon, France

One of the most interesting observations made on the last past years has been the improvement of "nanocomposites" mechanical properties. Nanocomposites can be divided into micro-nanocomposites (fine inclusions in a coarse matrix) and nano-nanocomposites (dispersion of two nanophases). The aim of this work is to improve the creep resistance of alumina-based micro-nanocomposites reinforced by SiC nanoparticles. The use of spark plasma sintering (SPS) provided us the possibility of developing highly creep resistant "intergranular" materials. In contrast with the few works already done on alumina-SiC materials processing by SPS ("intragranular" or "inter-intragranular" types), for the first time in this system our novel approach produced essentially intergranular positioning. The key point is to use a "coarse" alumina powder (instead of alumina nanopowder) and nano-SiC particles of 60 nm as raw materials. During this presentation, (a) the effect of some SPS parameters on the SPS densification and microstructure development, (b) the creep behavior and (d) the possible mechanism in charge of improving thermomechanical properties of alumina-based micro-nanocomposites will be discussed. The interest of using coarse alumina powder and SPS technology for preparing intergranular alumina-SiC micro-nanostructures will be supported.

3:40 PM

(ICACC-S1-028-2011) Thermal Shock Resistance of Yttria-Stabilized Zirconia with a Second Phase

J. P. Angle*, M. Mecartney, UC Irvine, USA

The lifetime of zirconia-based oxygen sensors can be dramatically shortened if water from the exhaust stream comes in contact with the sensor. The sensor operates at 900°C and the rapid change in external temperature can cause thermal shock and failure of the sensor. This project investigates the thermal shock behavior of 8 mol% yttria-stabilized zirconia (8YSZ) modified with second phases such as silica, alumina and mullite. Theoretical calculations show that the thermal shock resistance should increase with the amount of these second phases. Quenching experiments and three-point bending were used to determine the critical temperature difference (ΔTc) and flexural strength (σf) for each composition quenched from various temperatures. Increased thermal shock resistance was observed with an increase in the volume of the second phase, with the most significant improvement when the percolation limit of the second phase was reached for second phases with high thermal conductivity. Grain size analysis was determined by use of scanning electron microscopy (SEM), and it was found that increasing the amount of second phase particles was correlated with a decreased grain size and increased σf.

4:00 PM

(ICACC-S1-029-2011) Effects of Loading on Foreign Object Damage in Ceramic Matrix Composites

D. C. Faucett*, S. R. Choi, NAVAIR, USA

Foreign object damage (FOD) phenomena of oxide/oxide and SiC/SiC ceramic matrix composites (CMCs) were determined at ambient temperature with spherical ball projectiles using an impact velocity range of 100 to 400 m/s. CMC test coupons were impacted at a normal incidence angle while loaded under different levels of tensile stresses. Surface and subsurface impact damages, typically in the forms of craters, fiber breakage, delamination, and cone cracks, were characterized with respect to the levels of tensile loading applied. Effects of tensile loading on post-impact strength of test coupons impacted were also determined to better assess the severity of impact damage associated. Some analytical considerations regarding impact force and some experimental aspects related will be also presented and discussed.

4:20 PM

(ICACC-S1-030-2011) Fatigue behavior, bridging stresses, and fatigue reliability in Si3N4 ceramics

R. B. Greene*, J. J. Kruzic, Oregon State University, USA; S. Fünfschilling, T. Fett, Karlsruhe Institute of Technology, Germany

Silicon nitride ceramics doped with rare earth oxides exhibit excellent toughness and strength due to grain bridging. This contributes to increasing fracture and fatigue resistance curves (R-curves) dependent on crack size. Three Si3N4-RE ceramics were investigated containing

MgO-Y2O3, Al2O3-Y2O3, and MgO-La2O3. Fatigue crack growth experiments were conducted on compact tension specimens in order to determine the fatigue threshold for cracks with steady state bridging zones. Fatigue thresholds for the MgY and MgLa doped materials were found to be significantly higher than for the AlY doped Si3N4; however, when the data were normalized by the bridging stress intensity factor they all overlapped considerably. To further understand the role of the bridging stresses, micro-Raman spectroscopy was performed on the MgY specimens to measure the bridging stress distribution. By measuring a small shift in the 862 cm-1 Raman peak the full distribution was determined along the crack. The Raman results show a strong agreement with bridging stress distributions determined from fracture R-curves in the same Si3N4, although the peak bridging stress is degraded by fatigue loading. Using the combined fracture, fatigue, and Raman data the fatigue threshold R-curve has been calculated for this MgY containing Si3N4 to allow fatigue reliability predictions. Experiments are being performed to verify those predictions.

4:40 PM

(ICACC-S1-031-2011) Mechanical property characterization of a transparent spinel ceramic

R. W. Steinbrech, O. Tokariev*, J. Malzbender, Forschungszentrum Jülich GmbH, Germany; L. Schnetter, CeramTec-ETEC GmbH, Germany

The mechanical properties and failure mechanisms of transparent MgAl2O4 material are reported. In particular the elastic modulus of the material has been investigated using depth sensitive indentation, impulse excitation and ring-on-ring testing. The fracture toughness has been determined from the length of indentation cracks comparing different analysis methodologies. The fracture stress was derived from biaxial testing in a ring-on-ring loading arrangement. The fracture stresses were compared for different MgAl2O4 batches using Weibull statistics to permit an assessment of failure probabilities. The fracture mechanism and defects responsible for the failure have been investigated using light and scanning electron microscopy. Novel experimental methods were implemented for fracture determination and stress detection. An in-house developed indentation testing device permitted in-situ through thickness fracture observation. Particular attention was directed to the effect of inclusions and associated local stress fields as assessed using polarized light in photoelastic measurements.

5:00 PM

(ICACC-S1-032-2011) Mechanical and Thermal Properties of Copper-Alumina Interpenetrating Composites

J. S. Winzer*, L. Weiler, V. Salit, D. Gross, J. Rödel, Technische Universität Darmstadt, Germany

Copper-alumina interpenetrating composites have attractive thermomechanical properties with possible applications in car brakes and gears. In this work, the effect of Cu content and ligament diameter on the mechanical and thermal properties is assessed. Porous ceramics were produced using a variety of sacrificial preforms and infiltrated with Cu under gas pressure. The composites vary in Cu content from 20 to 60 vol% and Cu ligament diameter from 1 to 30 μm, giving a wide spread of properties. Young's modulus (E) was determined by obtaining the resonance frequency. The thermal expansion coefficient was determined via dilatometry and thermal conductivity with the Laser Flash method. These properties are compared to results of a numerical model, as well as to FEM analysis of real microstructures obtained via X-ray computer tomography. Fracture toughness (K) and R-curve behaviour were analysed using CT-specimens. Wear behaviour was investigated using a pin-on-disc test. It was found that E decreases with increasing Cu content. Thermal expansion coefficient increases with Cu content but is unaffected by Cu ligament diameter. Thermal conductivity increases with Cu content and ligament diameter. K is higher and R-curve behaviour more pronounced for higher Cu contents. Wear resistance decreased with increased Cu content and decreased Cu ligament diameter.

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

Environmental Barrier Coatings for Turbine Engines and Extreme Environments

Room: Coquina Salon G

Session Chairs: Rishi Raj, University of Colorado at Boulder; Joyce Dever, NASA Glenn Research Center

1:30 PM

(ICACC-S2-022-2011) Progress in Understanding and Mitigating the CMAS Attack of High Temperature Ceramic Coatings (Invited)

K. M. Grant, E. M. Zaleski, R. Jackson, C. G. Levi*, University of California, Santa Barbara, USA

CMAS degradation of ceramic coatings used for the protection of structural components in gas turbines is now recognized as a fundamental threat to progress in engine technology. In principle, the melting point of the silicate deposit (~1200°C) limits the ultimate temperature capability of the coating material. Both thermal and environmental barrier coatings are susceptible to the attack, although the mechanisms are significantly different. Current experience shows that state-of-the-art materials like 7YSZ and BSAS are severely degraded by CMAS, and the mechanisms are relatively well understood. Alternate materials like rare earth zirconates for TBCs and rare earth silicates for EBCs offer promise by reacting with molten CMAS and inducing its crystallization into products that nominally form a barrier to further penetration or reaction, but these solutions are arguably insufficiently robust. The reaction continues over time as long as there is silicate melt available, albeit at a much slower rate in the zirconates compared with the silicates. Moreover, both materials systems are susceptible to cracking and delamination upon cooling, especially after thermal cycling. This presentation will review the state of understanding of these problems and the paths being pursued to improve mitigation. (Funding: ONR grants N000140810522, N000140610322, monitored by Dr. David Shifler)

2:00 PM

(ICACC-S2-023-2011) Tailoring Polymer-derived Bond-coats For EBC On Silicon Based Ceramics

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

Previous work has shown that multilayer, environmental barrier coating (EBC) systems, based on polymer-derived bond coat layers, can improve the hydrothermal corrosion resistance of silicon nitride. Environmental barrier coatings are required to enable silicon-based ceramics to have usable lifetimes in propulsion and energy conversion systems. Use of silicon-based ceramics could dramatically improve efficiency in combustion systems by allowing increased operating temperatures and could reduce harmful emissions. As shown in the previous work, the composition, thickness, and density of the bond coat layer have significant impacts on the EBC performance. In the current work, additional data will be provided showing that the bond coat system can be adapted to monolithic and composite silicon carbide. In addition, the results of efforts to increase the maximum operating temperature of the bond coat will be described.

2:20 PM

(ICACC-S2-024-2011) Low Pressure Plasma Spray Thin Film (LPPS-TF) Deposition of Ceramics for Protective Coatings (Invited)

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

Thermal and environmental barrier coatings are necessary for the protection of metals and ceramics in high temperature turbine en-

gine environments. These coatings have become increasingly complex in composition and architecture in order to meet ever increasing temperature demands. In order to generate these multilayer protection systems, a new deposition process is needed to bridge the gap between conventional plasma spray, which produces relatively thick coatings on the order of 125-250 microns, and conventional vapor phase processes such as EB-PVD which are limited by slow growth rates, high investment costs, and vapor pressure requirements. The use of Low Pressure Plasma Spray-Thin Film (LPPS-TF) processing fills this gap and allows thin (< 10 μm) layers to be deposited and multilayer coatings of less than 100 μm to be generated. In this work, coatings of yttria-stabilized zirconia (YSZ) were applied to NiCrAlY bond coated superalloy substrates using the LPPS-TF coater at NASA Glenn Research Center. A design-of-experiments was used to examine the effects of the He/Ar process gas ratio and the total working pressure of the chamber during deposition. Samples were evaluated using scanning electron microscopy, X-ray diffraction, laser thermal conductivity measurements, and furnace cyclic testing.

2:50 PM

(ICACC-S2-025-2011) Self-healing Matrices for SiC Matrix Ceramic Matrix Composites

D. Poerschke*, L. Merrill, C. Levi, University of California, Santa Barbara, USA

Volatilization of SiO_2 in high-temperature moisture-laden environments necessitates the use of an environmental barrier coating (EBC) to protect silicon-based ceramics such as SiC matrix composites. While these coatings effectively limit volatilization, long-term protection is provided only as long as the EBC remains intact, since cracking or local loss of the coating exposes the matrix to the corrosive environment. A robust matrix, able to seal cracks and provide environmental protection, is desired to maintain the integrity of the component after EBC damage occurs. A candidate self-healing matrix material has been developed by incorporating yttrium oxide and boride, Y_2O_3 and YB_2, particles into the SiC matrix. Samples were oxidized at 1400°C in air to study the evolution of the resulting oxide scale. Material at the surface underwent oxidation producing an oxide scale containing yttrium silicate and borosilicate glass. The yttrium silicate provides protection against volatilization while the continuous borosilicate layer will fill cracks, preventing oxygen and water vapor ingress. This oxide layer is thus expected to provide better protection against environmental degradation than that formed on pure SiC.

3:30 PM

(ICACC-S2-026-2011) Polymer Derived Ceramics and Related Materials for Ultrahigh Temperature Coatings: The Science and the Technology (Invited)

R. Raj*, K. Terauds, J. Lonergan, University of Colorado at Boulder, USA; D. Marshall, Teledyne Scientific and Imaging Company, USA; B. Rashkova, G. Dehm, Austrian Academy of Sciences, Austria

Polymer Derived Ceramics can serve as a bond coat for protecting silicon based ceramics at ultrahigh temperatures. The outer coating that provides immediate protection against the environment is constituted from zirconium or hafnium oxide. While phenomenological measurements show the protection to be effective at least up to 1600oC, the scientific understanding of the constitution of the coating, which apparently evolves into new phases, that must be stable against the environment, and the atomistic mechanisms whereby it is effective, are just beginning to emerge. This exposition would cover both the phenomenological and the materials science of PDC based ultrahigh temperature coatings.

4:00 PM

(ICACC-S2-027-2011) Ultrahigh Temperature SiCN-HfO2 Environmental Barrier Composite Coatings on SiC up to 1600°C

K. Terauds*, R. Raj, University of Colorado, USA

Polymer derived ceramic–refractory metal oxide nanocomposites have recently been shown to be strong candidates for ultrahigh temperature environmental barrier coatings. This work demonstrates the potential for HfO2/SiCN/SiC composites as UHT hypersonic material structures. A 3μm film of hafnia was deposited on single crystal SiC with an intermediate layer of amorphous SiCN serving as a bond coating. Both films were deposited on the SiC substrate using a hot wall reactor pulsed CVD. Oxidation studies were performed on coated and uncoated samples up to 1600°C in air showing the SiCN/HfO2 coating completely suppressed the formation of silica on the SiC crystal. Wide angle xray diffraction and energy dispersive spectroscopy were performed to identify the formation of new phases during heat treatment and their concentrations at the interfacial boundaries.

4:20 PM

(ICACC-S2-028-2011) Creep and Fatigue Behavior of Hafnia and Ytterbium Silicate Environmental Barrier Coating Systems on SiC/SiC Ceramic Matrix Composites

D. Zhu*, D. Fox, L. Ghosn, B. Harder, NASA Glenn Research Center, USA

Environmental barrier coatings will play a crucial role in future advanced gas turbine engines because of their ability to significantly extend the temperature capability and stability of SiC/SiC ceramic matrix composite (CMC) engine components, thus improving the engine performance. In order to develop high performance, robust coating systems for engine components, appropriate test approaches simulating operating temperature gradient and stress environments for evaluating the critical coating properties must be established. In this paper, thermal gradient mechanical testing approaches for evaluating creep and fatigue behavior of environmental barrier coated SiC/SiC CMC systems will be described. The fatigue and creep behavior of Hafnia and ytterbium silicate environmental barrier coatings on SiC/SiC CMC systems will be reported in various environmental exposure conditions. The coating failure mechanisms will also be discussed under the heat flux and stress conditions.

4:40 PM

(ICACC-S2-029-2011) Oxidation Reactions and Kinetics of SiC, Si-C-N & Hf02 Ceramic Composites at Ultra High Temperatures

J. M. Lonergan*, R. Raj, University of Colorado, USA

There has been a recent interest and development of a new class of ultra high temperature materials capable of sustained structural and chemical stability at hypersonic speeds. A Silicon Carbide (SiC) fiber tow with a coating structure consisting of a Polymer Derived Ceramic (PDC) bond coat and Hafnia (Hf02) topcoat is being considered as an Environmental Barrier Coating (EBC). The fiber tow is dip coated with a PDC precursor, specifically Si-C-N, crosslinked at 200C and then pyrolyed at 1000C. The second coating of Hafnia is applied through a MOCVD process at 550C. SEM cross-sectional pictures show a PDC aggregate or filler that binds the individual SiC fibers together with an even coating of Hafnia encircling the fiber bundle. Oxidation tests conducted at 1500C in an open air box furnace show significant differences in the amount of oxide growth between the coated and uncoated samples. These SiC fiber tows combined with the Si-C-N/Hf02 coating system represents a new class of EBC for ultra high temperatures and harsh corrosive environments.

5:00 PM

(ICACC-S2-030-2011) An Yb2Si2O7 oxidation resistance coating for C/C composites by supersonic plasma spray

G. Lingjun*, Northwestern Polytechnical Uinversity, China; H. Minna, L. Hejun, L. Kezhi, Northwestern Polytechnical University, China

An efficient glass coating was prepared on the surface of SiC coated C/C composites by supersonic plasma spray to prevent them from oxidation at 1873 K. The structure of the as-obtained coating was characterized by XRD,SEM and isothermal oxidation test at 1873 K in air, respectively. Results show that the achieved Yb2Si2O7 outer coating was dense and it was bonded well with the SiC inner layer such

that the oxidation protective ability and thermal shock resistance were improved. After oxidation in air at 1873 K for 328 h and thermal cycling between 1873 K and room temperature for 17 times, the mass gain rate of the coated sample was only 0.28 %. A dense layer about 5 μm between the SiC inner coating and the Yb2Si2O7 outer coating was in favor of the enhancement of the oxidation resistance of the SiC/Yb2Si2O7 coating for C/C composites.

5:20 PM

(ICACC-S2-031-2011) Si-Mo-B oxidation resistance coating for SiC-coated carbon/carbon composites

Y. Zhang*, H. Li, K. Li, Q. Fu, Northwestern Polytechnical University, China

Abstract To improve the oxidation resistance of SiC-coated carbon/carbon (C/C) composites, the Si-Mo-B coating was prepared on the surface of SiC coated C/C composites by slurry method. The effects of B content on the microstructure and oxidation resistance of Si-Mo coatings were investigated. The results show that with the increase of B content in the coating, the oxidation resistance of the Si-Mo-B coating at 1173K increased gradually, the oxidation resistance at 1873K decreased contrarily. The multilayer coating with three-layer Si-Mo-B coatings and glass exterior coating also prepared, which could effectively protect C/C composites for 100 h at 1173 K and 150 h at 1873 K, and it could endure the thermal cycling between 1873 K and room temperature for 40 cycles. The excellent oxidation protective ability of the multilayer coating at broad temperature range could be attributed to the excellent self-sealing property.

S3: 8th International Symposium on Solid Oxide Fuel Cells (SOFC): Materials, Science and Technology

Reliability/Degradation

Room: Coquina Salon E

Session Chairs: Shailesh Vora, US Department of Energy; Yeong-Shyung Chou, Pacific Northwest National Laboratory

1:30 PM

(ICACC-S3-020-2011) Microstructural Change in Electrodes During Discharge Operation of Solid Oxide Fuel Cells (Invited)

T. Matsui*, H. Muroyama, K. Eguchi, Kyoto University, Japan

Ni-YSZ cermet is a conventional anode for use in solid oxide fuel cells, and its composition and microstructure are carefully controlled to achieve high performance and long-term stability. In this study, the performance stability of electrolyte-supported cell (Ni-YSZ | YSZ | LSM) was examined at 1000oC by feeding humidified fuel, x% H2O-(100-x)% H2. The influence of cermet composition on degradation was also studied. The degradation behavior was significantly dependent on the fuel humidity and cermet composition. In the case of Ni-YSZ with a volume ratio of 50 to 50, peculiar phenomena were observed. When the fuel of 30% H2O-70% H2 was supplied to the anode at the terminal voltage of 0.7 V, the current density decreased gradually soon after the discharge up to 69 h, followed by a sudden drop in current density. After the subsequent open-circuit holding, the performance was partially recovered in discharge operation. This behavior of degradation-recovery was reversibly repeated upon discharge-open-circuit holding operation. In the case of 40% H2O-60% H2, irreversible performance deterioration was observed accompanied with a drastic decrease in volume-specific triple phase boundary (TPB) length: the TPB length of degraded anode was evaluated to be 1.66-1.68 μm μm-3 by FIB-SEM technique, whereas that of as-prepared anode was 2.49 μm μm-3.

2:00 PM

(ICACC-S3-021-2011) Residual stress measurement on electrolyte of segmented-in series SOFC using X-ray stress measuring method

T. Somekawa*, K. Fujita, H. Yakabe, Y. Matsuzaki, Tokyo Gas Co., Ltd., Japan

In recent years, small scale SOFC systems have been developed for residential applications. Nickel grains in the anode layer of the cells could be oxidized when emergency shutdown happens due to a fuel outage. It is well known that a re-oxidation of the anode causes destruction of the anode layer. In order to develop a SOFC stacks which have the high tolerance against the re-oxidation, a detailed understanding of the processes of re-oxidation is very important. In this study, changes of the residual stress on the electrolyte were measured by using in-situ X-ray stress measurement method. A single cell clipped from segmented-in-series (SIS) stack was heated to 750 °C using 4%H_2-96%N_2 as a fuel and air as an oxidant. Then 4%H_2-96%N_2 gas was turn off and air was introduced into the anode. It has been found that almost no change of residual stress on the electrolyte was observed even when air was supplied to the anode instead of 4%H_2-96%N_2 gas. The performances of SIS-stack were measured after reduction and oxidation cycles. The stack showed the significantly low degradation rate by the cycles. These results suggest that the SIS stack have a high tolerance against the re-oxidation of nickel grains in the anode layer because of the electric insulated substrates which contain relatively small amount of nickel.

2:20 PM

(ICACC-S3-022-2011) Redox-Induced Performance Degradation of Anode-Supported Tubular SOFCs

Y. Heo, Korea Advanced Institute of Science and Technology, Republic of Korea; J. Lee, S. Lee, T. Lim, S. Park, R. Song*, D. Shin, Korea Institute of Energy Research, Republic of Korea

Porous composites of nickel and yttria-stabilized zirconia (YSZ) are the anode material of choice for solid oxide fuel cells (SOFCs) being developed or commercialized, owing to high catalytic activity, high electrical conductivity and excellent chemical/mechanical compatibility with YSZ electrolytes. The anode may be re-oxidized in the case of seal leakage, fuel supply failure or even very high fuel utilization. Therefore, the anode may undergo a number of reduction–oxidation (redox) cycles during long-term operation. The re-oxidation of Ni to NiO causes significant mechanical stress to be developed across the anode, which may destroy the integrity of the whole cell. In this study, the redox-induced performance degradation of anode-supported tubular SOFCs being developed at KIER was examined using various characterization techniques. The electrical and microstructure analyses indicated that as the anode experiences the redox cycling, well-dispersed Ni particles in the porous YSZ matrix coalesce into larger agglomerates. This results in a loss of continuous network for electronic conduction as well as a porosity increase, causing the degradation of electrical and mechanical properties. The anode-supported tubular cells with thin electrolyte and cathode were constructed and then the degradation of cell performance was analyzed under redox cycling conditions by using polarization and ac-impedance techniques.

2:40 PM

(ICACC-S3-023-2011) Numerical Modeling of Contact Material Densification

B. J. Koeppel*, W. N. Liu, E. V. Stephens, M. A. Khaleel, Pacific Northwest National Laboratory, USA

The objective of this work was to develop a numerical model for sintering of contact materials which are integral to the assembly of SOFC substrates and stacks. The joining of stack components using contact materials is critical to ensure that electrical and mechanical integrity is maintained during operation. Due to processing limitations from multiple fabrication steps, contact materials are being developed that can form a dense mechanical bond at temperatures below the typical range for good sintering rates. Within the stack, the layer to be sintered is constrained by the surfaces being bonded and subjected to different loading states based on the actual geometry and cell stiffness properties. Numerical modeling of the constrained sintering process will aid the design of uniform and dense contact layers. A finite ele-

ment model based on the continuum theory for sintering of porous bodies was developed and used to evaluate contact materials within planar SOFC stacks. This model accounts for the effect of kinematic constraints and remote loading on the local densification behavior. The effect of different contact materials and initial properties on the final density distributions was investigated, and the influence of the material volumetric changes on stresses within the cell and seal layers was characterized. The model implementation, material inputs, and stack thermal-mechanical stress results will be presented.

Sealant Glasses

Room: Coquina Salon E
Session Chairs: Shailesh Vora, US Department of Energy; Yeong-Shyung Chou, Pacific Northwest National Laboratory

3:20 PM

(ICACC-S3-024-2011) Performance of Glass-ceramic Sealant in Planar SOFC Short Stack Assemblies

F. Smeacetto*, M. Salvo, M. Santarelli, P. Leone, Politecnico di Torino, Italy; T. Moskalewicz, AGH University of Science and Technology, Poland; A. Chrysanthou, University of Hertfordshire, United Kingdom; M. Ferraris, Politecnico di Torino, Italy

Performance and testing of joined Crofer22APU bipolar plate/glass-ceramic sealant/anode-supported-cell (ASC) in dual atmosphere have been evaluated, in order to study the stability and effectiveness of the glass-ceramic (boron and barium-free silica-based) sealant used in the experiment. The time-evolution of the cell voltage was investigated with respect to chromium poisoning issues; the cell open circuit voltage was demonstrated to be fully achieved (at 800°C up to 500 hours) by employing the glass ceramic sealant. The Crofer22APU bipolar plate/glass-ceramic sealant/ASC cell was submitted to post mortem examination after the long-term experiment. Cross-sections of joined samples were characterized by SEM and TEM (with SAED). EDS analysis was carried out in order to detect any elemental diffusion into or away from the sealant after dual atmosphere exposure and to examine for any chemical interactions between Crofer22APU and ASC with the glass-ceramic sealant at their three-phase boundary under reducing and oxidizing conditions. The design and operation of an SOFC short stack (based on planar anode-supported cells) with the performance of the glass ceramic sealant inside the stack are also discussed.

3:40 PM

(ICACC-S3-025-2011) Compliant sealing glass for SOFC applications: thermal cycle stability and chemical compatibility with YSZ coating

Y. Chou*, E. T. Thomsen, R. T. Williams, J. P. Choi, N. L. Canfield, J. F. Bonnett, J. W. Stevenson, Pacific Northwest National Laboratory, 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 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 thermal cycle stability as well as thermal stability in dual environments at elevated temperatures. The SCN-1 glass is used to seal a NiO/YSZ anode supported YSZ bi-layer disc to an YSZ or Al2O3 coated SS441 substrate. High temperature leak rates will be reported as function of back pressure, temperatures, and coatings. Interfacial microstructure will be characterized to assess the compatibility of various coating.

4:00 PM

(ICACC-S3-026-2011) Interactions of Viscous Sealants with Solid Oxide Fuel Cell Components

M. O. Naylor*, J. E. Shelby, S. T. Misture, Kazuo Inamori School of Engineering, Alfred University, USA

Several silicate based glasses were studied for application as viscous sealants for SOFCs. Gallium and germanium containing silicates with zinc and strontium additions were prepared and studied. Several compositions retain a large amorphous content after 1400h at 850 °C in air. Powdered samples of the glasses have been heat treated up to 504h at 850 °C in air to evaluate crystallization and interactions with 8YSZ and aluminized stainless steel. Viscous flow behavior of powdered samples was studied using hot-stage microscopy, and weight loss under H2 was measured. The sealants all crystallize partially at 850C but most remain amorphous at 650C. Select sealants exhibit minimal interaction with 8YSZ substrates after 1500h. Initial test seals between 8YSZ and aluminized stainless steel survive thermal cycling, suggesting that some are appropriate for the SOFC application.

4:20 PM

(ICACC-S3-027-2011) Effect of environmental exposure on the microstructural stability of a barium silicate glass seal

A. Shyam*, R. Trejo, D. McClurg, J. Muth, M. Kirkham, E. Lara-Curzio, Oak Ridge National Laboratory, USA

Solid oxide fuel cell (SOFC) glass seals are expected to retain their functional properties for at least 40,000 hours under severe operating conditions. To assess the durability of an alkali barium silicate glass and its compatibility with SOFC-relevant materials, test specimens consisting of glass beads sintered onto alumina and 8YSZ substrates were exposed to air and a gas mixture of steam+H2+N2 at 800°C for various periods of time. The effect of long-term environmental exposure (~10,000 hours) on the phase and microstructural stability of the glass and its physical, thermal and mechanical properties was investigated and the results will be reported. This work was sponsored by the US DOE - SECA Core Technology Program at Oak Ridge National Laboratory.

4:40 PM

(ICACC-S3-028-2011) High-Temperature Viscous Sealing Glasses for Solid Oxide Fuel Cells

C. Kim*, C. L. Schwartz, J. Szabo, K. Barr, T. E. Day, MO-SCI Corporation, USA; R. K. Brow, Z. Tang, Missouri University of Science and Technology, USA

MO-SCI Corporation and the Missouri University of Science and Technology identified and tested several glass compositions that could be used as viscous seals for Solid Oxide Fuel Cells (SOFCs). The glasses possess desirable viscosity characteristics- that is, they have softening points in the temperature range expected for SOFC operations (650-850°C), so cracks that might form in the glass on thermal cycling should reseal upon reheating through a 'viscous healing' mechanism. The new glasses have relatively low liquidus temperatures (< 800°C) and do not exhibit significant crystallization when held at SOFC operational temperatures. Excessive crystallization could change the viscous behavior and may jeopardize the viscous healing characteristics of the seal. In addition, the new glasses wet both aluminized SS441 and NiO/YSZ substrates, forming hermetic seals that have survived, in one case, up to seventy five thermal cycles between room temperature and 750°C. The glasses have no significant weight loss from the molten state when held in ambient air.

5:00 PM

(ICACC-S3-029-2011) Effect of MgO addition on crystalline phase formation and thermal expansion of a barium aluminosilicate solid oxide fuel cell glass-ceramic sealant

N. Dasgupta*, B. Butler, E. Sorge, Materials & Systems Research, Inc., USA

The effect of addition of nano-MgO to BCAS glass was investigated with emphasis on phase development and thermal expansion with de-vitrification for SOFC sealing application. Glass-MgO compositions corresponding to 0%, 5%, 10% and 15% MgO additions by volume were de-vitrified at 800°C for various durations and evaluated for phase development and thermal expansion changes. The phase-mix changed with varying amounts of MgO addition and heat treatment conditions. The coefficient of thermal expansion (CTE) of the

glass-MgO compositions varied, depending on the crystalline phases present. The CTE of BCAS glass with 15 vol.% MgO was 12.4 x 10^{-6}/°C after de-vitrification at 800°C for 30 minutes and reduced by only 2.4% when maintained at this temperature for 900 hours. A perovskite based coating was developed for application on the sealing area of commonly used metallic interconnects. Sandwich structures consisting of YSZ – glass-MgO sealing composition – coated interconnect were heat treated at 800°C for different durations and were examined microscopically to assess the quality of sealing. The addition of an appropriate amount of nano-MgO to BCAS glass results in a sealing composition that is thermally stable with time and is non-reactive with a suitably coated interconnect.

S4: Armor Ceramics

Microstructural Design for Enhanced Armor Ceramics

Room: Coquina Salon D
Session Chair: Andrew Wereszczak, Oak Ridge National Laboratory

1:30 PM

(ICACC-S4-022-2011) Nature-Inspired Ultrahigh Toughness Ceramic-Polymer Structural Composites (Invited)

R. O. Ritchie*, University of California, Berkeley, USA; A. P. Tomsia, Lawrence Berkeley National Laboratory, USA

We present a novel approach for a generation of lightweight, high-performance structural materials with unprecedented combinations of strength and toughness. The approach is based on replicating Nature's hierarchical structures in synthetic materials. As a proof of concept, we have recently demonstrated how Nature's design concepts can be applied to bulk hybrid materials that comprise two conventional (low toughness) compounds, aluminum oxide and polymethylmethacrylate. Using freeze-casting, a technique pioneered in our Lab, we have created ice-templated hybrid structures with exceptional toughness that are over 300 times higher (in energy terms) than their alumina and PMMA constituents. These toughnesses far surpass what can be expected from the simple "rule of mixtures"; they result in alumina ceramic-based materials having a specific strength and fracture toughness comparable to that of aluminum alloys, i.e., a "yield" strength of 200 MPa with a fracture toughness of ~35 MPa√m. Our goal is to translate this approach to multiple material combinations including other ceramic/polymer and ceramic/metal composites, useful for armor and lightweight composites.

2:00 PM

(ICACC-S4-023-2011) Material design for superplasticity in covalent ceramics: Grain refinement and grain-boundary controlling (Invited)

Y. Shinoda*, Tokyo Institute of Technology, Japan

Covalent ceramics such as silicon carbide (SiC) and boron carbide (B4C) have excellence in high-temperature strength, and besides, its hardness belongs to the highest class following those of diamond and cubic-boron nitride (BN) ceramics. Therefore, they hold promise as heat-resistant or wear-resistant materials. However, its hardness and brittleness combined make them unworkable. The polycrystalline solids composed of fine grains can exhibit superplasticity, namely, an extremely large elongation in tension at elevated temperatures. The application of this nature has brought about the superplastic forming technology even for brittle ceramics. It is well known that the dominant mechanism of superplasticity is grain-boundary sliding of each grain. So the grain-boundary characteristics (structure and chemistry) have great importance on controlling the superplastic property. In this presentation, I will talk about the control of the grain size and the grain-boundary chemical composition for superplasticity focusing on SiC ceramics. Hot isostatic pressing equipment or high-pressure hot pressing technique at low temperature was utilized for grain refinement. The grain-boundary segregation of the additives and the impurity in SiC ceramics was clarified and its effect on superplastic property was investigated.

2:30 PM

(ICACC-S4-024-2011) Influence of Variations in the Starting Powders Chemistry and Crystallinity on Physical and Mechanical Properties of SPS SiC

V. Domnich*, R. A. Haber, Rutgers University, USA

To control plastic mechanisms in SiC ceramics, the ability to mix and form powders into uniform green bodies and sinter these structures into controlled, dense structures containing no macroscale defects and minimal microscale variability is required. These powders have to be well characterized and designed to minimize nano and microscale variability. In this work, we aim at quantifying the effects of precursor impurities, reaction time and spatial location on chemistry and crystallinity of SiC powders produced by carbothermic reaction. Raman spectroscopy, chemical, and x-ray diffraction analyses are used for obtaining structural and chemical information on the powders under consideration. Further, we use spark plasma sintering (SPS) to produce dense SiC structures made of powders with specified characteristics. The effect of powder variability on physical and mechanical properties of dense SiC structures is investigated and discussed.

3:10 PM

(ICACC-S4-025-2011) Tensile Failure Stress Anisotropy in Hot-Pressed Silicon Carbide

D. J. Vuono*, A. A. Wereszczak, P. J. Ritt, Oak Ridge National Laboratory, USA; J. Campbell, US Army Research Laboratory, Aberdeen Proving Ground, USA

The tensile failure stress of a hot-pressed silicon carbide (SiC) was measured using flexure testing with bend bars whose longitudinal axis was either parallel or perpendicular to the pressing axis. All bend bars were machined under the same conditions, had the same cross-sectional dimensions, and were tested with the same bend fixture and at the same crosshead displacement rate. Over 50 bars were tested of both orientations producing good statistical confidence in the results. Tensile failure stress was not isotropic. The average failure stress for the perpendicular bar set was approximately 16% higher than that of the parallel set. Not captured in that average failure stress difference was the fact that about 1/3 of the specimens in the parallel set failed at lower tensile stresses than the weakest specimen in the perpendicular set; namely, there was a large number of relatively low tensile failure stresses in the parallel set. These differences in failure stress distributions are discussed in context with fractographical observations, microstructure of the SiC, Weibull statistics, effective sizes, and other supportive mechanical evaluations. Possible ramifications of this tensile failure stress anisotropy on the fracture behavior in an impacted armor tile are also discussed.

3:30 PM

(ICACC-S4-026-2011) Fabrication of High Volume Fraction SiC_p / Al Metal Matrix Composites

R. McCuiston*, King Mongkut's University of Technology Thonburi, Thailand; S. Ngernbamrung, K. Dateraksa, K. Sujirote, National Metal and Materials Technology Center, Thailand; J. Wannasin, T. Sungkapun, Prince of Songkla University, Thailand

High volume fraction silicon carbide particle (SiC_p) - aluminum metal matrix composites were fabricated for use in a domestic armor application. A SiC powder mixture, consisting of three different average particle size powders (6.3, 2.2 and 0.68 microns), was designed in order to achieve high packing fractions, on the order of 60 to 70%. Near net shape porous SiC preforms were fabricated by die pressing. The preforms were bisque sintered to give them sufficient strength for infiltration. The bisque sintering was conducted either in air to produce an oxide film or by the conversion of a preceramic polymer polycarbosilane under an inert atmosphere. The preforms were infiltrated

by squeeze casting using 7075 aluminum in a semi-solid state. The infiltrated preforms were given a T6 heat treatment. Polished cross sections and fracture surfaces were observed using optical and electron microscopy to analyze the microstructure. The infiltrated preforms were found to have low residual porosity. Results on mechanical property evaluation and ballistic performance will be reported.

3:50 PM

(ICACC-S4-027-2011) Microstructural Design for Si-B4C-Diamond System

P. Karandikar*, S. Wong, G. Evans, M. Aghajanian, M Cubed Technologies, Inc., USA

Reaction bonded SiC (RBSC) and reaction bonded B4C (RBBC) materials have been used successfully for armor applications over the last decade. SiC is inert and does not react with molten silicon during the reaction bonding process. B4C however, can react with molten silicon during the reaction bonding process. These reactions can be used to tailor the microstructure and properties of resultant composite. Addition of alloying elements allows further manipulation of the reaction-synthesized phases. Finally, the properties of RBBC materials can be further tailored by using diamond reinforcement. Diamond is an extremely effective reinforcement due to its very high elastic modulus (1050 GPa), and hardness (12,000 kg/mm2). Diamond however, is heavier (density = 3.52 g/cc) and more expensive and thus its content needs to be minimized to keep the armor light and affordable. Also, similar to B4C, diamond can react with molten Si forming SiC. This study focuses on development of process-microstructure-property relation in the Si-B4C-diamond system. In this work, process parameters and particle sizes are systematically varied. The resultant composites are subjected to microstructural (optical, SEM, EDAX, and X-ray diffraction), physical, and elastic properties characterization. The resultant process-microstructure-property relationships will be presented in this paper.

4:10 PM

(ICACC-S4-028-2011) Mechanical Properties and Deformation Mechanisms of B_4C-TiB_2 Eutectic Composites

R. M. White*, E. C. Dickey, The Pennsylvania State University, USA

Directionally solidified eutectics are a unique class of in-situ composite materials, which may have improved properties over their monolithic counterparts. This study focuses on the boron carbide (B_4C) and titanium diboride (TiB_2) eutectic produced via laser processing. The composite nature of the material leads to the formation of residual stresses upon cooling from the solidification temperature, which is observed to effect the indentation-induced deformation, including preferential cracking at local tensile fields in the B_4C. Finite element models of the eutectic microstructure are used to calculate residual stress distributions, which are found to be qualitatively consistent with pre-deformation TEM strain fields and the subsequent deformation behavior. The B_4C-TiB_2 eutectic of has a Vickers hardness of 32 GPa at 9.81 N loads when the inter-phase spacing is on the order of 180 nm. The hardness of the composite is found to increase as the microstructural scale is decreased. A focused ion beam (FIB) is used to extract site-specific samples of both as-processed and indented materials for transmission electron microscopy (TEM), while Raman spectroscopy is used to analyze average deformation in the boron carbide phase. Both electron diffraction and Raman spectroscopy of deformed B_4C-TiB_2 eutectic materials suggest that the composite microstructure serves to suppress deformation in the B_4C.

4:30 PM

(ICACC-S4-029-2011) Mechanical Properties of Superhard Boride-Carbide Particulate Composites

E. W. Neuman*, W. Faherenholtz, G. Hilmas, Missouri University of Science and Technology, USA

The mechanical properties of hot pressed metal diboride - silicon carbide - boron carbide ternary composites were studied. For these materials, the metal diboride was either titanium diboride or zirconium diboride. The compositions consisted of particulate composites containing 20 to 70 vol% of one of the metal diborides with 30 to 80 vol% of silicon carbide plus boron carbide. The compositions were hot pressed to near full density at 2000°C under an applied pressure of 32MPa in a flowing argon atmosphere. Young's modulus, Vickers' and Knoop hardnesses, fracture toughness, and four-point bend strength were measured. The hardness of the composites were greater than expected base on rules of mixture calculations. For example, a TiB_2-SiC-B_4C and a ZrB_2-SiC-B_4C composition had Vickers' hardnesses (1 kg load for 15 sec) of 34 ± 3 GPa and 32+2 GPa compared to a predicted hardnesses of 26.2 GPa and 23.7 GPa. In addition to high hardness, some of the composite compositions had strengths as high as ~1.4 GPa with fracture toughness values as high as ~6 MPa√m. The influence of microstructure on the mechanical properties will be discussed.

4:50 PM

(ICACC-S4-030-2011) Structural Variations in Boron Carbide as a Function of Carbon Content: Raman Spectroscopy and X-Ray Diffraction Studies

V. Domnich*, D. W. Maiorano, R. A. Haber, Rutgers University, USA

Boron carbide is a material with extreme hardness, high Young's modulus and low specific weight that make it useful in lightweight armor applications. The main structural units in boron carbide are the 12-atom icosahedra located at the nodes of the rhombohedral lattice and the 3-atom chains connecting the icosahedra along the [111] rhombohedral direction. An ideal structure with the B4C stoichiometry would consist of eight B12 icosahedra and a C-C-C chain per unit cell. However, atomic similarity between boron and carbon allows large variations in boron carbide structure within the carbon content range of 8.8 to 20 at.%, including formation of such structural units as B12 and B11C icosahedra and C-C-C, C-B-C, and C-B-B chains. In this work, we use a combination of Raman spectroscopy and X-ray diffraction to investigate the structure and vibrational properties of boron carbide as a function of carbon content. Specifically, samples containing 9, 11, 13, 18, and 20 at.% C have been analyzed. Because Raman spectra of boron carbide are known to exhibit dependence on the excitation energy, four different wavelengths have been used in this study, extending from 325 nm (ultra-violet) to 785 nm (near infra-red).

S5: Next Generation Bioceramics

Advanced Processing of Bioceramics

Room: Ponce de Leon
Session Chairs: Roger Narayan, University of North Carolina; Akiyoshi Osaka, Okayama University

1:00 PM

(ICACC-S5-001-2011) Electrically Active Bioceramics (Invited)

I. Turner*, University of Bath, United Kingdom

Bone is a naturally piezoelectric material; the electrical potentials in mechanically loaded bone have been implicated as signals in the remodelling cycle. This has led to an interest in exploiting this phenomenon to develop electrically active bioceramics for use as bone substitutes with improved biological response. Both polarized hydroxyapatite (HA), whose surface charge is not dependent on loading, and piezoelectric ceramics, which produce electrical potentials under stress, have been studied in order to determine the benefits of using electrically active bioceramics as implant materials. The majority of piezoelectric ceramics proposed for use as bone substitutes contain barium titanate (BaTiO3). Composites of HA combined with barium titanate (BT) were thus manufactured for direct comparison with commercially available HA bioceramics. The attachment, proliferation, viability, morphology and metabolic activity of Saos-2

human osteoblast type cells cultured on HABT ceramics containing 90% barium titanate for one to seven days were compared with those observed on the HA ceramics. The behaviour of cells cultured on unpoled HABT was comparable to that observed on the HA samples at all time points. At one day after seeding, cell behaviour was modified on both the positive and negative surfaces of poled HABT. At three and seven days after seeding all parameters observed were comparable on poled and unpoled ceramics.

1:30 PM

(ICACC-S5-002-2011) Formation of Porous Zirconia and Titania with Self-assembling Agarose Templation (Invited)

X. Ma, M. Akinc*, Iowa State University, USA

Porous metal oxides, ZrO2 and TiO2, with high surface area have been synthesized by self-assembling agarose gel and employing ZrO(NO3)2 or TiOCl2 aqueous solutions as metal ion source. Porous metal oxides with the same open network structure as the gel are recovered by removing agarose polymer after a heat treatment at 500°C in air. For ZrO2, Phase transformation from amorphous to tetragonal occurs over a temperature range of 300-500°C as determined by XRD. FTIR revealed agarose/MO2 interaction. SEM reveals that the Agarose forms an open fibrous network structure after freeze drying. Agarose/MO2 nanocomposite as well as resulting MO2 after agarose burnout confirm the templation by Agarose. Porous MO2 fiber diameter is found to be around 10 nm. The specific surface area and pore size distribution of the sponge-like MO2 monoliths are determined by N2 adsorption isotherms employing BET and BJH methods respectively.

_____ This work was supported by the U.S. Department of Energy under contract number DE-AC02-07CH11358.

2:00 PM

(ICACC-S5-003-2011) Preparation of silica-based composite particles for blood purification therapy (Invited)

J. Li, Y. Shirosaki, S. Hayakawa, A. Osaka*, Okayama University, Japan

Sol-gel derived titania particles are promising candidates for blood purification therapy since they not only adsorb some pathogenic substances but also are highly blood compatible, or causing no blood clotting on direct contact with whole blood. For commercialization, such biologically active titania is to be developed on silica gel surface or involved in the surface layer. Thus, titania (anatase)-hybridized silica particles of 1~5 mm in diameter were prepared via the sol-gel route, using water glass, alginate and titanium tetraethoxide as the starting materials. Their bovine serum albumin and lysozyme adsorption was examined.

2:30 PM

(ICACC-S5-005-2011) Laser based additive processing of bioceramics (Invited)

S. Hoeges*, W. Meiners, Fraunhofer Institute for Laser Technology, Germany

Selective Laser Melting (SLM) is an Additive Manufacturing technique which enables the manufacture of parts on the base of individual three-dimensional data, including computer tomography models of anatomical structures. Full melting of the material results in serial properties of the generated parts. SLM has been successfully proved to be suitable for application in implant manufacturing for permanent bone substitution (e.g. titanium implants). Process development for bioceramics (e.g. Hydroxilapatit, Tricalciumphosphate) shows that direct processing via laser melting is not possible due to thermal properties of the materials. An alternative route for manufacturing of biodegradable implants is the use of composite materials. One material is chosen with a suitable melt phase, one material (bioceramic) for its excellent biological properties. The SLM process is developed for a composite material of Poly(D,L-lactide) (PDLLA) and β-Tricalciumphosphate (β-TCP). A suitable powder preparation method is developed and the processing parameters of the SLM technology are identified for the new material to produce dense parts. Porosity is integrated in the parts using CAD and reproduced via additive manufacturing. The properties of the parts concerning microstructure, mechanical, chemical and biological properties after processing are analyzed. Results of animal tests show the potential of the manufactured parts for medical application.

3:10 PM

(ICACC-S5-006-2011) Antibacterial, Abrasion-Resistant Micropatterned Alumina Surfaces

L. Treccani*, K. Rezwan, University of Bremen, Germany

Material surfaces employed in contact with fluids suffer typically from biofouling and surface abrasion induced by bacteria and abrasive particles naturally present in the environments. Biofouling and abrasion are respectively the main causes for epidemic outbreaks, efficiency loss and ultimately system failure. Here we present an innovative method to fabricate potentially long–lasting, antibacterial surfaces. Specifically designed alumina micropattern fabricated by a maskless aerosol printing technique, were functionalised with lysozyme, an antibacterial enzyme of the immune system. Such surfaces were tested for different time periods with solutions respectively containing bacteria, abrasive particles and aggressive chemical media. Biofunctionalised, micropatterned surfaces did not suffer abrasion, chemical degradation or any significant biocide activity loss. In particular, we showed that the micropatterns could efficiently protect the immobilised biomolecules from desorption, chemical denaturation and activity loss. Such biofunctionalised, micropatterned surfaces may present a feasible and highly efficient way to improve engineered systems e.g. biomaterials, biosensors or devices for biotechnological applications. Furthermore, the use of natural antibacterial agents represents a novel sustainable and safer alternative to antibiotics or other hazardous, synthetic biocides.

3:30 PM

(ICACC-S5-007-2011) Two photon polymerization for fabrication of small-scale medical devices out of organically-modified ceramic materials

R. Narayan*, A. Doraiswamy, S. Gittard, N. Monteiro-Riviere, University of North Carolina, USA; A. Ovsianikov, B. Chichkov, Laser Zentrum Hannover, Germany

The term rapid prototyping is used to describe additive processing of three-dimensional structures. Two photon polymerization is a rapid prototyping process in which ultrashort laser pulses are used for selective hardening of photosensitive materials. In this technique, near simultaneous absorption of two photons from a femtosecond laser is used to produce electronic excitation of material in a manner similar to that of a single photon with significantly higher energy. Solidification of material within the diffraction limit is possible as a result of the nonlinear nature of two photon absorption. Two photon polymerization technology is compatible with inexpensive and widely available photosensitive materials. This technique has been used to fabricate structures with a wider range of geometries than conventional microelectronics-based technologies. Recent medical applications of two-photon polymerization have involved fabrication of medically-relevant small-scale structures out of organically-modified ceramic materials. We have described fabrication of microneedles and microneedle arrays using two photon polymerization. In addition, we have described processing of small bone prostheses as well as scaffolds for regenerative medicine using this method.

3:50 PM

(ICACC-S5-008-2011) Effects of Electrical Modification on Phase Stability of Y-TZP Ceramics (Invited)

Y. Tanaka*, H. Hara, N. Enomoto, Kyushu University, Japan; K. Yamashita, Tokyo Medical and Dental University, Japan; J. Hojo, Kyushu University, Japan

Yttria-stabilized tetragonal zirconia (Y-TZP) is an important load-bearing bioceramic. However, a phenomenon called low temperature

degradation (LTD), in which a spontaneous phase transition occurs under moist conditions, reduces the reliability of Y-TZP as implants for long-term use. Since the exact mechanism of LTD is still unclear, this work was motivated by a search for influence of surface defects and static charges of Y-TZP ceramics on the LTD. Y-TZP ceramics were polarized under 1-1000 Vcm^{-1} and 100-400 ^{o}C to control the surface defects and static charges. The dipole formation on all of the polarized surfaces was proved with the successful detections of thermally stimulated depolarization current; the amount of charge storage, which was mainly originated in the displaced oxide ions and vacancies, was widely varied between 10^{-5}-1 Ccm^{-2} by poling conditions. Using the voltage and temperature above ca. 250 Vcm^{-1} and 200 ^{o}C changed the sample color from white to black with increasing electrical conductivity, indicating that the high external energy during the poling resulted in the electron or hole injections into Y-TZP as well as the ionic polarization. LTD durability was significantly influenced by the polarity on the surfaces; the positively-charged surface probably included holes and excess vacancies showed the good resistance for the LTD progress. The details will be presented at the conference.

4:10 PM

(ICACC-S5-009-2011) Synthesis and Characterization of Multi ion doped hydroxylapatite

A. Bahadir, C. Ergun*, G. Gunes, Istanbul Technical University, Turkey; T. J. Webster, Brown University, USA; I. Erden, Yildiz Technical University, Turkey

Synthetic Hydroxylapatite (HA) has a similar composition and structure to biological apatite. Therefore, synthetic HA has been extensively used for various biomedical applications like matrices for drug release control, bone cements, tooth paste additive, monolithic implants or coatings on metallic implants. Non-medical applications of HA include packing media for column chromatography, gas sensors, catalysis and host materials for lasers. Recently, much attention has been focused on nano-crystalline HA as an adsorbent for removing pathogenic proteins from blood for blood purification therapy since HA has good blood compatibility as well as a superior ability for selective protein adsorption. The major factors affecting the performance of HA on these applications are crystal morphology, density, porosity, pore size and distribution, chemical composition, and surface structure. As provided by the high flexibility of the apatite structure a great variety of cationic and anionic species can be substituted into HA structure which is specifically considered as an effective method to modify the properties of HA. In this research, multi ion doped HAs with a combination of Ag, Ti, Al and Cu ions will be synthesized via precipitation method and sintered in air at different temperatures. Then the samples will be characterized in terms of materials properties and biocompatibility.

4:30 PM

(ICACC-S5-010-2011) Fabrication of hydroxyapatite–calcite Nanocomposite

E. Girija*, G. Suresh Kumar, Periyar University, India; A. Thamizhavel, Tata Institute of Fundamental Research, India; Y. Yokogawa, Osaka City Unviersity, Japan; S. Narayana Kalkura, Anna University, India

Synthesis of nano and dispersed hydroxyapatite [HA, Ca10(PO4)6(OH)2] by sol-gel method is being done using organic modifiers like citric acid and after synthesis washing of the precipitate is an essential step to eliminate the byproducts and citric acid. Here we have employed sol–gel process in the presence of citric acid to fabricate dispersed nano HA at relatively low temperature. However instead of washing to eliminate the citric acid calcination was done at 400°C which resulted in the nanocomposite composed of hydroxyapatite and calcite. HA is known to be bioactive and bioresorbable but the rates are too low. On the other hand, CaCO3 is highly biodegradable. The combination of HA and CaCO3 compromised the demerits of each others. The dissolved Ca ions from CaCO3 enhanced the supersaturation of the surrounding fluid which resulted in higher bioactivity of HA.

4:50 PM

(ICACC-S5-011-2011) Functionalisation of calcium phosphate powders for protein delivery

V. Ozhukil Kollath*, H. Omari, R. Persoons, J. Luyten, S. Mullens, VITO, Belgium; R. Cloots, University of Liege, Belgium; C. Vervaet, B. De Geest, J. Remon, Ghent University, Belgium

With the aim to use CaP powders as a drug delivery biodegradable carrier, the interaction of CaP surfaces with proteins was studied. The first step in this study was the de-agglomeration of the CaP powders by planetary ball milling and ultrasonic treatment. The particle size distribution was measured by disk centrifuge. The surface characteristics of the obtained powder were studied by FESEM, FT IR, N2-adsorption/desorption, XRD and XPS and zetapotential measurements. After coating with BSA as a model protein, the quantity of adsorption was measured as a function of the pH. Because BSA and CaP are both negatively charged in physiological pH, the adsorption of amino acids and the accompanying shift in iso-electric point will be studied. In the future, the possibilities of a co-precipitation route will be evaluated.

5:10 PM

(ICACC-S5-012-2011) Collagen-templated sol-gel preparation of ultra-fine silica nanotube films and osteoblastic cell proliferation

S. Chen*, National Institute for Materials Science, Japan; T. Ikoma, Tokyo Institute of Technology, Japan; J. Li, H. Morita, National Institute for Materials Science, Japan; A. Osaka, Okayama University, Japan; M. Takeguchi, National Institute for Materials Science, Japan; N. Hanagataa, Hokkaido University, Japan

Novel scaffolds consisting of ultra-fine silica nanotubes (Silica NT) less than 100 nm in diameter were fabricated via sol-gel procedure using reassembled collagen fibril hydrogels, and their potential application to bone generation was investigated. The collagen fibril hydrogels were soaked in a sol-gel precursor mixture of tetraethoxysilane/ethanol/water/ammonium hydroxide/CaCl2 for 24 h at room temperature to produce silica- coated collagen fibril hybrids. They were subsequently calcined at 600 oC to produce silica nanotube films. They deposited apatite when soaked in Kokubo's simulated body fluid. Moreover, Silica NT films favored attachment and growth of MC3T3-E1 cells and exhibited good biocompatibility. The addition of Ca(II) stimulated cell proliferation and differentiation in vitro and led to the formation of apatite and collagen fibrils.

S7: 5th International Symposium on Nanostructured Materials and Nanotechnology: Development and Applications

Polymer Nanocomposite Technology and Nanoporous Materials

Room: Coquina Salon C
Session Chairs: Alan Weimer, University of Colorado; Christopher DiAntonio, Sandia National Laboratories

1:30 PM

(ICACC-S7-011-2011) Functionalization of Ultra-fine Particles with Nano-thick Controlled Films (invited) (Invited)

A. W. Weimer*, University of Colorado, USA

The functionalization of fine primary particles, including nanoparticles and nanotubes, is easily carried out using sequential self-limiting surface reactions. The self-limiting reactions result in the deposition of atomic or molecular layers, i.e. ALD or MLD. This functionalization process, referred to as Particle ALD/MLD, can be

used to deposit conformal and pinhole-free films of refractory oxides, non-oxides, metals, and hybrid polymer-based materials, among others. Precursor doses can be delivered to fluidized beds of particles sequentially and, in most cases, can be utilized at nearly 100% efficiency without precursor breakthrough and loss. The ability to use precursors with efficiencies approaching 100% opens the door for a unique opportunity to utilize precursors that previously might have been considered to be too expensive. Fluidized beds containing particles comprising hundreds of thousands, even millions of m^2 of surface area can be coated efficiently. Particle ALD/MLD has been demonstrated to place films on primary nanoparticles as small as 10 nm as well as on nanotubes having surface areas approaching 1000 m2/g and within the porous structure of polymeric materials having porosity near 95%. Physical, optical, electrical, and magnetic properties of the particles can be controlled in order to passivate, activate, or is some manner functionalize the particles.

2:00 PM

(ICACC-S7-012-2011) Novel Synthesis of Silicates from Silicone Resins filled with Oxide Nano-particles

E. Bernardo*, G. Parcianello, P. Colombo, University of Padova, Italy

Many silicates are of great interest due their characteristic partially covalent bonding, limiting interdiffusion, and thus leading to remarkable mechanical properties at high temperatures, low thermal expansion and high thermal shock resistance, optimum dielectric properties, etc. The poor interdiffusion, however, greatly complicates the obtainment of dense articles, by conventional sintering. A novel solution is represented by polymer-derived ceramics, in which a silicate article is obtained by direct thermal treatment in air (in the temperrature range of 1200-1500°C) of nano-composites consisting of silicone resins filled with suitable oxide nano-particles. The desired silicate is synthesized by the reaction of the oxide with the silica from the polymer; both residual porosity and glassy phase are very limited, and the grain size is typically below 200 nm. First adopted for the preparation of mullite, the approach was successfully applied to cordierite (2MgO.2Al2O3.5SiO2), yttrium silicates (Y2O3.SiO2 and 2Y2O3.SiO2), zircon (ZrO2.SiO2), here presented, as dense and porous components or coatings.

2:20 PM

(ICACC-S7-013-2011) Synthesis and Characterization of Nanoparticle Barium Titanate Based Nanocomposites

C. DiAntonio*, T. Monson, M. Winter, A. Roesler, P. Yang, T. Chavez, Sandia National Laboratories, USA

Ceramic based nanocomposites have recently demonstrated the ability to provide enhanced permittivity, increased dielectric breakdown strength, and reduced electromechanical strain making them potential materials systems for high energy density applications. A systematic characterization and optimization of a barium titanate based nanoparticle composite employing a polymer matrix will be presented. The work investigates and compares barium titanate nanoparticles solution-base synthesized by different routes that employ barium hydroxide, barium acetate or barium titanyl oxalate precursors. The results, based on the objective to synthesize a nanocrystalline barium titanate at or near its 'critical' size to potentially exploit a superparaelectric phase transition will be discussed. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

2:40 PM

(ICACC-S7-014-2011) Controlled amine functionalization of multi walled carbon nanotubes for the fabrication of PLA-CNT composites

S. Kesavan Pillai*, J. Ramontja, S. Sinha Ray, Council for Scientific and Industrial Research (CSIR), South Africa

Limited solubility of carbon nanotubes (CNTs) in most organic solvents limits their chemical manipulation, quantitative characterization, and wide application. Among various procedure developed, grafting of CNT surface with amines has been widely investigated in preparing soluble CNTs. The conventional approach of amine functionalization is tedious with a typical reaction time of 4-8 days which involves steps such as carboxylation, acyl chlorination and amidation which often leads to cutting of the tubes thus partly losing the high aspect ratio of CNTs. This work presents a two-step chemical functionalization of multi walled carbon nanotubes (MWCNTs) using mild acid treatment and hexadecyl amine (HDA). The major advantages of this direct procedure avoiding acid chloride formation is the control of HDA weight % in the functionalized samples. The method rendered full-length MWCNTs soluble in common organic solvents and the solubility is found to be dependant on the amine content. The CNT solution is used to prepare Polylactide (PLA) - CNT nanocomposite with improved thermal and mechanical properties. The materials were characterized with different techniques such as FTIR, TGA, SEM Photo luminescent spectroscopy and TEM.

3:20 PM

(ICACC-S7-065-2011) Mechanism of Enhanced Tenacity in Polymer Nanocomposite Studied by Small-angle X-ray Scattering and Electron Microscopy

J. Bandyopadhyay*, S. Sinha Ray, Council for Scientific and Industrial Research, South Africa

Poly[(butylene succinate)-co-adipate] (PBSA) nanocomposite containing 3 wt% organically modified montmorillonite exhibits improvement in tenacity (elongation at break) as compared to the pure PBSA. Nanocomposite also shows moderate improvement in tensile modulus and strength. The small-angle X-ray scattering and transmission electron microscopy are used to investigate the exact tenacity improvement mechanism in nanocomposite.

3:40 PM

(ICACC-S7-016-2011) Macro-scale and Highly Porous Conducting Polymer Composites for Efficient Oxygen Reduction

R. Parajuli, H. He*, Rutgers University, USA

Poly(3,4-ethylenedioxythiophene) (PEDOT) modified electrodes have been reported to catalytically reduce oxygen, which shows great potential to replace Pt based electrodes in fuel cells and metal/air batteries. However, the highest room-temperature current density observed (6mA/cm2) needed an extremely high overpotential 0.9 V versus standard calomel electrode (SCE), which largely decreased the output voltage of the batteries. In this work, we will first report our efforts to produce PEDOT/carbon nanotube composites with highly crystalline structures for low overpotential and high efficient oxygen reduction. Furthermore, even thought the highest room-temperature current density observed is sufficient for fuel cell and battery applications, higher current density applications of the PEDOT electrocatalyst concept would require extension of the three phase interface into a much thicker three dimensional highly porous and conductive structure, which is hard to achieve by using the nonconductive Goretex membrane. In this presentation, we would also share with you our recent exploration in fabrication of macroscale three dimensional PEDOT composite based on highly conductive and porous carbon nanotube sponges for more practical applications.

4:00 PM

(ICACC-S7-017-2011) Highly Porous SiCO NanoCeramics from Organically-bridged Alkoxysilanes

A. Parakkulam Ramaswamy, G. D. Soraru*, University of Trento, Italy

Due to their unique nanostructure in which silica nanosized clusters are encased into a graphene network, SiCO nanoCeramics combine very high temperature stability with un-usual functional properties such as semiconductivity, piezoresistyvity and luminescence. For these reasons porous SiOC ceramcs have been proposed as anode for Li-ion batteries and high temperaure sensors. Here we present a simple and

elegant synthetic route to produce highly porous monolithic SiCO without the usage of any templates. Different starting bis(trialkoxysilyl) alkanes and bis(triethoxysilyl)-arylenes were used to synthesize aerogels by non-supercritical drying avoiding the conventional supercritical process. The aerogels possessed low densities, surface areas in the range of 500-1000 m2/g and a narrow pore size distribution in the range 5-10 nm depending upon the type of organic spacer. Upon pyrolysis in argon atmosphere the aerogels yielded porous, monolithic silicon oxycarbide glass of different chemical composition with surface area above 400 m2/g and maintained a narrow pore size distribution. Standard techniques were employed for characterising the materials. Possible application of the porous SiCO as sensors will be discussed.

4:20 PM

(ICACC-S7-018-2011) Boron Carbide-Nanowires/Carbon-Microfiber Hybrid Structures and Composites from Cotton T-shirts

X. Tao, University of South Carolina, USA; L. Dong, ETH Zurich, Switzerland; X. Wang, University of South Carolina, USA; W. Zhang, Zhejiang University of Technology, China; B. J. Nelson, ETH Zurich, Switzerland; X. Li*, University of South Carolina, USA

Boron carbide-nanowire/carbon-microfiber hybrid structures have been fabricated using a cotton T-shirt as both the template and carbon source. The boron carbide nanowires exhibit a high elastic modulus of 428.1 GPa and elastic recovery after multiple high-strain bending cycles without brittle failure or obvious residual deformation for the strain up to 45%. The boron carbide-nanowire/carbon-microfiber hybrid structures can block 99.8% UV irradiation and achieve a superior reinforcing effect in their epoxy composites. The boron-nanowire formation mechanisms and corresponding synthesis techniques presented here can be extended to other carbide nanowires such as SiC, TiC, MoC, and WC by introducing suitable carbide-sources and catalysts.

4:40 PM

(ICACC-S7-019-2011) Nanodiamond-Polyaniline Nanocomposite: The Chemio-Physico Investigation and Application of New Frontier Films

H. Gomez*, M. K. Ram, A. Kumar, University of South Florida, USA

Nanocomposites of nanodiamonds particles with conductive polymers (i.e. polyaniline) displayed novel properties resulting from the molecular level interaction of diamond with polyaniline molecules. The choice of nanodiamond and polyaniline (PANI) was motivated by a wide range of technological applications of both components, i.e. transparent electrodes for photovoltaic, quantum information processing, magnetotometry, novel imaging, IR-fluorescence applications and electroluminescent devices. The ND-PANI nanocomposite films were characterized by UV-Vis, FTIR, electrochemistry, impedance, Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM) and electrical conductivity techniques. Current–voltage characteristics of nanodiamond-PANI nanocomposite show the ohmic junction. The electrochemical investigation on ND-PANI revealed the wider potential values with independent redox characteristics of polyaniline and nanodiamond. We have observed positive temperature coefficient (PTC) characteristics behavior on ND-PANI film. The ND-PANI films were also investigated for corrosion protection of mild and stainless steel, aluminum, copper, and in NaCl, H2SO4, HCl solutions.

5:00 PM

(ICACC-S7-020-2011) Unusual Crystallization Behavior of Biodegradable Polylactide in Presence of Functionalized Carbon Nanotubes

J. Ramontja*, S. Pillai, S. Sinha Ray, Council for Scientific and Industrial Research, South Africa; A. S. Luyt, University of Free State, Quaqua Campus, South Africa

The unusual crystallization behavior of biodegradable polylactide (PLA)/ functionalized carbon nanotubes (f-CNTs) composite will be presented. PLA/f-CNTs composite was prepared through solvent casting method using chloroform as a solvent. The crystallization behaviors of neat PLA and f-CNTs containing PLA composites were studied using differential scanning calorimeter, polarized optical microscope, and X-ray scattering. Results show that the nucleating role of f-CNTs for PLA melt-crystallization is very inactive. Such an observation is quite uncommon to the general understanding of the role of CNTs in polymer matrix melt-crystallization.

S8: 5th International Symposium on Advanced Processing and Manufacturing Technologies for Structural and Multifunctional Materials and Systems (APMT) in honor of Professor Katsutoshi Komeya

Novel Forming and Sintering II

Room: Coquina Salon B

Session Chairs: Morgana Fall, Ceralink Inc; Do Kyung Kim, KAIST

1:40 PM

(ICACC-S8-023-2011) Rapid limestone calcination using Microwave Assist Technology

M. Fall*, S. M. Allan, H. S. Shulman, Ceralink Inc, USA

Microwave Assist Technology (MAT) is being applied to the calcination of limestone for use in the cement, steel and glass industries. This presentation will include studies of microwave materials interactions through dielectric property measurements, process modeling, and lab scale microwave hybrid calcination tests. Microwave Assist Technology is a method to simultaneously apply traditional radiant heat and microwave energy in the same kiln, leading to fast volumetric product heating. Microwave thermal activation targets and directly heats limestone, eliminating the reliance on thermal conduction as a means of energy transfer. In addition less energy is wasted in heating non-product, such as the atmosphere and kiln lining. This technology has the potential to increase the speed of lime production by decreasing both the reaction time and temperature, further reducing energy consumption. Full scale implementation of microwave hybrid calcining of limestone is expected to save 46 trillion BTU/yr in the lime industry and 200 trillion BTU/yr in the cement industry.

2:00 PM

(ICACC-S8-024-2011) Pressureless microwave sintering of aluminum nitride

H. S. Shulman*, S. Allan, N. Vandervoort, M. L. Fall, M. Elmer, Ceralink Inc., USA

Microwave sintering is being explored as a low cost, alternative to hot isostatic pressing for thermal management materials. Pressureless microwave heating was used to sinter yttria-doped aluminum nitride (AlN) to full density in a fast process. Aluminum nitride doped with in-situ carbon nanotubes was also sintered. An ultrahigh temperature, microwave transparent thermal package was developed to reach temperatures above 1800 °C, needed to sinter AlN and other ultra-high temperature ceramics. In addition, a novel ultrahigh temperature microwave susceptor composition was used. Dielectric properties as a function of temperature were measured for AlN. The results and analysis of microwave sintered AlN compacts will be presented, including density, hardness, microstructure, dielectric properties, and thermal conductivity.

2:20 PM

(ICACC-S8-025-2011) Microwave Processing of Nanostructured Multilayer Ceramic Capacitors

B. Vaidhyanathan*, A. Ketharam, V. Venkatachalam, J. Binner, Loughborough University, United Kingdom

Interest in the fabrication of nanostructured ceramic devices has seen exponential growth in recent years owing to the requirements

of miniaturization, multifunctionality and improved reliability. The major hurdle in realising the full potential of nano ceramics is preventing the unwanted grain growth whilst achieving high densification during conventional high temperature processing. Microwave heating is fundamentally different from the conventional radiant heating techniques in that the energy can be deposited volumetrically throughout the material. Properly utilized, this can lead to greater micro/nanostructural control, improved products and reduction in manufacturing costs. Also electronic industries tend to move towards non-Pb based electronic materials such as barium titanate (BT) for device applications. Here a detailed study was performed on the microwave assisted synthesis of BT based formulations at the nano scale. >60 wt% nano BT suspensions were prepared and screen printed and the resultant capacitor devices were sintered using microwave, conventional and hybrid heating. Microwave power was identified as a new tool for controlling phase evolution during nano BT processing under identical thermodynamic conditions of T, P and time. With judicial selection of additives, X7R BT multilayer capacitors were fabricated and their electrical performance evaluated against commercial capacitor components.

2:40 PM

(ICACC-S8-026-2011) Microwave sintering of AlN ceramics with TiC/Al_2O_3 as susceptor material

Z. Zhang*, Shanghai Institute of Ceramics, CAS, China

AlN ceramics are difficult to sinter in a 2.45GHz microwave furnace, because these materials do not couple well with the microwave at low temperature. Possible solutions include pre-heating the sample with a resistance furnace or using hybrid heating mode with a resistance heater or susceptor material in the microwave furnace. However, when using SiC as susceptor in nitrogen atmosphere, the samples and the furnace are easily contaminated by carbon or silicon that formed in the nitridation of SiC. In this work, TiC/Al_2O_3 was used as susceptor material in the sintering of AlN ceramics. At high temperature, TiC was partly nitrided to Ti-N-C and Al_2O_3 reacted with the carbon to give Al-O-N phases. With this method, AlN was sintered to high density with excellent thermal conductivity without any contamination from the susceptor material.

3:20 PM

(ICACC-S8-027-2011) A Comparative Study on Microwave and Conventional Sintering Characteristics of Alumina and Alumina Matrix Nanocomposites

B. Kayiplar*, A. F. Dericioglu, Middle East Technical University, Turkey

In this work, monolithic alumina (Al2O3) and alumina matrix nanocomposites (Al2O3/SiCp and Al2O3/ZrO2p) fabricated by both microwave and conventional sintering techniques which have the potential of providing high temperature stability, strength and toughness, have been studied. Density, hardness and indentation fracture toughness measurements along with microstructural characterization using SEM were performed on monolithic Al2O3 as well as SiC and ZrO2 particle-dispersed alumina matrix nanocomposites obtained via microwave and conventional sintering techniques under identical process conditions. Microwave sintering was determined to be a remarkably effective method in the production of Al2O3 ceramics at considerably low temperatures (≤1400°C) compared to conventional sintering in achieving enhanced relative densities reaching to ~97% with improved microstructural characteristics and mechanical properties. Furthermore, in the case of SiC particle-dispersed nanocomposites fracture toughness improved considerably caused by the crack deflection at the dispersed particles and grain boundaries reaching to ~4 MPa.m1/2. Results have demonstrated that relative to conventional sintering, microwave sintering is more effective in the processing of alumina and alumina matrix nanocomposites.

3:40 PM

(ICACC-S8-028-2011) Shock Compaction and Characterization of Nanocrystalline Materials via Planar Shock Wave

H. Kim, KAIST, Republic of Korea; S. Chang, ADD, Republic of Korea; D. Kim*, KAIST, Republic of Korea

Nanocrystalline materials have been widely focused for the interesting subject of research for a few of decades, and their understanding has been advanced significantly in the last few years. The shock wave compaction (SWC) of powers using high pressure shock-waves generated by planar impact of explosives in considered to be a potentially important method for the synthesis and processing of bulk nanocrystalline materials. In this study, nanocrystalline bulk materials of Gd-doped ceria (GDC) and CNT/Cu composite were fabricated by planar shock wave compaction technique. Through the measurement of the electrical conductivity of shock recovered GDC was successfully obtained in spite of about 20 % porosity in the GDC compact and it confirmed that the SWC process has enough potential to fabricate the nanocrystalline bulk ceramics. And CNT/Cu mixture powder was synthesized and the crystallite sized is about 40~80 nm. TEM analysis of SWC-CNT/Cu revealed retention of nano-sized Cu grains (50~100 nm), and the presence of shear bands and homogeneous dispersion of CNTs in the Cu matrix. These findings explain the significantly enhanced hardness observed. A Vickers hardness and nanoindentation test for SWC-CNT/Cu indicated enhanced microhardness of 1190 and 1794 MPa, respectively, proving the efficiency of the SWC technique.

4:00 PM

(ICACC-S8-029-2011) Large, Near Net-Shaped Components by Field Assisted Sintering

C. Haines*, US Army ARDEC, USA; J. Singh, Penn State University, USA; D. Martin, US Army ARDEC, USA; B. DeForce, Penn State University, USA; D. Kapoor, US Army ARDEC, USA

Significant research has been done in the sintering of various materials by field-assisted sintering technology (FAST) also known as spark plasma sintering (SPS) over the past few years. A high percentage of this research has been done in understanding of the process and establishing structure properties relationships using small specimens (< 2 inches) with a simple cylindrical geometry. Limited research has been done in fabrication of larger sizes and more complex geometries that are required to promote FAST/SPS as a viable manufacturing technology. This paper will highlight the technical challenges faced when scaling up as well as abandoning simple geometries. We will report not only on the fabrication of larger specimens (6" diameter), but also on near-net-shape (NNS) components for a wide range of applications. We will also discuss the ability to fabricate multi-component, composites, and functionally graded materials with this technology with superior properties.

4:20 PM

(ICACC-S8-030-2011) Sintering and Forming Ceramics with Large Dimensions Using SPS

D. Jiang*, A. K. Mukherjee, University of California, USA

The ability of using SPS to sinter large-sized ceramics was evaluated. The major concern was non-uniformity of temperature on the specimen. Simulation of temperature distribution on the graphite die assembly reveals how the geometry can largely influence on temperature distribution, which is helpful for appropriate die design. The experiments on a transparent ceramic showed that the optical property can be fairly homogeneous along the diameter of a 75mm diameter disk, indicating the temperature distribution is uniform. Not only the large-sized flat disks can be sintered successfully by SPS, but also dome-shaped specimens with a diameter of 75mm was sintered by SPS with success. These promising results would encourage SPS users to make larger parts even with complicated shapes that may have important commercial applications.

4:40 PM

(ICACC-S8-031-2011) Influence of the pulse pattern on the spark plasma sintering of Si3N4 ceramics

M. Belmonte*, P. Miranzo, I. Osendi, Institute of Ceramics and Glass (CSIC), Spain

Despite the spark plasma sintering (SPS) technique, which is based on a pulsed electric current activated sintering process, is a powerful research tool for developing new materials, the complete understanding of the phenomena that take place during the sintering process is still one step behind. In order to gain some insight into SPS, we studied the effect of pulse voltage on the liquid phase sintering (LPS) process of silicon nitride (Si3N4) materials varying the sintering additives content and the pulse pattern of the SPS tests. Si3N4 compositions containing different amounts of sintering additives (from 1.7 to 4.9vol.% of Al2O3-Y2O3 mixture) were selected. SPS experiments were performed at 1600ºC for 5min, a heating rate of 133ºC.min-1 and 50MPa of uniaxial pressure. The pulse pattern was varied from 12:2 (12 pulses on, 2 pulses off) to 2:8. Shrinkage curves, microstructure evolution and α/β ratio were evaluated for all the materials. Compared to conventional techniques, SPS showed a marked enhancement of the particle rearrangement stage of the LPS process, especially at low additives content. Besides, a direct relation between the decrease in the rearrangement temperature and the pulse voltage was experimentally observed. Both phenomena were explained by the improved wetting of the grain boundary liquid phase, associated to electromechanical forces acting at the liquid-solid interface.

5:00 PM

(ICACC-S8-032-2011) Densification Mechanisms of Yttria-Stabilized Zirconia Based Amorphous Powders by Electric Current Assisted Sintering Process

T. Kumagai*, K. Hongo, National Defense Academy, Japan

Rapid densification behaviors (relative density; $\rho \leq 0.92$) of 3 mol% yttria-stabilized zirconia (3YSZ) and 3YSZ based powders by electric current assisted sintering process have been investigated. Although the starting 3YSZ powder was amorphous, the crystallization of tetragonal zirconia solid solution was completed before the appearance of rapid densification, indicating the impracticability of densification by amorphous viscous flow. The n (stress exponent) values estimated by a hot-pressing kinetic equation increase with decreasing effective external stress (i.e., increasing ρ), but n recalculated by taking into consideration the threshold stress (σ_0) show almost the constant value of 2. These recalculated values are quite similar to those of creep deformation with an accompanying σ_0 in the intermediate-stress region, suggesting that the rapid densification behavior is controlled by grain boundary sliding. The addition of boron changed the densification behavior drastically. The estimated n values without considering σ_0 show the similar values of 1.2 to 1.4, suggesting that the boron-rich glassy phase coexisting with the tetragonal (monoclinic at room-temperature) zirconia solid solution may relieve the stress concentration generated by grain boundary sliding.

S9: Porous Ceramics: Novel Developments and Applications

Structure and Properties of Porous Ceramics III

Room: Coquina Salon H
Session Chair: Thomas Watkins, ORNL

1:30 PM

(ICACC-S9-024-2011) Elastic Property Comparison of Porous Cellular Ceramics Using Multiple Test Methods (Invited)

R. Stafford*, Cummins Inc, USA; T. Watkins, A. Shyam, Oak Ridge National Laboratory, USA; P. Gloeckner, Cummins Inc, USA

The elastic properties of extruded porous ceramic materials are a critical input for reliablity modeling of honeycomb cellular structures used for exhaust aftertreatment devices. The measured elastic properties of porous ceramics from mechanical and resonance test methods will be compared. The elastic property measurements were performed on specimens fabricated from a single wall and also on multiple cell structures of cordierite and silicon carbide porous ceramic materials. The differences in the measured values of elastic properties from various test methods will be explained based on the geometry and elastic anisotropy of the test specimens.

2:00 PM

(ICACC-S9-025-2011) Properties and Thermal Shock Resistance of Fine Porous Alumina for Support Substrates of Ceramic Membranes

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

The thermal shock resistance and properties of alumina porous structures, the support substrates for permselective microporous ceramic membranes were studied. To study the influence of porosity on the thermal shock resistance systematically, porous alumina with different porosities were fabricated, and the thermal shock resistance samples were estimated by infrared radiation heating method. The mechanical and thermal properties related to the thermal shock resistance were also measured and the influence of porosity on the properties was carefully examined. The fracture strength and Young's modulus values remained steady in the measured temperature range, but decreased with increase in porosity of the samples. The fracture toughness, and thermal conductivity were also decreased with increase in porosity. Thermal shock resistance of porous alumina was estimated quantitively by the experimental thermal shock strength. The thermal shock parameters of porous alumina were decreased with increase in porosity owing to the decrease of fracture strength and thermal conductivity. The experimental thermal shock strength showed good agreement with that calculated from the material properties in this study. It is shown that, the thermal shock strength of porous alumina samples at service temperature could be estimated.

2:20 PM

(ICACC-S9-026-2011) Functionalized Fly Ash: A Recyclable Sorbent for Oil Spill Clean-up and Energy Recovery

D. Reid*, B. Ellis, L. Hench, S. Seal, University of Central Florida, USA

In 2007, 131 million tons of coal combustion products, mostly fly ash, were produced in the United States. Nearly 75 million tons were disposed of in landfills. Fly ash consists of spherical ceramic particles several microns in diameter. Due to its low specific surface area and hydrophilic alumino-silicate composition, fly ash has poor oil sorption capacity. A two-step process has been developed to transform this material into an effective oil sorbent. First, a reaction in an alkali solution increases the specific surface area by an order of magnitude, forming highly porous particles with nanoscale surface features. A second reaction functionalizes the particle surface with a hydrophobic monolayer. The product is a porous powder with a significant oil sorption capacity, well-suited for clean-up of spills such as the recent disaster in the Gulf of Mexico. Oil-saturated fly ash can be recycled into the combustion process of coal-fired power plants, thereby recovering the energy value of the oil. In this way, the use of functionalized fly ash as an oil sorbent is environmentally friendly and economically beneficial.

2:40 PM

(ICACC-S9-027-2011) Microstructural Study on Alumina Porous Ceramic Produced by Reaction Bonding of Aluminium Powder Mixed with Corn Starch

J. Anggono*, I. S. Shavitri, Petra Christian University, Indonesia

Addition of corn starch to the Al powders in a reaction bonding process has resulted in alumina porous ceramics. The corn starch

added was meant to create porosities during heating therefore they act as channels for oxygen to access the inner part of the samples for oxidation. The number of corn starch added to the Al powder was varied from 10%, 20%, and 30% wt. The green bodies of pellet samples with diameter of 20mm and 4 mm height were heated at various temperature of 1000oC, 1200oC, and 1400oC with a heating rate of 1.5C/minute in air. Microstructural study was performed using scanning electron microscope (SEM) and supported by phase identification using XRD and EDAX. XRD and EDAX have identified the presence of alpha-Al2O3, Fe, and Si which are impurities of Al powders. From SEM, it shows that the outer surface of all samples are denser than the inner part and identified as Al2O3. The thickness of this dense outer skin increases with an increase in heating temperature and the number of corn starch added.

Applications of Porous Ceramics

Room: Coquina Salon H
Session Chair: Thomas Watkins, ORNL

3:20 PM

(ICACC-S9-028-2011) Materials Science and Materials Chemistry for Large-Scale Electrochemical Energy Storage (Invited)

J. Liu*, Pacific Northwest National Laboratory, USA

This talk aims to discuss important cross-cutting, fundamental materials science and materials chemistry challenges that are applicable to a range of technologies encountered in electrochemical storage. This talk will attempt to highlight the critical materials problems using specific examples and results from recent efforts to reduce the cost and improve the performance of electrochemical energy storage devices. Specifically, this talk discusses 1) the characterization and understanding of the complex solution chemistry and redox reactions in concentrated, aggressive electrolyte solutions, 2) approaches to develop new battery designs and new chemistry combinations to reduce the cost, and 3) limitations and challenges of the electrode materials, nanoporous materials and ion selective membranes. In addition, the paper discusses the prospect of emergent technologies with ultralow costs on new energy storage materials and mechanisms.

3:50 PM

(ICACC-S9-029-2011) Use of Porous Ceramics to Enhance Water Cleanup using Nanomaterials

J. Schorr*, R. Helferich, S. Sengupta, R. Revur, MetaMateria Technologies, USA

Nano Technology has great promise as enablers for clean-up of waste water and purification of drinking water because of the high specific surface area of nanomaterials for selective removal; however, use of nanomaterials in commercial systems requires a suitable form. MetaMateria has developed a porous platform that is especially suitable for obtaining the enhanced performance available with nanomaterials. Testing has shown fast removal of contaminants (short contact times) allowing for more compact, lower cost water clean-up systems. This greatly enhances performance and can reduce the amount of active media needed to achieve a given level of performance. A lower cost, porous ceramic to carry the nanomaterials is used that allows high water flow at low pressures. Nano-enabled media has been shown to remove metal ions (e.g. As, Se, Fe, Mn), phosphate compounds, hydrogen sulfide, and even chlorinated contaminants (e.g. perchlorate). Nanostructured, thin films supported by the porous ceramic offers durable, high flow rate filters for the cleanup of contaminated water.

4:10 PM

(ICACC-S9-030-2011) High Porosity In Situ Catalyzed Carbon Honeycombs for Mercury Capture in Coal Fired Power Plants (Invited)

M. Ruffin*, M. Owusu, B. Y. Johnson, Corning, Incorporated, USA

Corning has developed a novel high porosity honeycomb sorbent that is effective at removing mercury from the flue gas of coal fired power plants. Highly porous activated carbons with pore size distributions in the micro – macro range are key for optimizing mercury adsorption potential. The use of pore formers in an extruded carbon honeycomb provides a technique that allows porosity to be tailored in a reproducible manner without removing active material as with chemical activation of carbon. We demonstrate that by adding a pore former to a synthetic resin or activated carbon powder we can develop materials that have a reproducible porosity that can be easily tailored to achieve between 10% and 40% porosity. Ten different pore formers were evaluated. Samples were extruded, dried, carbonized, and activated. They were then characterized based on weight loss, shrinkage, porosity and surface area. Ideal pore formers provided pore interconnectivity and overall porosity higher than 20% with minimal shrinkage. The porosity profile obtained via the use of pore formers was also compared to that using thermal processing alone to achieve high porosity. Comparable levels of overall porosity and pore distribution can be achieved via either technique without compromising mercury capture performance. A major advantage of pore formers is a 75% reduction in time required for chemical activation.

4:40 PM

(ICACC-S9-031-2011) Zirconia based ceramic honeycombs for the production of synthetic fuels by two-step thermochemical decomposition of CO_2 and H_2O at elevated temperatures

L. S. Walker*, University of Arizona, USA; J. E. Miller, N. P. Siegel, Sandia National Laboratories, USA; G. E. Hilmas, Missouri University of Science and Technology, USA; E. L. Corral, University of Arizona, USA

Two-step solar thermochemical decomposition of CO_2 and H_2O using zirconia based ceramic materials is quickly becoming a viable option for sustaining renewable fuel generation over the long-term. However, key obstacles preventing full-scale generation of synthetic fuel is limited to the production yield and efficiencies of ceramic substrate materials. Current substrate designs have moderately low surface area to volume ratios and limit the amount of exposed active material for reaction due to foam-based design. Therefore, our approach uses polymer co-extrusion of thermochemical active ceramics in order to fabricate dense honeycomb substrates with controlled open porosities and high surface areas of ~$10cm^2/g$. Preliminary CO generation results for 25-vol% Fe_2O_3/75-vol% YSZ composites that show the effect of surface area on reactivity will be discussed. In addition, the effect of increasing Y_2O_3 content from 3- to 8-mol% on the yield of CO production will be discussed. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000.

5:00 PM

(ICACC-S9-032-2011) Repair Segmental Bone Defects with Modified Tissue Engineering Method in Rabbit Radius

C. Lijia*, Key Laboratory of Transplant Engineering and Immunology, Ministry of Health,West China Hospital, Sichuan University, China

This study was performed to investigate whether recombinant human bone morphogenetic protein adenovirus (Ad.hBMP-2) gene and marrow cells were administered to hydroxyapatite/β-tricalcium phosphate (HA/β-TCP) ceramics could repair segmental defects quickly in rabbit radius, and saved lots of time of isolating and culturing seed cells. Ceramics were immersed in virus overnight, half an hour before surgery, autologous bone marrow aspirates were mixed with ceramics sufficiently. A 15mm radius was defected in the left limb of all animals. The critical-size defect was filled with: (1) Ad.hBMP-2 + HA/β-TCP + autologous marrow (group 1); (2) HA/β-TCP + Ad.hBMP-2 (group 2); (3) HA/β-TCP alone (group 3); (4) An empty defect as control (group 4). Histological and micro-CT analyses were performed on the specimens of week 2, 4, 8, 12 and 24. In group 1, four weeks after implantation, a small amount of new bone and cartilage tissues were found in the porous bioceramics, the images of micro-CT scanning

showed that materials integrated closely adjacent bone. Lots of new bone formation was observed at 12th week. In group 2 and 3, new bone and cartilage tissues were not seen until 8th week, however, it was significant less than that of group 1. In group 4, defects were not bridged after 12 week's repair. These results suggested that group 1 could repair segmental defects quicker than other groups.

S13: Advanced Ceramics and Composites for Nuclear Fusion Applications

Joining and Integration of Ceramic Structures

Room: Oceanview
Session Chair: Cristian Contescu

1:30 PM

(ICACC-S13-011-2011) Processing and characterization of SiC/SiC pin cladding for GFR

C. Sauder*, C. Lorrette, CEA, France; B. Humez, E. Rohmer, Laboratoire des Composites thermostructuraux, France

Owning to the recent progress in the fabrication of stoichiometric fibers with a good stability under neutron irradiation, SiC/SiC composites are candidate for nuclear applications as structural material for fuel containment in Gas Fast Reactor (GFR). At the beginning two concepts of fuel element were suggested by the French Altern. Energies and Atomic Energy Commission: (i) a plate concept and (ii) a pin concept. Preliminary studies led the CEA to focus on the pin concept which seems to be more adapted to ceramic/composites and processing (respect of geometrical tolerance). In this work, it is proposed to study different fibre structure boarding like filament winding and 2D or 3D braiding. Results on 3D braiding structure composites processing will be presented. Mechanical tensile behaviour of composites with different 3D braiding structure will be also investigated. At last, microstructure analyses will be performed and features of the stress-strain behaviour will be discussed with respect to fibre structure boarding.

1:50 PM

(ICACC-S13-012-2011) Joining of NITE SiC/SiC Composite and Metals for Nuclear Applications

H. Kishimoto*, T. Abe, T. Ono, Muroran Institute of Technology, Japan; T. Shibayama, Hokkaido University, Japan; Y. Kohno, A. Kohyama, Muroran Institute of Technology, Japan

Silicon carbide (SiC) is an expectant candidate of the structural material for the next generation fission and fusion reactors. A large issue of SiC/SiC composite for the applications is developments of joining techniques with metals. Nano-Infiltration and Transient Eutectoid (NITE) SiC/SiC composite is a best potential candidate for the Nuclear applications, the joining of dissimilar materials with NITE SiC/SiC composite need be developed. There are many situations where need the joining in the nuclear application. For the first wall of blanket and the armor on the divertor in fusion reactor, tungsten (W) is a candidate metal for the joining. Stainless steels and Reduced Activation Ferritic/Martensitic (RAFMs) steels will be the other candidates to join with NITE SiC/SiC composites. Because W with NITE SiC/SiC composites will be used at high temperature near or over 1000 °C, the diffusion bonding is appropriate for this joining. A large advantage of the W and SiC joining is their very closed coefficients of thermal expansion (CTE). Steels with SiC will be used in both room and elevated temperature, thus both mechanical and metallurgical techniques should be considered. In present research, seeking and developments of the joining techniques of dissimilar materials for nuclear system are introduced.

2:10 PM

(ICACC-S13-013-2011) Joining of SiC/SiC for nuclear applications

M. Ferraris*, V. Casalegno, S. Han, S. Rizzo, M. Salvo, A. Ventrella, Politecnico di Torino, Italy

Joining of silicon carbide based composites for nuclear applications can be of interest both for future thermo-nuclear fusion reactors and for new generation fission reactors components. In both cases, the main issues are the extreme thermo-mechanical loads on the joined components, the not completely known service conditions and requirements, their resistance to high temperatures, to neutron irradiation and to harsh chemical environment. Some joining techniques and joining materials for SiC/SiC will be described: results obtained by using non silica based glass ceramics, Ti-Si-C based ceramics and titanium as joining materials will be discussed. Results concerning the use of some pressure-less joining techniques will be shown: slurry and sintering, microwave assisted combustion synthesis and induction heating. The mechanical characterization of the joints will be discussed in terms of several torsion tests, in particular on joined miniaturized hour-glass shaped specimens, designed to fit irradiation capsules. Preliminary results from an international collaborative research on joining and mechanical test on joined SiC/SiC will be discussed.

2:30 PM

(ICACC-S13-014-2011) Assembly Technique for SiC/SiC Composite Compact Intermediate Heat Exchanger Utilizing SiC Slurry Sheet

T. Hinoki*, Y. Park, S. Konishi, Kyoto University, Japan

Silicon carbide (SiC) can be used in extremely harsh environments due to its excellent mechanical properties and chemical stability even at high temperature. Very dense SiC/SiC composites are available. Hermetic joining technique is required to have low tritium permeability and high temperature strength compact intermediate heat exchanger (IHX). The objective is to develop assembly technique for SiC/SiC composite IHX including hermetic joining technique utilizing the SiC slurry sheet. The slurry sheet consists of SiC powder and sintering additives. The slurry sheets were cut to fit to joint region. The SiC/SiC composites were machined to plates, frames and pins. The parts were assembled for IHX using the slurry sheets as joint inserts. The plates were grooved slightly for alignment of pin position and to prevent slurry from being forced out to channel. The assembled parts including the slurry sheets were hot-pressed. Uniform joint layer thickness is important to prevent stress concentration in particular for ceramic joint. The IHX scale model with 10 cm square was fabricated successfully utilizing the slurry sheet with uniform thickness. Present study is the result of "Development on Compact Intermediate Heat Exchanger Using Advanced Composite Material" entrusted to "Kyoto University" by the Ministry of Education, Culture, Sports, Science and Technology of Japan (MEXT).

2:50 PM

(ICACC-S13-015-2011) Joining of Thin SiC/SiC Composites by Local Heating

J. Elodie*, L. Maillé, Y. Le Petitcorps, E. Martin, LCTS, France; C. Lorrette, C. Sauder, CEA, France

The Gas Fast Reactor is a high temperature reactor cooled by helium. The excepted temperatures in operation are in the range of 1000°C but short time incursions at 1600 or 2000°C have to be anticipated. The use of a SiCf/SiCm composite as a tube containing the combustible is evaluated. One of the key issues is the joining of these composites to seal the tube. The present work describes the results for joining SiC substrates in solid state by reactive and non reactive compounds. As joining material, we have chosen two titanium silicides : TiSi2 (non reactive with SiC) and Ti5Si3 (reactive). The assembly was prepared by Spark Plasma Sintering. Cross section of the assembly was prepared to study the interface composition, the cracking and the crack deflection in the vicinity of the interface. Thermal treatments

have been also carried out at solid state. As expected for TiSi2 the bonding is too weak while for Ti5Si3 the joining is not stable in temperature. Solutions will be proposed to overcome these drawbacks. The advantage of local heating is the possibility to heat at high temperature (around 1800°C) for short time without damaging the composite structure. We focused on two main techniques : (1) a CO2 laser source and (2) micro-waves heating. The quality of the bonding will be evaluated by chemical and physical analyses (SEM, EDS, XRD).

Crystalline, Amorphous and Composite Materials for Waste Immobilization

Room: Oceanview
Session Chair: Kevin Fox, Savannah River National Lab

3:30 PM

(ICACC-S13-016-2011) Technology Development to Reduce Mission Life and Glass Volumes for US High Level Waste Vitrification Facilities (Invited)

D. Peeler*, SRNL, USA

Resolution of the nation's High Level Waste (HLW) legacy requires the design, construction and operation of large and technically complex, one-of-a-kind processing facilities coupled to equally complex waste treatment and vitrification facilities. Vitrification technology was chosen to treat HLW at Hanford and Savannah River sites, low-activity waste at Hanford site, and may potentially be applied to other defense waste streams such as INL tank waste or calcine. Joule-heated melters are being used at the Defense Waste Processing Facility (DWPF) and will be used at the Hanford Tank Waste Treatment and Immobilization Plant (WTP) to vitrify tank waste fractions. The loading of waste into glass and the glass production rates at WTP and DWPF are limited by either the current melter technology or process control models which link glass compositions to various properties. Significant reductions in glass volumes for disposal and mission life are only possible with refinement of current property models (or development of new models) and advancements in melter technology and glass formulations. This presentation will discuss the development of advanced silicate glasses, next generation melter technology and formulations, potential advantages of iron phosphate glasses, and model development efforts being performed under the DOE EM-31 Technology Development program.

4:00 PM

(ICACC-S13-017-2011) Layered Double Hydroxides for Anion Capture and Storage

J. Phillips*, L. J. Vandeperre, Imperial College London, United Kingdom

The technetium isotope, Tc-99, is a long lived radionuclide with a half life of $2.1x10^5$ years, produced with a yield of ~6% during nuclear fission which exists in solution as the pertechnetate anion, TcO_4^-. The pertechnetate anion does not bond well to soils and is highly mobile in groundwater as such it is highly desirable to capture and immobilise the TcO_4^- anion for long term storage. An integrated solution is proposed for the capture and disposal of this anion using layered double hydroxides (LDHs) as the capture medium. To this end, LDHs with the general formula $Ca_{(1-x)}(Al_{(1-y)},Fe_{(y)})_x(OH)_2\ xNO_3 . nH_2O$ were produced via a co-precipitation method from nitrate salts. This composition was chosen as it is suitable for thermal conversion to Brownmillerite, $Ca_2(Al,Fe)_2O_5$, a phase found in cements. LDHs with the composition $Ca_{0.67}(Al_{(0.5)},Fe_{(0.5)})_{0.33}(OH)_2\ 0.33NO_3.nH_2O$ were produced and exposed to solutions containing either single or pairs of anions (NO_3^-,Cl^-,CO_3^{2-} and ReO_4^- as a surrogate for TcO_4^-). It was found that exchange occurred in each case and the preference for intercalation was $Cl \approx CO_3 > NO_3 > ReO_4$. LDHs containing Ca, Al, and Fe are therefore suitable phases for the capture of anions, the composition of the LDH can be tailored for thermal conversion to ceramic phases.

4:20 PM

(ICACC-S13-018-2011) Functionalized Silica Aerogels: Advanced Materials to Capture and Immobilize Radioactive Iodine

J. Matyas*, G. E. Fryxell, K. Wallace, B. J. Busche, L. S. Fifield, PNNL, USA

The effective capture and safe storage of radiological iodine-129 remains one of the many concerns for the future expansion of nuclear energy. Various materials have been investigated but none of them can be effective for capturing iodine, and then sintered/densified to create a stable composite that could be a viable waste form. This presentation will address the development of chemically modified highly porous silica aerogels, which showed sorption capacities higher than 200 mg of iodine per gram at 150°C. The iodine uptake test in dry air containing 4.2 ppm of iodine demonstrated no breakthrough of the sorbent after 3.5 h and indicated decontamination factor in excess of 310. Preliminary tests showed the iodine-loaded aerogels retained more than 92 wt% of iodine after thermal sintering at 1200°C for 30 min. The capture efficiencies for iodine as well as iodine retention can be further improved with optimization of functionalization process and chemistry, and sintering conditions.

4:40 PM

(ICACC-S13-019-2011) Bottom-up design of a cement for nuclear waste encapsulation

L. J. Vandeperre, T. Zhang*, C. Cheeseman, Imperial College London, United Kingdom

The chemical interactions between waste and the cement, in which it is encapsulated, are dominated by the chemistry of the pore water in the cement. Hence tailoring the interaction between waste and cement requires designing the chemistry of the cement matrix. In this paper, the bottom up design of a new cement compatible with aluminium metal will be discussed. The starting point was the realization that hydration of magnesia to form brucite should yield a pH around 10 and that this is a favourable pH for aluminium passivation, certainly when compared with the much more alkaline environment induced by Portland cement. A range of fillers were studied and metakaolin and fused silica found to be compatible with the desired pH. Further work with fused silica showed that the brucite reacts with the fused silica to give magnesium-silicate-hydrate (M-S-H) gel. Contrary to expectation, strength measurements indicate that this phase gives rise to high strengths. Further work has encompassed additive selection for improved rheology, mortar design for dimensional stability and pH buffering, and encapsulation trials with aluminium. The results show that highly fluid cement with normal dimensional stability can be formulated, the pH can be controlled to remain close to 10 even in the presence of additives and aluminium metal in contact with this new cement shows no evidence of corrosion.

5:00 PM

(ICACC-S13-020-2011) Irradiation Damage Effects in Glass Ceramics for Advanced Waste Form Development

M. Tang*, A. Kossoy-Simakov, M. Zhou, J. Valdez, G. Jarvinen, K. Sickafus, Los Alamos National Laboratory, USA; J. Crum, L. Turo, Pacific Northwest National Laboratory, USA; K. Fox, A. Billings, K. Brinkman, J. Marra, Savannah River National Laboratory, USA

The safe and effective disposal and/or reuse and recycling of nuclear wastes has become a crucial issue in our increasingly globalized society. An important component of Fuel Cycle Research and Development program in the United States Department of Energy involves the development of advanced nuclear waste. In this presentation, we report on a project to develop glass ceramic and/or crystalline ceramic waste forms for fission products obtained from spent nuclear fuel, and concentrate on radiation stability on these materials. For this project, glass ceramics are fabricated using a borosilicate glass as matrix in which to incorporate fission products such as Cs/Sr, lanthanides and transition metal elements, and crystalline ceramics are fabricated using Al2O3 and TiO2 as matrix in

which to incorporate fission products. Transmission electron microscopy, Scanning electron microscopy, and X-ray diffraction are used to characterize the resultant microstructural characteristics (including crystallite size, composition, structure, and distribution) with processing procedures. We will also discuss results of electron, proton, and alpha irradiation experiments, which we are using to test the stability and durability of these glass ceramic and/or crystalline ceramic waste forms.

S14: Advanced Materials and Technologies for Rechargeable Batteries

Materials Design, Screening, and Electrode Architectures for Lithium-ion Batteries

Room: Coquina Salon F
Session Chairs: Veronica Barone, Central Michigan University; Mike Badding, Corning Incorporated

1:30 PM

(ICACC-S14-018-2011) Design of (thio)phosphates for high performance lithium ion batteries (Invited)

S. Adams*, R. Prasada Rao, National University of Singapore, Singapore

Strategies to enhance the power performance of safe low cost lithium ion battery (LIB) cathodes are explored by Molecular Dynamics simulations using a novel bond-valence based force field and ab-initio simulations, covering besides doping, tailoring the degree of disorder and interface engineering in cathode:electrolyte nanocomposites. The 1D Li^+ conductor $LiFePO_4$ is compared to tavorite-type "high voltage" cathodes $LiVPO_4F$ and $LiFeSO_4F$ that besides low-energy ion migration channels exhibit moderate energy thresholds for migration in perpendicular directions mitigating channel blocking. The interplay of blocking by $Fe_{Li}^{\cdot}$ and cross-linking pathways by $Li_{Fe}^{/}$ or $Na_{Fe}^{/}$ has a complex influence on the value and anisotropy of Li^+ mobility. Li^+ conductivity in Li_xFePO_4:$Li_4P_2O_7$ nanocomposites is discussed as a model for performance enhancement by interface engineering. To improve safety and stability, all-solid-state Li-ion batteries (ASS-LIBs) are attractive power sources for 'smart' cards etc. Designing fast ion conducting solids compatible with other battery components is key to the performance of ASS-LIBs. We investigate pure and halide doped thiophosphates incl. argyrodite-type Li_6PS_5X(X = Cl, Br) and $Li_7P_3S_{11}$ prepared via glass-ceramic processes. Li^+ mobility in Li_6PS_5Br nearly reaches values for liquid electrolytes. The performance of LIBs combining these cathode and electrolyte materials will be discussed.

2:00 PM

(ICACC-S14-019-2011) Finding Room for Improvement in Transition Metal Oxides Cathodes for Lithium-ion Batteries

K. C. Kam*, M. M. Doeff, Lawrence Berkeley National Laboratory, USA

Energy storage using rechargeable lithium-ion batteries has become an integral part of our modern lifestyle. They have been used or are being considered for use in a wide range of applications from portable electronics to vehicular applications. Since the commercialization of $LiCoO_2$, other layered transition metal oxide variants (*e.g.* NMC and NCA) have drawn major interest from battery companies. However, it is important to address performance and safety aspects and minimize the cobalt content in the material for reasons of cost and toxicity. These issues are particularly important for large-scale applications. Some of our work focuses on reducing the amount of cobalt in NMCs through metal substitution, without compromising their electrochemical properties. Recent findings show an improvement in capacity in certain circumstances. We present here some results and challenges toward improving these mixed layered transition metal oxides.

2:20 PM

(ICACC-S14-020-2011) Lithium batteries for EV: the challenges faced by electrolytes

J. Sanchez*, F. Alloin, C. Iojoiu, L. Cointeaux, J. Leprêtre, Grenoble INP, France; F. Toulgoat, UCBL, France; E. Paillard, Grenoble INP, France; R. Arvai, B. Langlois, UCBL, France; P. Judeinstein, Orsay, France; N. El Kissi, Grenoble INP, France

The innovative researches in solid state chemistry make available a variety of materials usable in positive or in negatives. While a high stability of electrolytes in reduction is required for batteries based on Li metal or Li graphite, the high voltage positives require electrolytes highly stable in oxidation. Now if one wants to associate, durably negative close to Li0 to high voltage positives it's like trying to square the circle. The bottleneck deals necessary with the electrolyte that must both exhibit a wide stability window and high conductivities. In addition to the search of new solvents and salts a special attention is currently paid to additives able to form stable electrolyte interfaces. EV and PHEV batteries will lay emphasis both on safety aspects and on eco-conception, in order to recycle and preferably to reuse most of the costly organic chemicals used in the electrolyte and electrodes. In the frame of this contribution we will present the issues related to the different concepts of batteries and some paths to overcome the bottlenecks.

2:40 PM

(ICACC-S14-021-2011) Autogenic Reactions for the Fabrication of Lithium Battery Electrode Materials

V. Pol*, M. Thackeray, Argonne National Lab, USA

Autogenic reactions, based on the decomposition of chemical precursors at elevated temperatures under self generated pressures are being used to prepare a wide range of materials with interesting structural, morphological and technological properties. The technique is highly versatile; it can produce core-shell carbon coated metal oxides, carbon-based materials, and various olivines, all of which are of interest as electrodes for lithium-ion battery applications. One interesting example is that spherical carbon particles can be prepared by the thermal decomposition of mesitylene (C9H12) or even plastic waste in an enclosed, but ventable, autoclave reactor under nitrogen at 700 °C. The as-obtained solid carbon spheres (2 – 5 μm diameters) are characterized as turbostratically disordered graphite sheets, the ordering of which can be increased by heating the spheres to 2400 °C under inert conditions. The initial electrochemical reaction of lithium with heated carbon spheres (2400 °C) occurs predominantly below 1 V, typical of a hard carbon electrode, generating a capacity of 275 mAh/g. The irreversible capacity loss on the first cycle (20%) is significantly less than that observed in unheated samples, typically 60 %. On cycling at 25 mA/g (~C/1 rate) between 1.5 V and 5 mV, the capacity of the carbon electrode increases steadily, reaching more than 250 mAh/g with >99% cycling efficiency.

3:20 PM

(ICACC-S14-022-2011) Lithium ion Conductive Solid Electrolyte with Porous / Dense Bi-layer Structure for All Solid State Battery (Invited)

K. Kanamura*, Tokyo Metropolitan University, Japan

All solid state rechargeable lithium ion battery has been prepared by using various kind of solid electrolyte, such as Li0.35La0.55TiO3 (LLT). The pellet or thin film of solid electrolyte has been applied to all solid state battery. However, an electrochemical interface between active material and solid electrolyte is small in such 2 dimensional configuration. In order to solve this problem, three dimensionally ordered macroporous (3DOM) solid electrolyte has been utilized to construct all solid state battery. The electrode system consisting of 3DOM solid electrolyte and embedded active material exhibits high discharge capacity at relatively high current. In order to construct the all solid state battery, a dense solid electrolyte layer is necessary to separate cathode

and anode. In this study, bi-layer type solid electrolyte with 3DOM and dense layers was prepared by using membrane filtration process of nano-size LLT particles and mono-disperse polystyrene beads for 3DOM layer and only nano-size LLT particles for dense layer. After the filtration, the obtained membrane was heated at 450 °C and then 1100 °C for 1 hour and 10 hours, respectively. By using the prepared bi-layer type solid electrolyte, all solid state battery with LiMn2O4 cathode and Li metal anode was constructed and tested.

3:50 PM

(ICACC-S14-023-2011) Multi-Scale Description of the Electronic Transport in a Composite Electrode for Lithium Battery

J. Badot*, CNRS - Chimie ParisTech, France; K. Seid, CNRS, France; O. Dubrunfaut, CNRS - UPMC - Paris Sud, France; S. Levasseur, UMICORE, Belgium; D. Guyomard, B. Lestriez, CNRS, France

The improvement of battery performance requires the rationale optimization of the composite electrode. The development of "new tools", i.e. experimental techniques as well as methodologies, is needed to understand the so-called composition-architecture-properties and performance relationships. The broadband dielectric spectroscopy (BDS) technique is applied for the first time to a composite materials used as an electrode for lithium battery. The electrical properties (permittivity, resistivity and conductivity) are measured from low frequencies (a few Hz) to microwaves (a few GHz). Model samples prepared from different LiFePO4 varying in particle size (from 50nm to 1μm) and carbon coating content (from 0 to 4wt%) are studied. The results demonstrate that the broadband dielectric spectroscopy technique is very sensitive to the different scales of the electrode architecture involved in the electronic transport, from interatomic distances to macroscopic sizes, as well as to the morphology at these scales, coarse or fine distribution of the constituents. This work opens up new prospects for a more fundamental understanding as well as a more rational optimization of the electronic transport in composite electrodes for lithium batteries as well as other battery technologies and conductor-insulator composite materials.

4:10 PM

(ICACC-S14-024-2011) Lithium Accumulator - Fully Inorganic Prototype Based on Three-Dimensional Electrodes

J. Prochazka*, L. Kavan, M. Zukalova, M. Bousa, B. Laskova, JHI, Czech Republic; J. Postler, HE3DA, s.r.o., Czech Republic; K. Neufuss, IPP, Czech Republic

New path to the higher lithium battery capacity is to increase the electrode thickness. To provide the accumulator with maximal safety, only inorganic materials are used for the construction (ceramics and metals). Before they are filled up with an electrolyte the organics-free cells can withstand temperatures over 400°C without any damage. The 3-D inorganic concept will be demonstrated on practical examples.

4:30 PM

(ICACC-S14-025-2011) Optimization of PVDF content and molecular weight for LiNi1/3Mn1/3Co1/3O2 composite cathodes

J. Li*, B. Armstrong, J. Higgins, C. Daniel, D. Wood, Oak Ridge National Laboratory, USA

A binder is one essential component in the processing of a composite cathode. It provides strength to the composite structure and ensures the adhesive strength between cathode and Al foil current collector while providing the appropriate rheological properties necessary for a variety of coating processes. The amount and type of binder also has significant effect on the electrochemical performance of composite cathodes, such as conductivity and cycle life. In conventional lithium-ion batteries, poly(vinylidene fluoride)(PVDF) is used as a binder due to its electrochemical stability over a large potential window. The use of PVDF in composite cathodes is ubiquitous in the literature. However, the effect of PVDF on composite cathode long-term performance and irreversible capacity loss is still poorly understood. In this study, the rheological properties of LiNi1/3Mn1/3Co1/3O2(NMC) slurries and the electrochemical performance of NMC composite cathodes are investigated. The effect of PVDF structure (molecular weight) and concentration on viscosity will be measured using a controlled shear stress rheometer. In addition, electrical conductivity, morphology and long-term performance of the NMC cathode will be measured by impedance spectroscopy, SEM and load cycling, respectively. The structure–property relationship of the PVDF critical concent and the cathode performance will be discussed.

4:50 PM

(ICACC-S14-026-2011) In-situ stress determination in LiCoO2 and LiCoO2 - MWCNT during electrochemical cycling

A. Mukhopadhyay*, J. Lahache, A. Tokranov, B. Sheldon, Brown University, USA

A major factor limiting capacity retention of Li-ion batteries is mechanical failure via cracking/disintegration of the active electrode materials and concomitant loss in electronic contact with the current collectors due to stresses generated during Li-ion intercalation/de-intercalation. To investigate the fundamental mechanisms and design solutions to such problem, our work focuses on in-situ quantitative determination of the stress developed in thin film electrode materials during galvanostatic charging/discharging cycles against Li metal in an electrochemical cell, using multibeam optical stress sensor (MOSS). Thin films of the most widely used cathode material (LiCoO2) has been grown on quartz substrate, with Au inter-layer acting as current collector, via sol-gel, spin coating technique. To explore the effects of multi-walled carbon nanotube (MWCNT) reinforcements on the stress development and cyclic stability, thin films of LiCoO2 containing MWCNTs have also been developed. It is believed that not only MWCNT can prevent fracture and disintegration of the cathode materials upon electrochemical cycling, but would also help to maintain electrical contact with the current collector upon disintegration of the cathode material. The differences in cyclic stability and stress response of monolithic LiCoO2 and LiCoO2 - MWCNT nanocomposites would be critically analyzed.

Poster Session A

Room: Ocean Center

(ICACC-PACRIM-P001-2011) Control of Microstructure and Thermal Conductivity of Large-sized, Hot-pressed AlN

S. M. Na, S. I. Kim, S. I. Ko, YJC Co., Ltd., Korea, Democratic People's Republic of; S. J. Lee*, Mokpo National University, Korea, Democratic People's Republic of

We have successfully fabricated 300 mm-diameter aluminum nitride (AlN) which shows a high thermal conductivity (≥ 200 W/mK) and a high strength (≥ 620 MPa) as well as a homogeneous, dense microstructure. In the trend of large-scaled silicon wafer, AlN electrostatic chuck and heater are also scaling-up and the fabrication processing is developing for satisfying demand quantity. In this study, the fabrication processing for a large-sized, hot-pressed AlN is examined with the control of the microstructure and the thermal conductivity. In the study of processing factors, the content of sintering aid, yttria, significantly affected the thermal conductivity more than the effects of sintering temperature and annealing time. All samples showed ≥ 98% relative density after hot-pressing at 1850 °C. In particular, the thermal conductivity and sintered strength were notably increased after addition of 3 wt% yttria, and about 15% increase of thermal conductivity was obtained through a 5 h annealing process. Inhomogeneous YAG phase was observed in the grain boundary of the hot-pressed AlN added 3 wt% yttria, and the YAG phase was distributed homogeneously with thin layer after the annealing process. In control of microstructure of the hot-pressed AlN, along with key properties, such as thermal conductivity, sintered density, strength and color will be presented. In addition, the processing variations will also be discussed to control the properties of the large-sized AlN. A fabrication of 450 mm-diameter AlN will be tried soon for future work.

(ICACC-PACRIM-P002-2011) SiOC Fiber of Fine Diameter Prepared by New Curing Process

D. G. Shin*, K. Y. Cho, Korea Institute of Ceramic Engineering and Technology, Republic of Korea; J. S. Hong, H. R. Lim, Y. R. Cho, M. S. Kang, D. H. Riu, Seoul National University of Technology, Republic of Korea

Ceramic fibers with diameters in the range of 10 to 20 μm have been developed as reinforcements. Their applications includes the gas turbines, heat exchangers, a first blanket walls for nuclear fusion reactors as well as candle filters for high temperature gas filtration. When the SiC fiber is used as reinforcement, it should have a high weavability and other related characteristics in order to make performs. SiC fibers with smaller diameter are now being issued in industries, but technologies can't come up to reduce lower than 10μm because it is very difficult to control the spinnability and curing mechanism of polycarbosilane, the precursor polymers. The weight average molecular weight (Mw) of polycarbosilane is around 1500-4000, which makes a spinning of the precursor fiber possible, and the smaller the Mw the better spinnability it is. However, precursor fibers having Mw lower than 2000 (means low melting point) are difficult to stabilize in air at around 200°C to produce cross-linking bondage due to its low melting temperature although it can make smaller diameter of precursor fiber easily. In this study, we report the fabrication of a small diameter of SiOC fiber derived from the spinning of low Mw PCS and a new curing process which can stabilize the low Mw precursor fibers at room temperature.

(ICACC-S1-P004-2011) Stress effect on the microstructure and vibrational properties of LaCoO3 based perovskites

Y. Chen, J. Dinan*, N. Orlovskaya, University of Central Florida, USA

LaCoO3 based perovskites are important electrochemically active materials used for cathodes in solid oxide fuel cells, oxygen separation membranes and catalysts. In a lot of these applications, the situations can arise when the material undergoes significant stress deformation. Therefore, it is important to study the effect of the stress on the microstructure and vibrational response of the LaCoO3 perovskites. In the current work, TEM is employed to study the defects, such as twins, stacking faults, dislocations, and grain boundaries, in the grains of LaCoO3. The LaCoO3 samples, which were mechanically tested over the significant period of time under the constant stress, were used to prepare thin foils. Then the microstructure of the as sintered and stressed samples was analyzed using TEM. At the same time, the vibrational response of as sintered and stressed samples was analyzed using micro-Raman spectroscopy. In addition, the LaCoO3 samples were loaded in 3 point bending in a specially designed in-situ bending device coupled with the Raman microscope, and then the changes in Raman spectra were studied under the stress as a function of time. We will report the results of our studies in the proposed poster.

(ICACC-S1-P005-2011) Processing of Continuous Al2O3 Nano-fibers

Y. Kagawa*, T. Saito, K. Matumura, R. T. Doloksaribu, The University of Tokyo, Japan; H. Kakisawa, Y. Tanaka, National Institute for Materials Science, Japan

Ceramic "nano-fibers" have been expected to use as a reinforcement of polymers, metals, and ceramics because they have large interface area between the fibers and matrix: expected to improve mechanical performances of composites. However, ceramic nano-fibers, which have nano-meter order diameter, are difficult to obtain and the fabrication process needs to be developed. Deposition of Al2O3 layer on carbon fiber surface is carried out using atomic layer deposition process (ALD). After deposition of Al2O3 layer, substrate carbon fiber is oxidized to obtain freestanding nano-Al2O3 fiber. During oxidation process of the fiber, deposited Al2O3 layer splits and sintered to form continuous freestanding nano-Al2O3 fibers. Using this two-stage process, fiber diameter smaller than 10nm is possible to fabricate and the diameter of the nano-fiber could be controlled by the thickness of deposited layer on a surface of fiber and oxidation process, i.e., heating rate and temperature etc. Discussions will be made on key parameters to obtain tailored continuous nano-Al2O3 fiber.

(ICACC-S1-P006-2011) X-Ray Transmission Characteristics of B4C Sintered Samples for High Hardness Windows Applications

C. A. Costa*, UFRJ, Brazil; V. M. Domingues, UFRJ, Brazil; A. F. Barbosa, CBPF, Brazil; J. B. de Campos, UERJ, Brazil; P. S. Cosentino, Army Evaluation Center, Brazil

X-ray window is a device which must have two simultaneous functions, namely, i) act as a barrier between the vacuum (or inert gas) environment inside an x-ray source tube and the external atmospheric conditions, ii) allow the x-rays to pass through it. Beryllium has widely been used for this kind of application, since it is a light material - nonetheless, it is toxic and cancerigenous. Boron carbide (B4C) is composed of boron and carbon, which are the next light elements in the periodic table, and posses a very good mechanical strength. So, the use of B4C to substitute beryllium and carbon is potentially interesting for a base material for x-ray transmission windows. The present study investigated the use of B4C to substitute Be and C in X-ray transmission window applications. B4C was produced by pressureless sinter and the density was 99%. X-ray transmission experiments were performed using a home-made apparatus, which includes a 55Fe x-ray source and a bidimensional gas detector. The B4C, Be and C samples were exposed to radiation during 15, 30 and 60 minutes. Two dimensional transmission images were acquired for each sample and the results showed that B4C was comparable to Be and C materials, indicating a possible application for windows x-ray transmission.

(ICACC-S1-P007-2011) In situ, high temperature, synchrotron studies of monoclinic to tetragonal phase transformation in HfO2 and Ta2O5 – doped HfO2 system

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

The transformations of hafnia (HfO_2) are described analogous to the transformations in zirconia (ZrO_2) because of the similar crystal structures, although the phase transformations in hafnia occur at higher temperatures. In this study, the monoclinic to tetragonal transformation in HfO2 (~1800°C, compared to 950°C in ZrO_2) was studied in situ, in air, by high temperature X-ray diffraction using synchrotron radiation. In the past, high temperature studies have been conducted in an inert atmosphere which results in structural modifications caused by the formation of oxygen vacancies. In order to utilize the material in air it must be studied in a similar atmosphere. A quadrupole lamp furnace (QLF) was used, in conjunction with three state of the art X-ray detectors, to study HfO2 in situ at the transformation temperature in air. Results will be presented to show the complex thermal expansion as it relates to the crystal structure of monoclinic HfO_2, the hysteresis of the transformation and the high temperature structure as studied for the first time in air. The effect on the transformation temperature of doping with penta-valent Ta5+ will be ascertained in the HfO_2 - Ta_2O_5 binary system. The use of reflection geometry diffraction on highly absorbing samples, as well as pair distribution function analysis will be discussed.

(ICACC-S1-P008-2011) CTEAS - Program to Determine Thermal Expansion Properties of Materials from High Temperature X-ray Diffraction

R. Haggerty*, P. Sarin, Z. A. Jones, W. M. Kriven, University of Illinois Urbana-Champaign, USA

It is very common to describe the thermal expansion (TE) of a material by calculating the expansion of the lattice parameters of a crystal. For many systems this method is satisfactory and describes the anisotropies in expansion that the crystal exhibits, but for systems of low symmetry (i.e. monoclinic or triclinic symmetry crystals) the TE can be much more involved than the expansion of the lattice parameters can describe. The Coefficient of Thermal Expansion Analysis

Suite (CTEAS) program provides a simple method to visualize and understand the 3-D TE in low symmetry and high symmetry crystals in the same easy way. It also provides a simple interface for converting structural x-ray analysis into TE that can be related back to the crystal structure of the material. The program calculates a best fit TE in a generic rank two tensor form that relates to the symmetry of the crystal, while taking into account the temperature dependence of the TE. Besides producing figures and movies that can describe TE qualitatively and quantitatively, the program is capable of describing the TE along any single crystallographic plane so that it can be easily related to the crystal structure and chemistry of the material. In summary, CTEAS makes TE of the most complex crystals easy to study and understand, thus making it an excellent tool for research as well as for teaching.

(ICACC-S1-P009-2011) How Do You Measure That Ceramic Property?

J. Salem, NASA GRC, USA; J. Helfinstine*, Retired, USA; G. Quinn, NIST, USA; S. Gonczy, Gateway Materials Technology, Inc., USA

To help answer questions of "how do I properly measure property X of that 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. 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-P010-2011) Synthesis and characterization of Ta-doped lead free Bi0.5(Na0.5K0.5)0.5TiO3 piezoelectric ceramics

K. Kumar*, B. Kumar, crystal lab, India

Lead free sodium bismuth titanate, Na0.5Bi0.5TiO3 (NBT) based ceramic is one of the promising candidate having good dielectric and ferroelectric properties. It shows a high Curie temperature (Tc ~ 320 oC), remnant polarization (Pr ~ 38 μC/cm2) and conductivity. On the other side, Potassium bismuth titanate, K0.5Bi0.5TiO3 (KBT) is a ferroelectric material with a higher Curie temperature (Tc~380 oC). So, a binary system of KBT and NBT were expected to posse good dielectric and ferroelectric properties. BNKT is one of those material having very high Tc and reasonably good piezoelectric properties as compared to other lead free piezoelectric materials. Pure and Ta (0.2, 0.4, 0.6,0.8 &1 %) doped BNKT ceramics were synthesized by solid state reaction technique. Crystalline structures of the compound at the room temperature were studied by X-ray diffraction (XRD) technique in which shown a pure perovskite phase was confirmed. The dielectric studies in wide temperature range (20 – 550 0C) showed an increase in the depolarization temperature (Td) and transition temperature (Tc) with doping concentration in BNKT ceramic. The remnant polarization (Pr) value was found to increase with increasing Ta content in BNKT ceramic. The other characterizations like piezoelectric charge coefficient (d33), Hysteresis loop, SEM etc have been analyzed and discussed in detail.

(ICACC-S1-P011-2011) Local Damage Detection in SiC/SiC Composites by Thermal Imaging Technique

S. Sadohara*, Y. Kagawa, The University of Tokyo, Japan

A woven fabric SiC fiber/SiC matrix composite has heterogeneous microstructure, and therefore, local damage caused under service is highly dependent of microstructure. To understand this micro damage, local damage evolution process in woven fabric SiC fiber/SiC matrix composites has been monitored using thermal imaging method. Local damage was introduced by spherical indentation or Vickers indentation under various conditions; static, impact etc. Damage models are developed based on the damage caused by the indentations observed both macro- and microscopically and the damage is quantitatively analyzed by damage parameter. The composite with damages are illuminated by IR light source and thermal imaging, which corresponds thermal conductivity change, is monitored as a function of time. The change of thermal image is correlated with the local damage parameter and this parameter seems useful for local damage prediction. Potential of thermal imaging method is compared with that of ultrasonic C-scan and electromagnetic wave methods. Discussions will be made on the potential of thermal imaging technique to determine local damage in the composite.

(ICACC-S1-P012-2011) Damage Characterization in SiC/SiC Composites using Electrical Resistance

C. Smith*, Ohio Aerospace Institute, USA

Ceramic matrix composites (CMCs) envisioned for high-temperature structural applications require reliable structural health monitoring techniques to prevent catastrophic failure. The lifetime of these materials is limited mainly by the formation of transverse, in-plane matrix cracks that expose the fiber/matrix interface to environmental degradation and also result in increased load on surrounding fibers. Many conventional techniques, such as ultrasound and x-ray, have limited capability to detect such damage. Electrical resistance has already been shown to correlate with material degradation in SiC/SiC CMCs. Since there are many mechanisms occurring that contribute to the overall electrical resistance, it is necessary to quantify the effect of matrix crack formation, crack depth, and oxidation. Tensile testing results will be presented for both monotonic and creep loading in air and vacuum, coupled with in-situ resistance monitoring.

(ICACC-S1-P013-2011) Synthesis of Ceramic Materials and Compositions with Soft Mechano-Chemical Assistance

R. Yu*, The Chinese Ceramic Society, China

This paper reviews recent developments on synthesis of various ceramic materials and compositions (such as oxide, biomaterial, electronic and electric intermetallics, microwave dielectric composite, battery compounds and sialon compositions) with soft mechano-chemical assistance. Further studies in this aspect are also proposed.

(ICACC-S1-P014-2011) Glass Composites Containing Carbon Nanotubes: Processing, Characterisation and Prospects for Toughening

T. Subhani*, J. Cho, Imperial College London, United Kingdom; F. Inam, M. J. Reece, Queen Mary University of London, United Kingdom; W. E. Lee, Imperial College London, United Kingdom; A. R. Boccaccini, University of Erlangen-Nuremberg, Germany; M. S. Shaffer, Imperial College London, United Kingdom

Due to their remarkable electrical, thermal and mechanical properties, carbon nanotubes are potentially attractive reinforcement in a variety of composite materials. The effect of diameter and aspect ratio of CNTs on the mechanical properties of brittle systems, particularly glass is a research area to be explored. Dense silica glass matrix composites reinforced with multi-walled carbon nanotubes (MWCNTs) were produced by colloidal processing by heterocoagulation to exhibit the true effect of CNTs as reinforcing filler in brittle matrices. By controlling the surface chemistry, the quality of the diphasic suspension was maintained during mixing, ensuring electrostatically-driven coating of silica nanoparticles onto the MWCNTs. Both pressureless and spark plasma sintering were performed for densification of the composites to theoretical density whilst minimising devitrification of the silica glass matrix material. As-produced composites with MWCNTs of different diameter / aspect ratio and loadings upto 15 wt.% were characterised microscopically and mechanically. In addition to SEM, XRD, hardness and fracture toughness, the composites

were also characterized for thermal and electrical conductivities. The possible toughening mechanisms associated with CNT pull-out, CNT bridging, and crack deflection were investigated.

(ICACC-S1-P015-2011) FEM and Experimental Studies on the Optimization of Fiber Volume Ratio in SiC Fiber Reinforced SiC Ceramics under Hertzian Stress

T. Kim*, J. Park, I. Kim, K. Lee, Kook-Min Universiity, Republic of Korea

FEM analysis and experimental studies on the effect of soft coating layer on SiC fibers under indentation contact stresses are studied. Boron nitride (BN) and Pyrocarbon (PyC) materials are selected as coating materials for SiC fiber. Especially, this study attempts to find the optimum fiber volume ratio in SiC fiber reinforced SiC ceramics under Hertzian stress. Various SiC matrix/coating/fiber /coating/matrix structures are modeled, and analysis is performed by changing a type of soft coating layer. The stress changes for composites with coating in the contact axis or radial direction are analyzed. The same structures are fabricated by hot process, experimentally, and the mechanical behaviors of load-displacement are evaluated using Hertzian indentation method. The results show that the behaviors of experimental results are the same with FEM results. Additionally, FEM analysis on thermal stress due to differences in thermal conductivity or coefficient of thermal expansion conducted on the same modeling structure will be included in this presentation. Ultimately, the optimized fiber volume ratio in SiC fiber reinforced SiC ceramics will be discussed.

(ICACC-S1-P016-2011) Evaluation of mechanical property in polycrystalline translucent ceramics

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Microstructure and mechanical property of translucent Al2O3-based ceramics have been investigated. Several kinds of polycrystalline spinel were fabricated by various sintering temperature, and single crystal spinel and sapphire were used for comparison. Bending strength was measured at room temperature and high temperature (1273K). Fracture toughness and Vickers hardness were measured by indentation fracture (IF) method at room temperature. Microstructure characterization was performed using scanning electron microscopy (SEM), and the mean grain size of the each specimen was evaluated by measuring the sizes of approximately 100 grains. Bending strength at high temperature tended to be lower than that of room temperature. The grain size dependence of Vickers hardness and fracture toughness was not clearly observed, but bending strength of spinel decreased with increasing grain size, and reached the minimum when the grain sized was 20 μm, and over 20μm, the value became constant. At the presentation, the effect of the microstructures developed by various sintering conditions on the mechanical properties of the spinel will be discussed from a viewpoint to develop novel translucent Al2O3-based ceramics.

(ICACC-S1-P017-2011) Effect of Reactive Heat Treatment on Properties of Al-Mg-B4C Composites

M. K. Aghajanian*, A. L. McCormick, M. Waggoner, M Cubed Technologies, USA

Metal matrix composites consisting of boron carbide (B4C) particles in an Al alloy matrix have been well studied due to their utility in various structural and nuclear (neutron absorbing) applications. In addition, prior work exists where such composites have been reactively heat treated to yield lightweight and hard ceramic-like materials consisting of Al-B-C ternary phases. The present work aims to expand on this prior work and examine the quantnary Al-Mg-B-C system. The advantages of this system are reduced density due to the presence of Mg, and the ability to form the ultra-hard AlMgB14 phase under the correct processing conditions. Composites will be made by infiltrating preforms of B4C particulates with molten Al-Mg alloy. Key variables will be Al:Mg ratio of the alloy and residence time at temperature (i.e., reaction time) after infiltration. The aim is to demonstrate the fabrication of lightweight composites that range in behavior from metal-like (low reaction time) to ceramic-like (high reaction time). Microstructures, mechanical properties and phase composition will be presented.

(ICACC-S1-P018-2011) Pressureless Sintering of Boron Carbide Using Amorphous Boron and SiC As Additives

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Boron carbide (B4C) is a structural ceramic material with a relative small world-wide production. Process B4C and to obtain high density is a difficult task, since the nature of the covalent bonds leads to very low diffusion rate. Consequently, high temperatures, atmosphere control and proper sintering additives must be used. Sintering additives reported in the literature are AlF3, Be2C, TiC, TiB2, W2B5, SIC, Al, Mg, Ni, Fe, Cu, Si and C; and C has been considered the most effective among all of them. The present study evaluated the processing of B4C with addition amorphous boron (Bam) and SiC, which might have been added as nanoparticles. The B4C and Bam where high energy milled with SiC spheres during 15, 30 and 60 minutes, and SiC were added to the composition, possibly as nanoparticles. The materials were pressed and sintered at 2150 C for 30 minutes. The results showed that the density was higher than 95% for all milling times and the elastic modulus measured was 276, 333, 365 and 420 GPa as the milling time varied from zero, 15, 30 and 60 minutes, respectively. This data shows a very promising route to obtain a dense material with high elastic modulus.

(ICACC-S1-P019-2011) Optical and Mechanical Properties of Rare Earth Oxides Doped Polycrystalline Silicon Nitride Ceramics

B. Joshi*, S. W. Lee, Sun Moon University, Republic of Korea

Transparent ceramics are used in new technology because of their best mechanical properties over glasses. Transparent ceramics are now days widely used in armor, laser windows and in high temperature applications. Silicon nitride ceramics have excellent mechanical properties and if transparent silicon nitride is fabricated, it can be widely used in many fields. Y2O3, Er2O3, La2O3, Dy2O3 and Nd2O3 doped polycrystalline silicon nitride were prepared and their optical transmittance were investigated in visible and in infrared region. Translucent silicon nitride ceramics were obtained. Mechanical properties and microstructure were also investigated. Grain growth in silicon nitride was reduced with addition of Y2O3 and Nd2O3. Glassy phase of silicon nitride was reduced with doped rare earth oxides. (0.1-1) wt.% of each rare earth metal oxides were sintered with 3 wt.% MgO, 9wt.% AlN and 87 wt.% of α-Si3N4. Adding these rare earth oxides shows good mechanical properties as high hardness, fracture toughness and strength.

(ICACC-S1-P020-2011) Determination of Apparent Porosity Level of Refractory Concrete Using Ultrasonic Pulse Velocity Technique and Image Analysis

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Concrete which undergoes thermal treatment before and during its life-service can be applied in plants operating at high temperature and as thermal insulation. Progression of sintering process can be monitored by the change of the porosity parameters determined with nondestructive test method - ultrasonic pulse velocity and computer program for image analysis. Experiment has been performed on the samples of corundum and bauxite concrete composites. Apparent porosity of samples thermal treated at 110, 800, 1000, 1300 and 1500 C was primary investigated with standard laboratory procedure. Sintering parameters were calculated from the creep testing. Loss of strength and material degradation occurred in concrete when it was subjected to increased temperature and compressive load. Mechanical properties indicate and

monitor changes within microstructure. Level of surface deterioration after thermal treatment was determined using Image Pro Plus program. Mechanical strength was determined using ultrasonic pulse velocity testing. Nondestructive ultrasonic measurement was used as qualitative description of changing porosity in specimens. Ultrasonic pulse velocity technique and image analysis proved to be reliable methods for monitoring of micro-structural change during thermal treatment and service life of refractory concrete.

(ICACC-S1-P021-2011) Effect of Reaction Time on Composition and Properties of SiC-Diamond Ceramic Composites

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Composites of reaction bonded silicon carbide (RBSC) and diamond have huge potential because of the high hardness, high thermal conductivity and high stiffness they exhibit. There is a strong drive to increase the quantity of diamond powder incorporated, thereby improving the properties of these composites. The addition of up to 20% diamond to the RBSC composites poses technical challenges that must balance higher final properties with increasing processing difficulties. The thermal stability of diamonds is such that high processing and/or longer reaction times can degrade their properties. X-ray diffraction of diamond powders has shown an increasing transformation to graphite during elevated processing temperatures. Analytical techniques (ICP-AES) have also shown decreasing silicon content with increasing reaction temperatures in SiC-Diamond composites. The current study relates isothermal reaction time to microstructure and properties of the SiC-Diamond composites. These physical properties are directly related to the final composition (e.g. remaining diamond and silicon content) of the composite. The effect of initial carbon content on the microstructure and residual silicon content is also discussed.

(ICACC-S1-P022-2011) Mechanical and Microstructure Characterization of Reaction Bonded Silicon Carbide Processed With Petroleum Coke

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Reaction bonded silicon carbide (RBSiC) shows some advantages over conventional sintering of silicon carbide, namely, the temperature and time of processing are significantly reduced. To achieve a successful material it is necessary to have a well adjusted combination of raw materials and processing parameters. For instance, to use of petroleum coke requires total degassing of this carbon source, which happens at 1900°C. The present study evaluates the mechanical properties and microstructure of a RBSiC obtained by processing SiC particles with average size of 0.51 μm and petroleum coke as carbon source. The green body was processed at 1450 and 1600°C, resulting in material with density of 2.8 g/cm<3>, average hardness 2415 HV and ultrasound elastic modulus of 265 GPa.

(ICACC-S1-P023-2011) Frequency and Hold-Time Effects On Durability of Melt-Infiltrated SiC/SiC

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With the growing interest in ceramic matrix composites for multiple applications, the response of the material to service conditions needs to understood. A range of durability testing was undertaken on Melt Infiltrated (MI) SiC/SiC Ceramic Matrix Composite. MI SiC/SiC was tested under 30 Hz fatigue, 1 Hz fatigue, dwell fatigue (2 hour hold cycle) and creep loading. The applied stresses ranged from microcracking point to well above the saturation stress of the material. Test temperatures included room, 815C and 1204C. The effects of fatigue loading frequency and dwell (hold) time on the durability of the composite will be presented.

(ICACC-S1-P024-2011) Durability Comparison of Two Ceramic Matrix Composites with a Sequenced Matrix

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Ceramic matrix composites (CMC) are being considered for aerospace turbine engine applications where durability at elevated temperature is critical and needs to be thoroughly understood. One unique class of CMC is fabricated with a sequenced layered matrix. The layers are structured such that various oxides and glasses form to fill matrix cracks providing protection of the interface coating and the fiber. The protection of the fiber interface coating is critical for the performance of the composite in long term applications. Two different ceramic matrix composite systems were studied in various durability tests. Testing consisted of creep testing, dwell fatigue testing, and 30 Hz fatigue testing at RT to 1315C. The two CMCs studied in this investigation had the same exact matrix, but one was manufactured with a SiC fiber while the other had a C fiber. This work presents the results of the testing for the two systems and compares the high temperature performance of the two CMC.

(ICACC-S1-P025-2011) Study of Cohesive Strength of Powders by Means of Rheology

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In many industries, powders are a vital step in the processing toward manufacturing the final product. A challenge arises in the ability to predict the transport properties of these powders. One such ceramic product would be cordierite catalytic converters, where the flowability of the powder precursors, alumina, talc, and hydrous clay, leads to breaking of aggregates. The particle sizes and distributions of the precursors are important to the characteristics of the produced cordierite. The solution is the development of a test to simulate the flow behavior of dry powders. Powder flowabilty is controlled by interparticle cohesion, which for dry, inert particles are the Van der Waals forces. Particle size, shape, and bulk density will all affect the flowabilty of the powder. To determine relative flowability, measurements such as find the Angle of Repose may be used to provide a bulk scale characterization, but flow behavior of powders depend upon different operations and the measurement may not be representative of the powder under the actual process. The use of a rheometer allows for the collection of viscoelastic data of the cohesive powders, as well as finding data at multiple axial load, better representing powders which may be compacted during the manufacturing process. From this data, cohesion is predicted by determining the shear strength powder.

(ICACC-S1-P026-2011) Property and Microsctructural Correlations to Wear on Reaction Bonded Materials

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Composites of silicon carbide (SiC) and silicon (Si); boron carbide (B4C) and Si; and SiC, diamond and Si are fabricated by the reactive infiltration of molten Si into preforms of said particles and carbon. Depending upon the application, these materials can be used in many situations due to their favorable properties including high hardness, low thermal expansion and high stiffness. Particularly, these materials display minimal wear owing to their high hardness and high stiffness. In this study, grit size, material, and material loading will be studied to garner an understanding of the effects on wear properties in these systems. The wear mechanisms will be determined through the use of SEM analysis.

(ICACC-S1-P075-2011) High Temperature Strength and Corrosion Resistance of Joints Used in Silicon Carbide Heat Exchangers

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Ceramic heat exchangers are increasingly important for use as high temperature recuperators or chemical synthesis modules where effi-

cient heat transfer is required. Common applications may include gas turbines, Solid Oxide Fuel Cells or synthesis gas generators. Heat exchangers require thermal gradients which drive heat between the flow streams. These thermal gradients create differential stresses and strains in joints where materials and thermal conditions can be discontinuous. In most cases, the joint material is characterized for strength at room temperature, yielding comparable data; however, as these joints are used at high temperatures, other factors influence the strength of the joint. Examples include possible reactions or corrosion of the joint with the fluids, thermal stresses, high temperature creep, or slow crack growth. These factors render the room temperature strength data incomplete for use in ceramic heat exchangers. This research discusses the room temperature and high temperature strength of various joining materials used for joining silicon carbide heat exchange devices and also the effects upon the strength after joint exposure to various corrosive environments.

(ICACC-S4-P027-2011) Ultrasonic Nondestructive Characterization of Oil-Based Clay

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Oil-based modeling clays are commonly used as a backing material for high strain-rate testing applications. After an initial test, the extent of which the clay properties may have changed has not been extensively studied. The change in properties after an initial test may affect the outcome of subsequent tests. This research utilizes ultrasonic nondestructive characterization techniques to examine the properties of a clay backing material before testing situations. Sample sets were fabricated to isolate the effect of different variables, including pressure, layering, and foreign material contamination. Controlling these variables leads to a better understanding of how each affects the acoustic properties of the clay. Ultrasound testing includes sonic velocity and frequency-based attenuation coefficient measurements. Specifics of the dominant acoustic loss mechanism in the frequency range of 10-30MHz is also investigated.

(ICACC-S4-P028-2011) Microstructure Property-Relationship for Ceramic Armor Materials

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A study was conducted to correlate the relationship of non-destructive evaluation with microstructural variability and defect distributions for a series of sintered SiC plates. Plates were divided into groups having similar acousto-elastic properties based upon the results of ultrasound C-scans. Selected tiles were machined into bend bars for modulus of rupture testing. Microstructural analysis and fractography have been carried out to determine the effect on strength of carbonaceous inclusions and other second-phase features. Characteristic acoustic spectra have been realized for different microstructural configurations.

(ICACC-S4-P029-2011) Examining Characteristics of Silicon Carbide through Various Powder Processing Techniques

R. Bianchini*, S. Mercurio, R. Haber, Rutgers University, USA

Silicon carbide powder is processed using coprecipitation and various milling techniques. These powders are, then, densified using the spark plasma sintering in order to determine the effectiveness of the powder creating methods. The sintering of the silicon carbide powders produce different resultant characteristics, such as microstructure, hardness, and densities, which are evaluated for each powder sample. The characterization helps determine the presence of defects in the silicon carbide samples.

(ICACC-S4-P030-2011) Boron carbide sintered with metallic carbides

P. A. Cosentino, Brazilian Army, Brazil; C. Costa, Federal University of Rio de Janeiro, Brazil; J. Brant*, State University of Rio de Janeiro, Brazil

Boron Carbide (B4C) is an important ceramic material, which has been used for structural and nuclear applications. However, its covalent nature and corresponding low diffusion mobility allied with high melting point (2427oC) make it one of most difficult material to sinter, namely, reach high density. The prevailing covalent character of the crystalline bonds of boron carbide determines its unique mechanical properties and low sinterability, which has been surrounded by the use of hot pressing, the most used method for obtaining high-dense boron carbide by the industry. Another approach to improve the final density is by powder activation, which can be performed by the combination of physical and chemical methods. An alternative approach for additives is based on carbides. They have been observed to improve the B4C sintering, but inducing reactions that lead to second phase precipitation, which might affect fracture toughness, strength and hardness. One critical step when carbides are used is to identify the new phases formed during sintering. The milling process introduced high quantity of ZrO2 nanoparticles from the milling balls. The present study evaluated the phases formed when B4C was fluxed with VC, Cr3C2 or carbon when hot pressed. Also it was used two kinds of powder: one as received and the other was submitted to high energy milling in order to produce submicron boron carbide (B4C) particles.

(ICACC-S4-P031-2011) Submicron Boron Carbide Synthesis Through Rapid Carbothermal Reduction

S. Miller*, W. Rafaniello, F. Toksoy, D. Maiorano, S. Mercurio, Rutgers University, USA; T. Jessen, Army Research Laboratory, USA; R. A. Haber, Rutgers University, USA

Highly pure submicron boron carbide powder has been synthesized by rapid carbothermal reduction. A specially designed furnace maintains the temperature of a boron oxide containing precursor below its melting temperature until just prior to entering the furnace hot zone at 1600-2000°C. The rapid heating of the precursor results in increased nucleation and the subsequent formation of small crystallites. The powder morphology is similar to those produced though vapor phase reactions.

(ICACC-S4-P032-2011) Development of Nano Alumina and Zirconia Toughened Alumina for Ceramic Armour Applications

S. Huang*, J. Binner, B. Vaidhyanathan, Loughborough University, United Kingdom; C. Hampson, Morgan Technical Ceramics Ltd, United Kingdom; C. Spacie, Morganite Electrical Carbon Ltd, United Kingdom; P. Brown, Defence Science and Technology Laboratory, United Kingdom

The brittle nature of ceramics can restrict their capability to resist multiple ballistic impacts. Alumina is widely used for ballistic protection and the present work focuses on investigating the effect on the properties of alumina arising from decreasing the grain size and also forming a zirconia toughened alumina (ZTA) nanocomposite via the addition of nano yttria stabilised zirconia (nanoYSZ). It is expected that a degree of plasticity could be achieved in dense ceramics with a very fine grain size, which could significantly improve the high strain rate performance and multihit capability. To date, dry and wet formed green bodies with densities above 55 wt% have been achieved with both ceramic systems via controlling the pH and solid content of the nano-suspensions. A two-stage hybrid microwave sintering method was used to achieve full density and a fine sub-micron grain size in the alumina and a nano grain size in the YSZ additions. The samples were subjected to a wide range of strain rate tests using split Hopkinson pressure bar, gas gun and ballistic tests. Variables, such as the grain size of the alumina matrix and YSZ, the yttria content in the YSZ and the YSZ fraction in ZTA, were found to affect the quasi-static and dynamic properties of alumina and ZTA, including hardness, fracture toughness, bending strength, dynamic toughness and high strain rate performance.

(ICACC-S4-P033-2011) Attempts to Quantify the Plasticity of Ceramic Materials

C. Hilton*, J. McCauley, J. J. Swab, U.S. Army Research Lab, USA

Studies have suggested that inelastic deformations play a very important role in the impact performance of ceramic materials. However, complete understanding of the deformation mechanisms and techniques for quantifying the "bulk plasticity" of these brittle materials

are extremely limited. Hardness testing has long been recognized as a useful method of investigating indentation response of engineering materials and some researchers have recently begun investigating its potential as a method to estimate the amount of plastic deformation that a material experiences during an impact/penetration event. Two approaches have been proposed to quantify the amount of plasticity in ceramic materials during a hardness test and relate this value to impact performance. A comparison of the results from these two approaches for SiC and AlON is presented and discussed.

(ICACC-S4-P034-2011) Strength Testing of Coarse-Grained Transparent Spinel

J. J. Swab*, G. Gilde, US Army Research Laboratory, USA; S. Kilczewski, Data Matrix Solutions, USA; R. Pavlacka, Oak Ridge Institute for Science and Education, USA

Spinel materials are being developed for a variety of applications including transparent armor, electromagnetic windows and as laser hosts. A property that is commonly measured for all of these applications is flexure strength. This is measured using prismatic beam specimens subjected to four-point flexure as outlined in ASTM C1161 and/or circular disks or square plates in equibiaxial flexure as outlined in ASTM C1499. In both instances the flexure specimens tested are usually only a few millimeters thick. However, the spinel materials being developed are typically comprised of grains hundreds of microns in size. Does the grain size to specimen thickness ratio influence the flexure strength measurements? This presentation examines the flexure strength of a spinel with an average grain size in excess of 350 microns applying flexure testing methods to specimens of different thicknesses.

(ICACC-S4-P035-2011) Modifying the Cracking Behavior of Silicon Carbide through Advanced Processing and Grain Boundary Engineering

S. R. Mercurio*, R. Bianchini, S. Miller, Rutgers University, USA; T. Jessen, U.S. Army Research Laboratory, USA; R. Haber, Rutgers University, USA

A coprecipitation process has been utilized in order to introduce sintering aids into silicon carbide samples. The improved mixing and fine, reactive sintering aids introduced in this way serve to reduce the presence of anomalous defects and modify the microstructure versus conventionally prepared silicon carbides. The versatile processing method also allows for control over the amount, structure, and properties of the grain boundary phase present. Further control of the sintering behavior through use of spark plasma sintering has been shown to also influence the crystallinity of the grain boundaries in silicon carbide, reduce the grain size, and allow for the use of even lower additive contents. Mechanical properties of the varied silicon carbides were investigated and related to changes in the grain boundary properties, and observations of different cracking behaviors were used to determine the importance of grain boundary characteristics in liquid phase sintered silicon carbides.

(ICACC-S4-P036-2011) Implications of Ceramic Fracture on the Transition from Dwell to Penetration

J. C. LaSalvia*, U.S. Army Research Laboratory, USA

Recently, a number of researchers have reported their observations on fundamental ballistic interactions between high-velocity projectiles and ceramic bodies. These experiments which have focused on projectile dwell and penetration, have provided insight into the fundamental mechanisms governing the ballistic and material response of thick ceramic bodies subjected to high-pressure, high-rate, transient loads. With respect to the transition from dwell to penetration, fracture can be a dominant mechanism. In particular, a number of observations have shown that the formation of cone cracks is an important process which can lead to the onset of penetration of an impacting projectile. An analytical model to aide exploring the implications of cone cracking on dwell and penetration onset has been developed based on assumed applied stresses, boundary-integral method for cone crack stress-intensity calculation, and dynamic fracture mechanics. Predictions for the velocity for penetration onset and dwell duration above this velocity are presented. Additionally, the effect of surface flaw statistics on the transition from complete dwell to penetration is also discussed.

(ICACC-S4-P037-2011) Impact Failure Mechanism Hierarchies in Armor Ceramics

B. G. Compton*, E. A. Gamble, F. W. Zok, UCSB, USA

This study probed dynamic and quasi-static stress states generated in an armor ceramic by high velocity impact with ductile spheres. Finite element simulations and analytical models enabled the relation of impact velocity, target geometry and material properties to specific ceramic failure mechanisms such as microcrack comminution, cone cracking, radial cracking and spall. From these models an impact failure mechanism map for ceramic materials is generated. Further, by accounting for the appropriate time scales required for each failure mechanism, hierarchies between mechanisms are established and the implications for armor material design and selection are discussed.

(ICACC-S4-P038-2011) Modeling ceramic compressive impact loading with a flaw-driven model

C. Zingale*, L. Graham-Brady, K. T. Ramesh, Johns Hopkins University, USA

A model for impact of brittle materials has been created for ceramics with circular flaws following the model of Paliwal and Ramesh (2008) for rectilinear flaws. This two-dimensional, flaw-driven, elastic model is used to predict material strength under constant strain rate loading. The models have previously been show to capture expected trends in material strength: increased strength with increase in loading rate, decreased strength with increasing flaw size, and decreased strength with increasing flaw density. Model results for circular and rectilinear flaws are compared. This comparison suggests that, when materials contain flaws on the order of 10 microns, rectilinear flaws may control material strength. However, in materials with large (100 micron) circular flaws, the model suggests that both flaw types need to be considered. Work integrating the two flaw types into a single model and work comparing the model to experimental data will also be discussed.

(ICACC-S4-P039-2011) Deformation damage in alumina after ballistic impact

S. Ghosh*, Loughborough University, United Kingdom; C. J. Dancer, R. I. Todd, University of Oxford, United Kingdom; H. Wu, Loughborough University, United Kingdom

Alumina is a popular structural ceramic which is used extensively for armour application. Alumina ceramics under high stress fail through intergranular fracture. Twinning is the primary defect identified in alpha alumina along with low dislocation density. However, deformation of alumina under very high strain rates is not completely understood. Ballistic tests carried out on alumina generate a large number of fragments which carry the signature of the defects that caused the failure of the material. In the present study, commercial alumina tiles (Sintox CL) were exposed to ballistic impact. Microstructural analysis of the fragments was carried out using FIB, SEM and TEM, and confocal Cr^{3+} fluorescence microscopy to measure residual stress and plastic deformation. Cr^{3+} fluorescence indicated a difference in the extent of plastic deformation for the impact site compared to both the edge of the damaged zone and the virgin material. TEM of specimens lifted out from fragments of different sizes revealed extensive ductile deformation underneath the surface. A high dislocation density was observed in these fragments indicating a possible mechanism change during high strain rate deformation.

(ICACC-S4-P040-2011) Intermediate-Rate Fracture Toughness of Ceramic Materials

D. Casem*, U.S. Army Research Lab, USA; C. Hilton, Oak Ridge Institute for Science and Education, USA; J. J. Swab, U.S. Army Research Lab, USA

We investigate techniques for performing intermediate-rate fracture toughness tests in a servo-hydraulic load frame using a variety of di-

agnostics and the test methodologies outlined in ASTM C1421. Of primary interest is the measurement of the bending stress local to the fracture initiation site and the assurance that initiation is not affected by inertia local to the site. If there is no inertial affect then a quasi-static analysis can be applied. The applied load is measured at each support point using quartz crystal force transducers installed directly beneath the rollers. This replaces the force measurement made by more traditional load cells. The specimen is also instrumented directly with semi-conductor strain gages, and specimen deflection is measured with a line-laser extensometer. The results of these diagnostics are used to infer when dynamic effects become large enough to lead to errors in the measured fracture toughness. The effect of specimen size on specimen equilibrium is also considered.

(ICACC-S4-P041-2011) Effect of Load on Surface and Sub-Surface Features Characteristic of Knoop Indents in Ceramics

E. R. Shanholtz*, J. C. LaSalvia, J. J. Swab, U.S. Army Research Laboratory, USA

Changes in surface and sub-surface features characteristic of Knoop indents in several commercial ceramics are explored in an effort to better understand the mechanisms governing the variation of hardness with load. Knoop indentation was conducted at various loads in a hot-pressed boron carbide (B4C), a gas-pressure sintered silicon aluminum oxynitride (SiAlON), and a hot-pressed silicon carbide (SiC) to characterize the effect of load on the hardness of each material. All materials exhibited a strong indentation size effect. The indents were characterized using optical and scanning electron microscopy to determine dominant inelastic deformation mechanisms on the surface and underneath the indents. Efforts were also made to quantify the variation of bulk inelasticity and fracture at the various loads. Experimental procedures and results will be presented.

(ICACC-S4-P042-2011) Further Observations on Solid-State Amorphization in Sphere-Impacted B4C and β-SiC

J. LaSalvia, S. Kilczewski*, U.S. Army Research Laboratory, USA

High-velocity hard-sphere impact damage sub-surface observations on polished cross-sections of a hot-pressed boron carbide (B4C) and a modified chemical vapor deposition (CVD) silicon carbide (SiC) were reported previously. In addition to severe multi-scale cracking and fragmentation typically observed in other ceramics, evidence for solid-state amorphization was observed in these ceramics. In this investigation, regions which displayed evidence for solid-state amorphization were examined in more detail using field-emission electron microscopy, energy-dispersive spectroscopy, micro-Raman spectroscopy, and nano-indentation. The purpose is to gain a better understanding of previous observations and shed light on possible governing mechanisms. Findings from these experimental techniques will be presented and discussed.

(ICACC-S4-P043-2011) Densification and Microstructural Properties of Boron-Carbide in Spark Plasma Sintering

M. Toksoy*, R. Haber, Rutgers University, USA

This study examines the densification of a series of commercial boron carbide powders by spark plasma sintering. The starting powders varied somewhat in particle size, particle size distribution and crystalline purity. Spark plasma sintering parameters – temperature, pressure and dwell time were varied. Results will relate hardness, elastic properties, density and grain size to the SPS process parameters. X-ray diffraction was performed to provide phase identification.

(ICACC-S4-P044-2011) The Effects of Temperature and Pressure Profiles on the Densification and Microstructural Properties of Transparent Magnesium Aluminate Spinel Fabricated by SPS Processing

M. Vu*, R. Haber, Rutgers University, USA

Mixtures of high-purity magnesium aluminate spinel fine powder and 1 wt % LiF as the sintering aid were sintered by means of the SPS processing technique. The effects of different temperature and pressure profiles on the densification and microstrucstural properties of the fabricated transparent polycrystalline magnesium aluminate spinel were investigated. Very high densification and transmittance were archived under appropriate conditions. The effect of impurities on the optical properties of the transparent spinel was also determined and discussed.

(ICACC-S4-P045-2011) Boron Carbide Amorphization as a Function of Powder Processing

D. W. Maiorano*, V. Domnich, R. A. Haber, Rutgers, The State University of New Jersey, USA

Previous work has shown that powder processing of mass produced boron carbide is capable of introducing severe microstructural changes to the powder. The present work examines the occurrence of the so-called "amorphization" event during typical powder processing, an event previously assumed to only occur under conditions of extremely high stress and strain rate, such as ballistic impact or nanoindentation. Samples densified using the spark plasma sintering technique are then studied for changes in bulk microstructure and mechanical properties as a result of the processing-induced amorphization.

(ICACC-S4-P046-2011) Theoretical Investigation of Stacking Fault Dynamics in Al, N, O, and B-Doped SiC under External Loading

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Assessing the behavior of SiC under dynamic loading is crucial for understanding its ballistic performance. SiC exhibits high degree of ductility which may be attributed in part to the formation and mobility of large numbers of stacking faults (SF) in the SiC structure. In this work, we investigate the effect of additives (Al, B, N, O) on SF dynamics in 3C, 2H, 4H, and 6H SiC polytypes and the resultant plasticity of the material under external loading. Both hydrostatic pressure and pure shear stress are considered. The calculations are performed for both zero and room temperatures. Additives are considered as point defects substituting for either Si or C atoms in the SiC structure. To assess the SF energy values, we use a combination of an axial next-nearest-neighbor Ising model and single-point energy calculations within the scheme of density-functional theory. The results of our simulations imply that the (3111) SF in 6H SiC has the highest energy of all possible stacking faults among the SiC polytypes considered, which apparently results in the onset of plastic deformation around 20 GPa in 6H SiC at zero temperature. To various degrees, additives (Al, B, N, O) are found to facilitate SF induced plasticity in 6H SiC. The role of additives in promoting plastic deformation in SiC in a wider pressure range is discussed.

(ICACC-S4-P047-2011) Mesoscale modeling of dynamic failure of polycrystalline armor ceramics

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Dynamic failure mechanisms at the scale of individual grains are investigated for ceramic polycrystals via continuum models and computational micromechanics. Behaviors of individual grains are modeled with anisotropic elasticity and crystal plasticity for dislocation slip. Cohesive zone models are used to represent intergranular fracture. Finite element calculations are performed with a parallel Lagrangian code incorporating contact interactions among distinct grains. Materials of study include aluminum oxynitride (AlON, idealized as having cubic crystal symmetry) and silicon carbide (SiC, polytypes with hexagonal crystal symmetry). Polycrystals consisting of numerous grains are subjected to compressive loading conditions at various strain rates and various confining pressures. Coupled pressure-shear loading may also be considered. The following physical phenomena are investigated via computation: effects of lattice orientation and anisotropy, effects of grain boundary failure properties, effects of specimen size, effects of

loading rate, effects of confining pressure, and competition between plasticity and fracture. Statistics of important physical phenomena are analyzed.

(ICACC-S4-P048-2011) Modeling Heat Transfer during Sublimation Growth of Silicon Carbide Single Crystals by Physical Vapor Transport

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Numerical simulation has been very useful in predicting the temperature distribution and subsequent growth kinetics in various vapor growth processes and can augment difficult or inadequate in situ measurements. Multidimensional models of silicon carbide (SiC) sublimation growth systems of varying levels of complexity have been developed to aid in the design, manufacture, and optimization of these growth systems. Since it is well known that SiC defect density and growth rate are strongly influenced by the temperature distribution, particularly with respect to the seed temperature and the temperature difference between the source and seed, an accurate assessment of this temperature distribution is required. In this work we present a transient heat transfer model accounting for conduction, convection, radiation, and radio frequency induction heating, to numerically investigate the temperature distribution within an axisymmetric apparatus during sublimation growth of SiC bulk single crystals by physical vapor transport (modified Lely method). Here, the evolution of the temperature gradients is studied numerically during the heating process and, where feasible, compared with existing experimental data. Variations of the numerical model, including the effects due to the choice of heat transfer mechanisms, input coil voltage, frequency, and coil placement, are analyzed.

(ICACC-S4-P049-2011) Simulation of the Ballistic Impact of Tungsten-Based Penetrators on Confined Hot-Pressed Boron Carbide Targets

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The rapid advancement of the computational power and the recent advances in the numerical techniques and materials models have resulted in improved simulation tools for ballistic impact into single and multi-layer armor configurations. 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. LaSalvia et al. [1] studied experimentally the interaction of confined hot-pressed boron carbide targets impacted by laboratory-scale tungsten-based long-rod penetrators. To better understand the physics involved, modeling and simulation will be used. The strength and failure models will be iteratively modified until satisfactory reproduction of the experimental data has been achieved. Also, the contribution and sensitivity of the various parameters on the accuracy of the solution, such as such as the fractured strength constant and fractured strength exponent of σf, and the hydro tensile limit will be considered as well. The final goal of this effort will be to develop a better understanding of the importance of being able to accurately model tensile failure in order to accurately simulate the ballistic response of ceramics. [1] 34 ICACC, Daytona Beach, FL, January 25-29, 2010

(ICACC-S4-P050-2011) Multi-Scale Computational Investigations of SiC/B_4C Interfaces

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Computational tools are used to cross spatial and temporal scales during investigations of ballistic events on armor materials. The ensuing weakening of these materials after such an event is of particular interest, and recent investigations of boron carbide (B_4C) inclusions in silicon carbide (SiC) showed that weaknesses in these materials did not originate at the grain boundaries. In an effort to characterize the development of structural changes, a multi-scale computational approach is employed. Several samples of varying B_4C concentrations in SiC matrices are studied with density functional theory molecular dynamics (DFT-MD) simulations to determine the stability at the B_4C/SiC interface under several high temperature and pressure regimes. DFT calculations employing molecular clusters to represent single sites along the interface are also presented, and this smaller-scale approach aims to isolate the structural changes that occur at each site and their contribution to the stabilities of these B_4C/SiC samples. These two spatial and temporal scales provide insight into how interface dynamics play a role in the development of structural weaknesses, and a comparison with experimental observations is also included.

(ICACC-S4-P051-2011) Static and Dynamic Indentation Response of Basal (c) Plane and Pyramidal (a) Plane Sapphire

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Static and dynamic indentation experiments are conducted on EFG sapphire along the c and a crystallographic axes to determine the loading rate dependence on material properties. Static hardness is measured using a conventional Vickers tester while the dynamic hardness is measured using a custom test fixture based on Split Hopkinson Pressure Bar techniques with the capability to produce single indentations at strain rates of roughly 103 s-1. Static and dynamic hardness values as well as the resultant fracture response for both axes are compared at a range of indentation loads. The results indicate that dynamic hardness is 12-15% greater than the static hardness for both a and c plane configurations. A comprehensive analysis of crack system development is presented in which the characteristic cracks are confirmed to preferentially propagate along the r and c axes and a new discussion of lateral cracks bridging separated r axes is discussed. Although cracking is found to occur preferentially along the r and c axes for both static and dynamic indentations, the dynamic indentations yielded shorter cracks along crystallographic axes with an increased amount of localized spalling surrounding each indentation site. This would indicate a shift of energy dissipation from major crack system propagation to localized spalling under higher strain rate indentations.

(ICACC-S4-P052-2011) Dynamic indentation response of Chemically Strengthened Ion-Armor™ Glass

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A lithium aluminosilicate glass was surface strengthened using a patented ion-exchange process. The resulting glass, named Ion Armor™, was reported to have surface compressive stresses approaching 1 GPa. The depth of compressive zone layer was determined using photoelasticity. The influence of this surface compression on static and dynamic Vickers indentation hardness measurements was investigated and compared with the unstrengthened glass properties. All static hardness measurements were conducted utilizing a standard Vickers hardness tester at 15 seconds load duration, while all dynamic indentation hardness measurements were performed at loading duration of 60 microseconds using a custom-made Dynamic Indentation Hardness Tester (DIHT). The variation in hardness with depth was also examined by conducting Vickers indentations on a surface perpendicular to the strengthened face. It was found that there is a 15.3% increase in static hardness (900 MPa) from the raw glass to the strengthened glass. The dynamic hardness was 33.9% (2.12 GPa) greater than the static hardness. The hardness profile on the unstrengthened surface revealed that the effect of strengthening extends much farther beyond the compression zone depth determined using photoelasticity.

(ICACC-S5-P053-2011) Co-substitution in Hydroxyapatite: an approach to control physio-chemical properties like degradation, bioactivity and thermal stability

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Hydroxyapatite (HA) is an inorganic compound with chemical formula close to that of bone mineral and is widely used as a biomaterial due to its bioactivity and biocompatibility. Ionic substitutions have been proposed as a tool to improve the properties of hydroxyapatite for more potential applications. In the present study, we have made an attempt to synthesize zinc and carbonate co-substituted HA by using the precipitation method. Comparative studies on HA, zinc substituted HA and carbonate substituted HA were also carried out. Characterization of the synthesized products by XRD, FT-IR, XRF and SEM confirmed them to be nanostructured HA with corresponding zinc or/and carbonate substitution. Substitution of carbonate in HA leads to a remarkable increase of in vitro degradation and bioactivity. When zinc is substituted simultaneously with carbonate it exerted a control over these properties. Zinc substituted HA formed considerable amount of β-TCP and α-TCP at 1000°C and 1400°C respectively. Co-substitution of carbonate along with zinc reduced the conversion to β-TCP to a greater extent at 1000°C and conversion to β-TCP and α-TCP at 1400°C. It may be possible to tailor the degradation, bioactivity and thermal stability of HA by regulating the concentration of zinc and carbonate for more biomedical applications.

(ICACC-S5-P054-2011) Effect of surface roughness of 45S bioactive glass on gene expression of MC3T3 pre-osteoblast cells

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Several glass compositions upregulate the expression of genes involved in bone formation. This remarkable bioactive response is established from the use of ions leached from glass powders. Now we have investigated the effect of 45S Bioglass surface roughness (Ra= 0.05 to 1.8 μm) on the bioactivity of MC3T3 pre-osteoblasts, using qRT-PCR analysis. The culture medium of the samples is changed every other day, thereby minimizing the effect of different dissolution rate of various surfaces. This information is particularly valuable for improving the performance of glass coating on titanium implants currently under development. The expression of six genes, runx2, bglap, osteocalcin, collagen-1A, alkaline phosphatase (ALP) and connexin-43 is compared at 4, 11, and 17 days with borosilicate coverglass as the reference substrate and GAPDH as the housekeeping gene. These genes are markers of different stages of bone cell differentiation and mineralization. The expression of ALP passes through a maximum at 11 days, but the kinetics is slower for smoother samples. Regarding connexin-43, initially the roughest surface promotes the highest amount of gene expression. For other genes, the roughness of Bioglass has little effect on their expression. Interestingly, the control borosilicate coverglass stimulates higher expression of ALP, bglap, and osteocalcin than any Bioglass sample.

(ICACC-S5-P055-2011) A newly formulated Lactic acid and Na lactate-buffered body fluid solution for the biomimetic coating of titanium alloy surfaces with calcium phosphate

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A new solution was hereby developed for the biomimetic coating of Ti6Al4V plates with CaP. The new synthetic body fluid (Lac-SBF) contained appropriate amounts of sodium lactate (NaL) and lactic acid (HL), as well as all the other ionic constituents of the human blood plasma. The inorganic ion concentrations of the Lac-SBF solutions were perfectly identical with those of human blood plasma (i.e., 142 mM Na, 103 mM Cl, 27 mM HCO3, 5 mM K, 1.5 mM Mg, 2.5 mM Ca, 1 mM HPO4, and 0.5 mM SO4). The new Lac-SBF solution of this study eliminated the need for using Tris/HCl or Hepes/NaOH buffers. Prior to biomimetic coating with Lac-SBF, Ti6Al4V substrates were chemically treated in NaOH and/or NaOH+H2O2 solutions and then heated at 600C for 1 h in air. Solution properties were evaluated by using turbidimeter, pH meter and rheometer. The coatings were characterized by using Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM), and a scratch tester.

(ICACC-S5-P056-2011) Fabrication of porous Ag doped Hydroxylapatite coating with antibacterial properties Electrostatic Spray Deposition (ESD) method

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The materials used in manufacturing of medical implant and prosthesis must be biocompatible. This means that the materials used to manufacture them should: not be toxic and carcinogen to human body, have enough mechanical properties depending on the location they are applied, not cause any foreign body reactions, not undergo any corrosion, permit to control dissolution rate depending on their application. Importantly, the long term stability of calcium phosphate derived materials will depend to a great extent on their ratios of calcium (Ca) to phosphorous (P). the Ca/P ratios of calcium phosphates in bulk or in coatings vary according to which of the following phases are present: alpha and beta-tricalcium phosphates (TCP), tetracalcium phosphates, octacalcium phosphates, and Hydroxylapatite (HA or Ca10(PO4)6(OH)2). Among these phases, pure 100% crystalline HA is known to be the most stable and strongest phase. Many different coating methods have been applied so far. These are plasma spray coating, sputtering, dipping, sol gel, electrophorecit deposition, hot isostatic pressing, etc. The objective of the current study is to coat titanium surface with antibacterial Ag doped Hydroxylapatite. In order to do that, electrostatic spray deposition (ESD) technique will be used.

(ICACC-S5-P057-2011) Fabrication of nanoporous glass fiber for flexible bioscaffolds and other products

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Recently, a heat+chemical treatment method based on spinodal decomposition followed by devitrification was developed in our laboratory for introducing multi-modal, interconnected nano-macro porosity in bulk 45S bioactive composition. For making flexible bioscaffolds and other biocompatible products, glass fibers of similar nanopore structure are needed, which can be used to fabricate felt, cloth, etc. Unfortunately, 45S glass is unsuitable for fiber drawing, and hence other fiber-based products. Now we report successful demonstration of our method for fibers of bioactive 20.9Na2O-7.1K2O-18CaO-P2O5-52SiO2 (S520) composition, thus introducing nanoporous fiber for bioactive applications. After successfully drawing S520 glass fibers, the samples are heat treated at 600-950°C and then leached in an acid at various temperatures. Scanning electron microscopy and porosimetry show that the fibers consist of interconnected nanopores ~tens nm in size. The present novel processing protocol establishes potential applications of bioactive glass in the regeneration of flexible tissues, and other areas of tissue engineering.

(ICACC-S9-P058-2011) Porous Hybrid Al2O3-Based Ceramics Prepared by Freeze Casting and Organic Surface Modifications

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Porous hybrid materials, combining the properties of organic and inorganic materials, have shown potential advantages such as toughness, high strength and low density, in many applications. A new type of porous hybrid Al2O3 ceramic was prepared by a freeze-casting process that produced a porous scaffold, followed by surface modifications with PMMA, yielding dense composite structures. Our goal is to utilize the organic-inorganic grafting technology in the interior structure of the porous ceramic to tailor the thermal properties of hybrid materials.

(ICACC-S9-P059-2011) The Characteristic Study of Porous Glass-Ceramics for High Transmission of Sun Light

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To exploit efficiently solar energy for any applications, improving the transmission of incident sun light at all wavelengths and all directions is one of common solution but critical. In this study, we investigate the transmission at visible, NIR and IR regions from various incident angles of sun light as function of various characteristics of porous glass-ceramics. The characteristics of porous glass-ceramics to be studied include porosity, pore size, pore size distribution, index distribution and mechanical strength. The ultimate goals are to reveal the effect of porous on transmission and scattering and then optimize the characteristics of porous glass-ceramics for high transmission of sun light for solar energy application.

(ICACC-S9-P060-2011) SiC foams for high temperature applications

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Si-SiC open cell ceramic foams with porosity >80% and pore size from 40 to 10 PPI are industrially employed as active zone in porous burners for heat radiation applications. Si-SiC open cell foams product range is increasing in terms of geometry, foam architecture, and base materials, continuously broadening their fields of application. From the first radiative burners, Si-SiC open cell foams are nowadays empolyed in catalysis, heat transfer, mechanical and optical applications. This work presents Si-SiC foams main characteristics as well as an overview of their applications in high temperature hostile environments. New SiC filament foams, able to realize different foam morphologies, are also presented. This new class of foams demonstrated higher thermal conductivity and thermal-shock resistance, making them promising for even more extreme applications.

(ICACC-S9-P061-2011) Macrocellular silicon carbide foam with hierarchical porosity

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Macro-cellular silicon carbide foams with hierarchical porosity were produced by using a polycarbosilane, foaming agent and transition metal halide as a catalyst. The presence of a catalyst resulted in the formation of 1D-nanostructures (nanowires) on the wall surface of foam. The composition, nanostructure and amount of the nanowires could be varied depending on the type of catalyst, gaseous atmosphere, pyrolysis temperature and the presence of an inert filler. This led to an increase of the specific surface area of the cellular ceramic substrates and various morphologies. The mechanical strength, BET surface area and thermal stability of the obtained monolith were investigated. This process enables the decoration of macrocellular structure with nanostructures directly through a simple one step pyrolysis. Macrocellular silicon carbide foam with hierarchical porosity is good candidate for various engineering applications.

(ICACC-S9-P062-2011) Intentionally Porous Alumina

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Porous ceramics have been increasingly used for industrial filters, catalyst supports, and gas sensors. There have been quite a few reported methods for the preparation of porous ceramics. Carbon particles are used as pore formers to prepare porous alumina through a dry powder pressing process. Porous bioceramics are fabricated by a foaming method involving in-situ polymerization of a foamed slurry. Porous alumina ceramics have been prepared by coating a cellulose sponge with an alumina slurry, followed by sintering in air. Alumina scaffolds have been produced using polymer scaffolds prepared by fused deposition modeling. With the development of nanoscale material research, porous alumina has been paid increasing attention, because it is a good template to fabricate nanometer-sized fine structures. The geometry of such materials may be described as a honeycomb structure, which is characterized by a close-packed array of columnar hexagonal cells, each containing a central pore normal to the substrate. In this paper we present steps towards preparing impermeable light weight alumina plates or rods of potentially closed porosity for mobile refractory components. Classical slurry routes are combined with conventional (e.g. polyethylene balls) and unconventional pore forming agents spanning the nanometer to millimeter range.

(ICACC-S9-P063-2011) Fabrication and characterization of ceramic foams produced on polymer templates

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Ceramic foams with controlled porosity and strength have been used for a wide range of applications such as filters. In this study, ceramic foams were produced by low-cost method using natural clays and alumina as raw materials and organic polymer sponges as templates. Polymer sponges with different pore sizes were dipped into ceramic slurry with controlled specific gravity and slurry content, followed by squeezing, drying and sintering to give porous structure. Sintering was carried out at 1500 C for 4, 8 and 12 hours respectively. The studied properties include linear shrinkage, pore size, bulk and apparent density, porosity and compressive strength. In addition, phase analysis and grain structure were investigated using X-ray diffraction (XRD) and scanning electron microscopy (SEM). This study found that clay contents at 70-75 wt% and alumina content at 25-30 wt%, with sintering time of 4 hours optimized compressive strength. Phases and grain size in the sintered bodies did not show a significant effect on the mechanical strength. However, pore sizes and pore distribution after sintering of polymeric sponge templates strongly affected the physical and mechanical properties of porous ceramics in this study.

(ICACC-S9-P065-2011) Materials from particle-stabilized foams and emulsions

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Already at the beginning of the 20th century, Ramsden and Pickering observed the ability of fine particles to adsorb to oil-water interfaces and drastically improve emulsion stability1, 2. For efficient emulsion and foam stabilization, the particle surface energy needs to be tailored in order to promote particle attachment to the liquid-liquid or liquid-gas interface, but also to avoid particle agglomeration in the bulk. In-situ hydrophobization3-6 is a powerful method to deliberately control the wettability of colloidal particles of all kind through adsorption of short-chain amphiphilic molecules in order to enable the formation of stable wet foams and emulsions. This poster gives an overview over our activities in the field of particle-stabilized ceramic foams and emulsion and describes the method and processing in more detail. Special attention is given to the parameters controlling foam formation and microstructure as well as the wide variety of structures achievable via this platform technology. That includes the fabrication of highly porous ceramics with outstanding mechanical and microstructural properties as well as the harvesting of millions of hollow microcapsules with controlled porosity in the particle shell.

(ICACC-S9-P066-2011) High Contrast Tomography of Soft material, Membranes and Porous Composites beyond Sub micron Resolution

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3D Imaging of soft materials such as polymers, membranes, coatings and biological tissue at high resolution is difficult in most imaging modalities. Visualizing these materials, involves contrast agents, elaborate and destructive sample preparation techniques. While conventional x-ray computed tomography (CT) has the advantage of imaging buried structures within materials in 3D, it works predominantly with hard materials under absorption contrast mode. Soft materials

and unstained biological tissue for instance, lack the contrast to be of much utility. To overcome the submicron resolution barrier and contrasts limitation of soft materials, it is necessary to resort to Synchrotron Radiation X-ray submicron and nanotomography, employing a combination of hard, soft or tunable x-ray energies and phase contrast. We describe a suite of novel lab based x-ray computed tomography system which overcome the resolution and contrast limitation of conventional CTs. The novel suite of CTs provides multiscale resolution from 50 microns to 50 nm including soft x-ray energies, absorption and phase contrast. Comparison of data from the novel CTs with synchrotron based sub-micron and nanotomography and other imaging modalities such as SEM, SEM/FIB, optical microscopy will be demonstrated for a variety of soft materials, biological cells, membranes, coatings and porous composites.

(ICACC-S13-P068-2011) Preparation of C/B4C/SiC composites using self sintering materials

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C/B4C/SiC composites have good mechanical properties and high oxidation resistance to temperatures higher than 1000 C without the need of using a protective layer. The fabrication of this kind of materials usually involves the use of a carbon filler, usually coke, a binder pitch and carbides particles. This preparation method usually leads to inhomogeneities in the material due to the different behaviour of coke particles and binder pitch during thermal treatment but also to the low sinterability of carbon with the ceramic particles. In this work a self-sintering carbon material containing B4C and Si nanoparticles have been developed to produce this kind of material.

(ICACC-S13-P069-2011) Strength Evaluation of Ultra-fine Grained Graphite by Miniature Equibiaxial Flexural Test

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Equibiaxial flexure is an alternative flexural test configuration to conventional four-point bending of brittle materials. This test method is particularly suitable and attractive for irradiation effect study on fine-grained, isotropic nuclear graphite due to 1) the applicability of very small specimens, 2) freedom from the edge effect, and 3) lack of anisotropy effect on biaxial strength. In the present work, an equibiaxial flexural test procedure for using miniaturized specimens was first developed. Influences of the test configurations, loading conditions and the Young's modulus to fracture stress ratio on the stress uniformity were studied by a finite element analysis and validated by an experiment. Based on that and the recommended standard practice in ASTM C1499, a statistically significant population of miniature specimens suitable for some of the planned irradiation programs were tested. The material used was Tokai Carbon grade G347S isotropic, ultra-fine grained nuclear graphite. Uniaxial flexural tests were also conducted in a four-point-1/3 configuration using the full-size (ASTM C651) and the 1/2 size (ASTM C1161) specimens machined from the same graphite block. The results obtained from different test configurations and different specimen dimensions are compared and discussed in terms of the size scaling.

(ICACC-S13-P070-2011) A new single-step brazing for joining CFC to copper

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Carbon fiber composites (CFC) offer a high thermal shock resistance and a good compatibility to fusion plasma. They are foreseen as plasma facing material for the strike point region of the ITER divertor during its start-up phase. At the moment, two configurations involving a joint of the CFC with a Cu/Cu-alloy heat sink have been studied for two divertor geometries: flat-tile and monoblock. The second one is the reference geometry for ITER and comprises a pipe shaped heat sink made of Cu alloy passing through a hole in CFC tiles. Because of curved surface and thermo-mechanical properties at ceramic/metal interface, the monoblock geometry is affected by higher thermal stresses during manufacturing than the flat-tile one. A pure copper interlayer (1–2mm thick) is used to mitigate, by plastic deformation, the stresses due to the thermal expansion mismatch. This paper deals with the development of a new single step brazing process suitable for both flat tile and monoblock concepts. The brazing of the three materials (CFC/Cu/Cu-alloy) can be performed in a single heat treatment by using the same Cu-based brazing alloy. RF-sputtering and galvanic processes have been used to coat the brazing alloy by Cr, in order to increase its wettability on CFC. The results of this new joining process have been compared with those obtained by other techniques.

(ICACC-S13-P071-2011) Comparative studies of radiation resistance of the Boron Nitride and C2C ceramics Al2O3 on Plasma-Focus PF-1000 device

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BN and Al2O3 are used in TAE Antenna coil on MAST spherical tokamak. We undertake experiments to compare their radiation resistance. Samples of the materials (bulk for BN and 20-μ film on Al substrate for Al2O3) were exposed on the axis of the Plasma-Focus PF-1000 device to intense streams of hot plasma ($v \sim 10^7$ cm/s and $Npl \sim 10^{18}$ cm-3) and fast deuterons (Ei~100 keV). Time of the interaction ~ 0.2...1.0 μs. The irradiation process was diagnosed by fast optical cameras and optical spectrometry. Experiments were performed at $10^9 \ldots 10^{10}$ and $10^8 \ldots 10^9$ W/cm2. Irradiated specimens were investigated by optical microscopy and X-Ray structure analysis. Results: 1. At 10^{10} W/cm2 Al2O3 coating is completely evaporated. Surface of BN was smoother than in virgin samples. 2. Direct comparison of both samples at 10^8-W/cm2 pulses has shown that there are no cracks of BN and Al2O3 specimen, yet a wave-like structure become apparent more profoundly in Al2O3. However weighing of samples has shown, that evaporation of BN was ~ 2 times higher than of Al2O3. 3. The X-ray phase analysis has shown no evidence of cracking of Al2O3. So the insulation properties of Al2O3 did not decline. Evaporation of BN under fast ion irradiation may create potential source of impurities. So, the Al2O3 coating may be potentially more beneficial if it is kept below melting point.

(ICACC-S13-P072-2011) Effect of neutron radiation on mechanical properties of B4C

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B4C is an important material used in the nuclear reactors. During the reactor's operation, the B4C undergoes severe neutron radiation and defects are generated in the structure. These defects are responsible for the degradation of mechanical performance of B4C and can make this material unsuitable for further exploitation. Therefore, both crystal structure and mechanical properties of B4C were studied before and after radiation, as well as for the case when irradiated by neutrons B4C samples has been annealed in order to heal the defects introduced by the radiation. B4C fully dense (99% density) ceramics were produced by hot pressing at 2100 C, 30MPa, and 45 minutes dwell time. 4-point bending strength, SEVNB fracture toughness, hardness and indentation fracture resistance have been measured on as received B4C, B4C radiated by soft neutrons, and B4C after radiation and annealing at 400 C for 1 hour. The Weibull parameters were determined for the each set of the samples. The fracture surfaces of the materials have been analyzed using SEM.

(ICACC-S13-P073-2011) Compositional effect of ceramic breeder on compatibility with SiC under HFIR irradiation

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In the advanced design of HCPB in a fusion reactor, SiC is required to be compatible with the ceramic breeder under neutron irradiation at high temperature. The composition of ceramic breeder should change due to nuclear reactions of Li(n, α)T during irradiation. In this study, the effect of compositional ratios of Li/Al in lithium aluminate on compatibility with SiC was investigated by using HFIR. Samples used were monolithic β-SiC pellets fabricated by Rohm and Hass, and sintered pellets of 4 different compositional lithium aluminate, Li_xAlO_{2-y} (x = 1.00, 0.95, 0.90 and 0.80), fabricated by TYK Corp. A lithium aluminate pellet, sandwiched by two SiC pellets, was loaded in a TZM subcapsule purged by helium gas. Irradiation was performed in HIFR at 800 °C at a fluence of 7×10^{25} n/m^2. The X-ray diffraction pattern prior to irradiation showed that the intensity ratios of $LiAl_5O_8$ phase to $LiAlO_2$ phase in the 4 lithium aluminate samples (x = 1.00, 0.95, 0.90 and 0.80) were 0.014, 0.39, 0.25 and 1.06, respectively. Assuming all of the ^{6}Li atoms burned up by irradiation, the composition of x in Li_xAlO_{2-y} should change to 0.92, 0.88, 0.83 and 0.74. Reaction product was observed especially on the surface in SiC in contact with lithium aluminate of lower-x after irradiation. It was considered that formation of $LiAl_5O_8$ phase in lithium aluminate deteriorated the compatibility with SiC.

(ICACC-S13-P156-2011) Fabrication of SiC Inert Matrix Fuel though a Polymer Precursor Route with Controlled Porosity and Superior Mechanical Properties

C. Shih*, J. S. Tulenko, R. H. Baney, University of Florida, USA

A process for the fabrication of silicon carbide (SiC) inert matrix fuels at a low temperature of 1050 °C is reported which utilized a liquid pre-ceramic polymer precursor and SiC powder of various sizes. The process parameters include the polymer contents, the SiC powder size variations, the cold pressing pressure and different mixing methods. The polymer infiltration and pyrolysis (PIP) process was used to further densify the fabricated pellet. The density, pore size distribution, microstructure and mechanical properties of the fabricated pellets were characterized. The maximum theoretical densities achieved before and after PIP process were 81% and 87% respectively. The fabricated pellets can be prepared with superior mechanical properties to the currently used mixed oxide fuels.

(ICACC-S13-P157-2011) Reprocessing Silicon Carbide Inert Matrix Fuel by Molten Salt Hot Corrosion Enhanced by Water Vapor

T. Cheng*, R. H. Baney, J. Tulenko, University of Florida, USA

Silicon carbide is one of the prime candidates as the matrix material in inert matrix fuels (IMF) being designed to reduce plutonium inventories through transmutation. Since complete transmutation is not practical in a single in-core run, it is necessary to reprocess the inert matrix fuels. The current reprocessing techniques of many inert matrix materials involve dissolution of spent fuels in acidic aqueous solution. However, SiC cannot be dissolved by that process. New reprocessing techniques are required. An efficient process has been developed for separating transuranic species from the silicon carbide (SiC) matrix. Silicon carbide can be corroded in molten potassium carbonate (K2CO3) and form water soluble potassium silicate. Water vapor was introduced in the SiC/K2CO3 corrosion system in order to determine whether water vapor can accelerate the SiC reprocessing process. The SiC corrosion rates under CO2, O2 and H2O are compared to determine the most efficient atmosphere for reprocessing SiC IMFs and to obtain a better understanding of the reaction mechanism. The SiC pellets with 5 wt% of CeO2, a surrogate for plutonium were fabricated. Ceria was successfully separated from the SiC matrix by applying the molten salt reaction/dissolution strategy.

(ICACC-S14-P074-2011) Ultrahigh Rate Capability and Phase Stability of Spinel $LiMn_2O_4$ Nanowires as Cathode Materials for Li-ion Battery

H. Lee*, M. Pandurangan, KAIST, Republic of Korea; R. Ruffo, Universita degli Studi di Milano-Bicocca, Italy; D. Kim, KAIST, Republic of Korea

The high energy and power density capability of lithium ion battery technology have been attracted widespread interest over the past few years due to potential applications in both hybrid electric vehicles and full electric vehicles. Spinel $LiMn_2O_4$ is a promising candidate to replace layered Ni or Co oxide materials as cathode in lithium ion batteries because of its intrinsic low-cost, environmental friendliness, high abundance and better safety. However, the application of $LiMn_2O_4$ in high power systems requires the development of fast kinetic electrodes, which appears nowadays possible using nanostructured morphologies. In this regard, spinel $LiMn_2O_4$ nanowires were successfully synthesized using a facile two step process: a solvothermal reaction to prepare α-MnO_2 nanowires followed by solid state reaction. The nanowire structure and morphology have been correlated to the electrochemical characterization and the possibility of high rate capability as well as phase stability will be discussed. Galvanostatic battery testing showed that the material delivers 100 and 78 mAh/g at very high rates (60C and 150C, respectively) in a larger potential window (2.4/4.4 V) with very good capacity retention and outstanding structural stability. Such performances are due to both the favorable morphology and the high crystallinity of nanowires.

Wednesday, January 26, 2011

S1: Mechanical Behavior and Performance of Ceramics & Composites

Composites: Fibers, Matrices, Interfaces and Applications

Room: Coquina Salon A
Session Chairs: Walter Krenkel, Universitat Bayreuth; Dileep Singh, Argonne National Laboratory

8:00 AM

(ICACC-S1-033-2011) Ceramic Composites for Hypersonic Applications (Invited)

D. B. Marshall*, B. N. Cox, O. Sudre, S. Lucato, J. B. Davis, Teledyne Scientific, USA

The use of textile methods to optimize fiber architecture in ceramic composites provides new opportunities for the design of hot structures for hypersonic vehicles. Examples will be discussed of actively cooled composites, thermal protection structures, and shape morphing structures. Material limitations and degradation mechanisms will be discussed, along with approaches for modeling performance and lifetime.

8:30 AM

(ICACC-S1-034-2011) Ultra-high-temperature ceramics for aerospace and solar energy applications

D. Sciti*, S. Guicciardi, L. Silvestroni, A. Bellosi, National Research Council - CNR, Italy

UHTCs are considered a class of promising materials for several applications, the most appealing ones being in the aerospace and energy sectors. Beside the well known characteristics that make UHTCs attractive as TPS, there is a strong interest in their applications as sunlight absorbers operating in the high temperature regime. The first part of this work is thus focused on characterization of various carbides and borides, in terms of room temperature and high temperature mechanical, thermal and optical properties. The discussion on properties relevant to solar applications will help

to select the most promising matrices and/or composites for this application. The second part of this work is dedicated to toughening of UHTCs, which is another crucial step for application of UHTC in aerospace. This work will present the different strategies developed to increase this property, including incorporation of elongated reinforcement such as SiC chopped fibers or in-situ development of SiC platelet-reinforced materials. The mechanical properties will be compared to those of the un-reinforced materials and the effect of different kinds of sintering aids amongst Si3N4, MoSi2 and ZrSi2 will be analyzed.

8:50 AM

(ICACC-S1-035-2011) Novel High Temperature Wound Oxide Ceramic Matrix Composites manufactured via Freeze Gelation Process

T. Machry*, EADS Innovation Works, Germany; D. Koch, Univ. of Bremen, Germany; C. Wilhelmi, EADS Innovation Works, Germany

Ceramic Matrix Composites based on oxide materials are of interest for high-temperature application due to, not only their inherent oxidative stability, but also to their damage tolerance and thermal shock resistance. The development of a new oxide CMC with Nextel 610 fibers and mullite matrix manufactured via filament winding and freeze gelation process is presented. The ceramic matrix is produced using the sol gel technique combined with the freeze gelation process. Solid nanoparticles are dispersed into a liquid and filler particles are added. The infiltration of the fiber bundles by the suspension is then conducted via filament winding. The nanoparticles from the sol form a three-dimensional network due to its gel transition which is forced by freezing of the solvent, resulting in ice crystals growth. At moderate temperatures just above room temperature the green body is dried and ice crystals are evaporated or sublimated. Knowledge on fiber filament infiltration and binding between layers was evaluated via microstructure and REM analysis. Interlaminar and composite strength were tested. Results show that slurry impregnation of the individual fiber bundles is successfully achieved and the mechanical tests on the CMCs indicate that the concept of this manufacturing route is promising and that fiber properties can be transferred to composite properties effectively.

9:10 AM

(ICACC-S1-036-2011) Processing of Advanced Oxide/Oxide Composites for Gas Turbine Applications Based on Tailored Textile Technologies

C. Wilhelmi*, T. Machry, EADS Innovation Works, Germany; R. Knoche, ASTRIUM Space Transportation, Germany; D. Koch, Univ. of Bremen, Germany

New concepts for aerospace applications such as gas turbine aero-engines require advanced lightweight structural materials with superior high-temperature environmental stability in order to increase operation efficiency and to reduce CO2 emission. Oxide/oxide CMCs can fulfil these demands for high performance turbines due to their inherent oxidation resistance, good thermo-mechanical properties at elevated temperatures and low density. For some decades now EADS IW uses the standard PIP process (Polymer Infiltration Pyrolysis) for manufacturing of a specific oxide/oxide CMCs termed UMOX. Continuous oxide fibres are impregnated with pre-ceramic slurries via filament winding technique and further processed to a green body following by high temperature treatment where the matrix is converted to a ceramic state. Besides specific advantages such as excellent reproducibility the main drawback of this process is based on high manufacturing costs due to long process times. To overcome this disadvantage and the strong demand for high performance materials a new process with a tailored textile technique was successfully developed and investigated for the fabrication of advanced oxide/oxide CMCs. This new process and the CMC characteristics will be presented and the potential for the processing of cylindrical structures such as for gas turbine applications will be evaluated.

9:50 AM

(ICACC-S1-037-2011) Design and Development Approach for Gas Turbine Combustion Chambers made of Oxide Ceramic Matrix Composites

R. Knoche*, E. Werth, M. Weth, J. Gomez-Garcia, ASTRIUM Space Transportation, Germany; C. Wilhelmi, EADS Innovation Works, Germany; M. Gerendas, Rolls-Royce Germany, Germany

Higher efficiencies and reduced CO2 emission in gas turbine engines require the turbine cycle to operate at higher pressures and temperatures. A safe operation of high performance turbines can only be achieved by using HT materials with effective cooling methods. Accordingly the introduction of oxide Ceramic Matrix Composites (CMC) for combustor liners appears promising due to elevated thermo-mechanical performances and low densities. Moreover oxide CMC are inherent resistant to oxidation which enables an acceptable lifespan. Thus the development of these CMC and tailored cooling schemes is one of the main tasks for increasing efficiencies in gas turbines. This scope has led to the cooperative project HiPOC (High Performance Oxide Ceramics) consisting of 3 companies and 4 research institutes. In HiPOC ASTRIUM focuses on the structural design of representative turbine components made of CMC including attachment systems. This activity strongly interacts with the further development of an oxide CMC (termed UMOX) performed by EADS IW. The paper describes the design for structural components in turbine applications which obviously is influenced by CMC characteristics and its manufacturing. The development approach is presented together with results from the FEM verification of the design. The paper concludes with the next steps in developing CMC components for gas turbines.

10:10 AM

(ICACC-S1-038-2011) Effect of microstructure on room and high temperature properties of oxide/oxide composites developed for gas turbine applications

D. Koch*, K. Tushtev, K. Rezwan, C. Wilhelmi, S. Denis, J. Göring, Univ. of Bremen, Germany

Oxide/oxide composites are developed for high temperature applications in oxidizing atmosphere. In general their mechanical long term stability is assured not exceeding 1000°C which is not only attributed to type of fiber but also to matrix composition and reinforcement architecture. Therefore three different types of composites, all reinforced with Nextel 610 fibers, are investigated produced via different reinforcement concepts (filament winding, UD crossply layup, fabric layup) and matrix processing (liquid slurry infiltration, liquid polymer infiltration, resin transfer molding). It turns out that different microstructures result in specific advantages of individual composites under various loading conditions. Stiff but porous matrices induce high tensile and interlaminar strength while off axis loading provokes lower strength. In this case anisotropy of the material has to be considered in design of components. A weaker matrix with smaller pores results in lower stiffness but higher off axis strength. If specimens are loaded in compression mode straight orientation of fibers allow higher strength compared to woven or fabric structures. The high temperature properties are again correlated to the individual matrix performance and to the fiber architecture especially to the effect of kind of roving cross-overs where stress concentrations occur.

10:30 AM

(ICACC-S1-039-2011) Oxide Fiber Coatings for SiC/SiC Composites

E. E. Boakye*, P. Mogilevsky, T. A. Parthasarathy, UES Inc., USA; M. M. Cinibulk, Air Force Research Laboratory, Materials Directorate, Wright Patterson Air Force Base, USA; H. S. Randall, Air Force Research Laboratory, Materials Directorate, Wright Patterson Air Force Base, USA; M. Ahrens, Air Force Research Laboratory, Materials Directorate, Wright Patterson Air Force Base, USA

Current SiC-based ceramic-matrix composites (SiC/SiC CMCs) rely on carbon or boron nitride fiber coatings to control fiber-matrix interface properties. However, both carbon and boron nitride are susceptible to oxidation in the environments of most applications for which CMCs are intended. A potential alternative oxidation resistant fiber coating for SiC fibers is the γ-polymorph of the rare-earth disilicates (RE2Si2O7, where RE = Y, Ho, or Er). Rare-earth disilicates exist up to seven polymorphic forms and are refractory, melting at over 1750°C. The mechanical properties of yttrium disilicate (γ-Y2Si2O7) are comparable to those of monazite. It is soft and deforms plastically at room temperature. This combination of properties suggests γ-Y2Si2O7 as a suitable oxidation-resistant interface for SiC/SiC CMCs. Coatings of Y2Si2O7 and Ho2Si2O7 were made on SCS-0 SiC fiber using silica/yttrium hydroxide and silica/holmium hydroxide dispersions. The coatings were converted to the γ-polymorph by heat treating in argon - 497ppm oxygen mixtures. Coated and uncoated SCS-0 fibers were put in SiC/Re2Si2O7 matrix and densified at 1200 °C/1h using the pulse electric current sintering technique (PECS) with a force of 20KN in vacuum. Push-out testing was conducted to infer the weakness of the γ-Y2Si2O7 interface.

10:50 AM

(ICACC-S1-040-2011) Transmission Electron Microscopy of Damage to Rare Earth Orthophosphate Fiber-Matrix Interphases that Deform with Transformation Plasticity during Fiber Push-Out

R. Hay*, G. Fair, AFRL, USA; E. Boakye, P. Mogilevsky, T. Parthasarathy, UES, Inc., USA; M. Ahrens, T. Godar, Wright State University, USA

Oxide-oxide CMCs with rare-earth orthophosphate interphases have been successfully demonstrated. The major concern for these interphases is the high fiber pull-out stresses, typically ~80 - 200 MPa. An approach to lowering pullout stress uses interphases that weaken by transformation plasticity during a –ΔV martensitic phase transformation. The xenotime → monazite martensitic phase transformation induced by indentation for TbPO4 and (Gd,Dy)PO4 solid-solutions was characterized by TEM. Coatings of(Gd,Dy)PO4 xenotime were applied to single-crystal alumina fiber. These fibers were hot-pressed in alumina matrices and fiber push-out tests were conducted. Push-out stresses from 10 to 80 MPa were measured. Deformation in the (Gd,Dy)PO4 fiber-matrix interphase was characterized by TEM. A band of deformed material several microns thick was present in the interphase. Deformation mechanisms were dominated by cataclastic flow with attendant intense deformation of small grains. Electron diffraction confirmed that many of the deformed grains had transformed to monazite. Grains with a fine lamellar structure were ubiquitous in the deformed area; their characterization is discussed. The relationships between push-out stress and fiber-matrix interphase microstructure are also discussed.

11:10 AM

(ICACC-S1-041-2011) Toughness Optimisation of a Metallic Fibre Reinforced Ceramic Composite (MFC)

S. R. Pemberton*, T. W. Clyne, University of Cambridge, United Kingdom; L. Marston, Fiberstone Products Limited, United Kingdom

Little research has hitherto been undertaken into the fracture behaviour of metal fibre reinforced ceramic composites (MFCs). A commercially available MFC, using melt-extraction 304 grade stainless steel fibres in an alumina, alumino-silicate matrix, was therefore investigated. This was manufactured by a slip-casting based technique allowing easy and cheap manufacture of net-shape ceramic matrix composites. This work studies the fracture behaviour of such composites via single fibre tensile testing, a novel method of fibre pull-out testing and Izod impact testing of the composite. Using these three methods it was possible to analyse the composite fracture behaviour and produce a model to predict the fracture toughness of an MFC, combining the contributions from frictional fibre pull-out and plastic deformation to failure of the metal fibres. The addition of metallic fibres to a ceramic matrix is shown to create a dramatic increase in the toughness of the resulting composite (up to 40 kJ m-2), making this a promising material for applications demanding high impact and corrosion resistance at moderately high temperatures. Experimental results additionally show that increasing fibre volume fraction, fibre diameter (for a given fibre aspect ratio) and fibre work of deformation (via changing the stainless steel fibre grade used) increased the fracture toughness of the MFC.

11:30 AM

(ICACC-S1-042-2011) Structural behaviour of bamboo composites

B. N. Muthuraman*, Rajalakshmi Engineering College, India

Nowadays, composites sandwich panels are used extensively due to their high strength to weight ratio, smooth exterior, high load carrying capacity and corrosion resistance. The objective of this work is to examine the feasibility of employing alternative composites material made of natural fibres as the flooring material for lightweight businessjet aircraft. Particularly, among all natural fibres, bamboo has been widely used for structural purposes due to its lightness and strength. In order to get the first hand experience, an experimental work on Bamboo-EPS-Bamboo and glass fibres sandwich panel is carried out by using Universal Testing Machine of 50KN load capacity subjected to American test standards. The experiments includes materials subjected to tensile load, flexural load and compressive load, from which the tensile strength, flexural strength and compressive strength are determined. It is found that bamboo sandwich panel is capable of carrying compression load of one tonne for an area of 0.01 sq.m. The structural behaviour of the composites are reported through the two dimensional models and displacement is determined using ansys. All the results have been plotted in graphs and compared for different composites materials. The author wishes to express gratitude to Composites Technology Park, Bangalore for providing the necessary facilities for this project with sincere thanks to Dr. R. Gopalan, Executive Director, for permitting him to carry out this project.

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

Functionally Graded Coatings and Interfaces

Room: Coquina Salon G

Session Chairs: Jow-Lay Huang, National Cheng Kung University; Yongho Sohn, University of Central Florida

8:00 AM

(ICACC-S2-032-2011) Growing Integration Layer [GIL] Method: Coating and Joining of Functional Ceramic Layers on Metallic Materials in Solution without Firing Processes (Invited)

M. Yoshimura*, N. Matsushita, Tokyo Institute of Technology, Japan

In the ceramic/metal joining and coating, the most difficult problem is how to overcome poor adhesion of ceramic layers by their cracking and /or peeling arising from their intrinsic brittleness. On the basis of accumulated results and discussion, we propose a novel concept and technology of the formation "Growing Integration Layer" [GIL] be-

tween ceramics and metallic materials to improve the adhesion performance. Those GIL(s) can be prepared from a component of the metallic materials by chemical and /or electrochemical reactions in a solution at low temperature of RT-200°. They have particular features:1)Widely diffused interface(s),2)Continuously graded layers grown from the bulk(substrate),3)Low temperature process,etc. BaTiO3 or 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.1) The GIL strategy is effective for many metallic alloys and bulk metallic glassed 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°[2]. Similarly, bioactive oxide layers could be prepared on different Bulk Metallic Glasses. The GIL methods are typical "Soft Process" and "Green Process" using aqueous solutions, and applicable for various functional and structural ceramics layers.

8:30 AM

(ICACC-S2-033-2011) Development of Oxide Ceramic APS Coatings for Microwave Absorption (Invited)

M. Floristan*, University of Stuttgart, Germany; P. Müller, A. Gebhardt, A. Killinger, R. Gadow, IFKB University of Stuttgart, Germany; A. Cardella, European Commission, Germany; C. Li, Max-Planck-Institut für Plasmaphysik, Germany

Thermonuclear fusion is a promising source of clean energy for the future. The extreme operating conditions of fusion reactors have lead to an increasing interest on the field of high performance materials. Research has focused on the development of materials which can function under thermal and mechanical loads or strong radiation. The present work describes the development of coating systems acting as absorbers for 140 GHz radiation on the water-cooled baffle for the stellarator Wendelstein 7-X. Several types of ceramic coatings were applied on copper substrates by Atmospheric Plasma Spraying. Different powders in composition and grain size were used as feedstock material. The influence of the process parameters on the coating properties and microwave absorbing capability was analyzed. The coatings mechanical properties were characterized in terms of porosity, microhardness, roughness, adhesion and residual stresses. XRD and SEM were carried out. It was found that thickness and microstructure of the coatings have a significant influence on microwave absorption behaviour. For Al2O3/TiO2 coatings, absorption values over 90% were obtained. After optimization of the coating structure for maximum microwave absorption, the coating procedure had to be adapted to the complex water baffle geometry. With this aim, the robot kinematics were designed to achieve a regular coating regarding thickness and microstructure.

9:00 AM

(ICACC-S2-034-2011) Functionalization of silica surface with silane coupling agent for rubber composite

J. Yoo*, Korea Institute of Ceramic Engineering & Technology, Republic of Korea; G. Lee, Korea University, Republic of Korea; D. Yun, Korea Institute of Ceramic Engineering & Technology, Republic of Korea

Silica has been used for improving property of rubber composite as filler. However, strong filler-filler interaction caused by silanol of silica surface leads to aggregation of silica filler in the rubber and the result is causing reduction of mechanical properties of rubber. In this study, nano silica particle was modified with silane coupling agent to improve dispersion ability of silica in the rubber through chemical reaction between silica and coupling agent. Various functional groups containing sulfur chain or alkyl chain were used to modify silica surface. FT-IR, TGA and 29Si CP/MAS NMR confirm modification of silica surface with silane coupling agent chemically or physically. Silane coupling agent on the silica surface is analyzed by infrared spectra peaks at 2962, 2927, 2855 cm-1 due to stretching vibration modes of the C-H bonds. After modification, amount of physisorbed water on the silica is decreased, while organic amount on the silica is increased. From SEM analysis, unmodified silica is agglomerate in the rubber, however, modified silica is well dispersed in the rubber composite because filler-filler interaction was reduced by modification.

9:20 AM

(ICACC-S2-035-2011) Interfacial structure of V2AlC thin film on (0001) and (11-20)-sapphire

D. P. Sigumonrong, J. Zhang*, Materials Chemistry, RWTH-Aachen University, Germany; Y. Zhou, Shenyang National Laboratory for Materials Science, Institute of Metal Research,, China; D. Music, J. M. Schneider, Materials Chemistry, RWTH-Aachen University, Germany

Polycrystalline V2AlC thin films have been deposited on (0001) and (11-20) α-Al2O3 substrates by magnetron sputtering from elemental targets at 750oC. The structure of the interface between V2AlC films and sapphire substrates has been determined by high-resolution transmission electron microscopy (HRTEM). A 12-nm-thick transition layer was observed between V2AlC thin film and (0001)-sapphire substrate; while local epitaxial growth was indentified between V2AlC thin film and (11-20)-sapphire with the orientation relationship of [11-20](0001) V2AlC // [0001](11-20) α-Al2O3. HRTEM showed that the epitaxial interface was a semicoherent interface with a lattice match of 8.97%, which can be accommodated greatly by misfit dislocations. Our ab initio calculations suggested that the most stable interfacial structure was characterized by the stacking sequence …C-V-Al-V // O-Al…, exhibiting the largest work of separation for the configurations studied and hence strong interfacial bonding. Therefore, it is proposed that interfacial design based on misfit minimization and interface stabilization by strong interfacial bonding may enable local epitaxial growth.

Advanced Coating Charcterization Methods and Non-Destructive Evaluation

Room: Coquina Salon G
Session Chairs: Yongho Sohn, University of Central Florida; Jow-Lay Huang, National Cheng Kung University

10:00 AM

(ICACC-S2-036-2011) Evolution of Raman lines of t'-YSZ with high-temperature aging

A. M. Limarga, Harvard University, USA; J. Iveland, University of California, USA; M. Gentleman, Texas A&M University, USA; D. M. Lipkin, GE Research, USA; D. R. Clarke*, Harvard University, USA

Raman spectroscopy is typically used for phase characterization in YSZ-TBC because of its sensitivity to the presence of monoclinic phase in the metastable tetragonal (t') zirconia obtained in the as-deposited coatings. We observed that even before the onset of monoclinic phase formation, the Raman peaks shift and undergo sharpening with annealing. The evolution of the Raman lines of metastable tetragonal yttria-stabilized zirconia with high-temperatures aging has been monitored and the data analyzed using a Larson-Miller parameter. This normalization allowed the shift and sharpening of the Raman peaks of tetragonal zirconias having different stabilizer concentration and produced by different methods with different microstructures to be described by a common curve. The observed Raman shifts are consistent with evolution of the metastable phase into a coherent mixture of tetragonal and cubic phases.

10:20 AM

(ICACC-S2-037-2011) Monitoring Delamination of Thermal Barrier Coatings During Interrupted High-Heat-Flux Laser Testing Using Luminescence Imaging

J. I. Eldridge*, D. Zhu, NASA Glenn Research Center, USA; D. E. Wolfe, The Pennsylvania State University, USA

Both near-infrared (NIR) and upconversion luminescence imaging of thermal barrier coatings (TBCs) have been shown to successfully

monitor TBC delamination progression during interrupted furnace cycling. However, because furnace cycling alternates between two isothermal conditions, it does not adequately model engine conditions where TBC-coated components are subjected to significant through-thickness temperature gradients that may produce a different delamination progression path. Therefore, new data and analysis are presented based on luminescence imaging of TBC-coated specimens subjected to interrupted high-heat-flux laser cycling exposures that much better simulate the thermal gradients present in engine conditions. The TBCs tested were composed of 7wt% yttria-stabilized zirconia (7YSZ) that incorporate a base sensor layer co-doped with erbium and ytterbium (7YSZ:Er,Yb), both deposited by electron-beam physical vapor deposition (EB-PVD). The high-heat-flux exposures were performed using a high power CO_2 laser operating at a wavelength of 10.6 μm. Each laser cycle consisted of 1 hr hot time (laser on) followed by 5 min cooling (laser off). The debond progression observed by luminescence imaging is correlated with apparent changes in the TBC thermal conductivity.

10:40 AM

(ICACC-S2-038-2011) Deposition Gas Turbines Thermal Barrier Coatings with Thermographic Phosphors for Temperatures Measurement

E. H. Jordan*, M. Majewski, C. Kelley, M. Renfro, University of Connecticut, USA

Temperature can be determined from fluorescence decay time of rare earth doped oxide ceramics. Doing so in Aircraft turbine environments is particularly challenging because of the high temperatures and the need to have phosphors compatible with the thermal barrier coating. A program is underway to accomplish this goal. Dy doped YAG has been made by solution precursor plasma spray (SPPS) and has the requisite temperature range which based on decay time measurement is from 1100 C to about 1600 C. Many other phosphors were tested and a method to collapse all data to one line has been found and some implications of this will be discussed. The range can be made extended to from 50 C to 1000 C by using peak height ratios. The thermal barrier coating is made of yittria stabilized zirconia (YSZ). YSZ and YAG have different coefficients of thermal expansion that may lead to durability problems. The doped Dy-YAG is applied over the YSZ coating by SPPS. In preliminary cyclic furnace tests to 1121 C no durability problems have been seen. We have also established a method to make composite coatings that are primarily YSZ with Dy doped YAG inclusions using twin injectors if better durability is needed. In the resulting micro composite the stresses due to expansion miss match will be at the micro level where there are far less likely to lead to unstable fracture.

11:00 AM

(ICACC-S2-039-2011) Thermal Imaging Measurement Accuracy for Thermal Properties of Thermal Barrier Coatings

J. Sun*, Argonne National Laboratory, USA

Thermal barrier coatings (TBCs) are being extensively used for improving the performance and extending the life of combustor and gas turbine components. TBC thermal properties, thermal conductivity and heat capacity (the product of density and specific heat), are important parameters in those applications. These TBC properties are usually measured by destructive methods, involving separating the ceramic coating layer from the substrate and performing density, specific heat, and thermal diffusivity measurements. Nondestructive evaluation (NDE) methods, on the other hand, allow for direct TBC property measurement on natural TBC samples so they can be used for inspecting the quality of as-processed components as well as monitoring TBC degradation during service. For this purpose, a multilayer thermal-modeling NDE method has been developed which analyzes data obtained from pulsed thermal imaging to determine thermal conductivity and heat capacity distributions over the entire surface of a TBC specimen. The measurement accuracy can be affected by many factors from experimental and sample condition variations. These factors are investigated in this study based on numerical simulations and experimental results for thermal imaging. When relevant, their effects to standard test method such as laser flash are also discussed.

11:20 AM

(ICACC-S2-040-2011) Determination of Average Surface Temperature of Thermal Barrier Coatings During Engine Operation and its Application to Assessment of Ex-Service Parts

G. Witz*, H. Bossmann, M. Schaudinn, S. Bachegowda, Alstom (Switzerland) ltd, Switzerland

Assessment of ex-service parts is important for power generation industry; giving the opportunity to correlate part conditions to specific operating conditions like fuel used, local atmospheric conditions, operating regime, temperature load, etc.; it also allow to check and validate thermal as well as mechanical models. One of the most valuable parameter for the part assessment is the knowledge of the local thermal condition; something that is not trivial to measure during engine operation or determine by modeling. In Alstom, a method has been developed, allowing determination of an ex-service part average surface temperature. The method has been validated by comparing it to thermal models and to base metal temperature mapping, showing a good correlation with both types of data. Data showing how this method can be applied for assessment of ex-service combustor liner condition will be also presented.

11:40 AM

(ICACC-S2-041-2011) Thermal Diffusivity Measurement by Thermographic Technique for the Non Destructive Integrity Assessment of TBCs Coupons

F. Cernuschi*, Enea Ricerca per il Sistema Elettrico, Italy; P. Bison, S. Marinetti, CNR-ITC, Italy; S. Capelli, L. Lorenzoni, Enea Ricerca per il Sistema Elettrico, Italy; E. Campagnoli, Politecnico di Torino, Italy

For thin (<200 micron) air plasma spray (APS) and electron beam physical vapor deposition (EBPVD) ceramic thermal barrier coatings (TBCs), some non-destructive techniques indicate damage at the bond coat-TBC interface during either ageing or cyclic oxidation tests. However, no technique is available for thick (>200 micron) APS TBCs. In this work, a semi-quantitative estimation of cracks at the interface of TBCs is obtained from thermal diffusivity values measured on coupons subjected to thermal cycling by using a single side thermographic technique. In fact, during thermal cycling, two phenomena occur: sintering that promotes a significant increase of thermal diffusivity, and cracking that, representing an additional thermal resistance, causes an apparent decrease of thermal diffusivity. The idea presented hereinafter consists in removing the effects of sintering from apparent thermal diffusivity to estimate cracking at the interface.

S3: 8th International Symposium on Solid Oxide Fuel Cells (SOFC): Materials, Science and Technology

Electrodes II

Room: Coquina Salon E
Session Chairs: Nguyen Minh, Consultant; Tatsumi Ishihara, Kyushu University

8:00 AM

(ICACC-S3-030-2011) Modification of SDC-LSCF cathode functional layer by solution infiltration

S. Lee*, N. Miller, H. Abernathy, K. Gerdes, M. Manivannan, U.S. Dept of Energy, National Energy Technology Laboratory, USA

Solution infiltration was used to modify a commercial SOFC cathode composed of a Sm_2O_3-doped CeO_2 (SDC) – $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-d}$ (LSCF) functional layer and an LSCF current collecting layer. Intro-

ducing a highly electrocatalytic Co-containing perovskite into the cathode increased the triple phase boundary length and decreased the electrode overpotential by 30 mV for a current density of 0.25 A/cm^2 at 750°C. Cathode performance was not greatly improved for the infiltrant loadings over 6 wt%, implying that only a couple of infiltration steps would be enough to significantly raise the oxygen reduction rate of the cathode. For over 200 hrs operation, the Ni-YSZ anode-supported fuel cell having a YSZ electrolyte and SDC-LSCF cathode infiltrated with Co-containing perovskite showed a change in polarization resistance of less than 0.02 Ωcm^2. Based on a comparative study on the infiltration of an electrocatalytic active component, the cobaltite perovskite, and an insulating phase, a Sr-doped lanthanum zirconate, we can discuss the electrochemical behaviors of the infiltrated cathodes based on relative electrocatalytic activity and mixed conductivity of the infiltrants.

8:20 AM

(ICACC-S3-031-2011) In-situ XRD of Operating SOFC Cathodes

J. Hardy*, J. Templeton, Z. Lu, J. Stevenson, Pacific Northwest National Laboratory, USA

A solid oxide fuel cell (SOFC) test fixture has recently been developed that makes it possible to measure the performance of an operating SOFC while simultaneously performing x-ray diffraction on its cathode. The evolution of this research tool will be presented together with SOFC performance data that was acquired from anode-supported cells while XRD patterns were being collected from their lanthanum strontium cobalt ferrite (LSCF) cathodes. The XRD measurements were performed over a 2-theta range of 25 – 85° and will be correlated to the performance data from the cell.

8:40 AM

(ICACC-S3-032-2011) Influence of the operation parameters on LSCF and LSF cathodes degradation

A. Arregui*, University of Trento, Italy; L. Rodriguez, IKERLAN S.Coop., Spain; S. Modena, M. Bertoldi, SOFCPOWER S.r.l., Italy; J. van Herle, EPFL, Switzerland; V. Sglavo, University of Trento, Italy

One of the key points in SOFC commercialization is to enhance the longterm stability of cathode materials. In this regard, higher performing [(La,Sr)(Co,Fe)O3-δ] and LSF [(La,Sr)FeO3-δ]-cathodes constitute a promising electrode material to decrease operation temperature in comparison to the conventional LSM. Nevertheless, LSCF and LSF cathodes have revealed intrinsic degradation mostly due to the perovskite instability and Sr segregation. As far as the chromium poisoning is concerned, mixed ionic-electronic conducting cathodes are probably more resistant than the conventional LSM, because electrochemically active area is not restricted to the triple phase boundary. In the present work, a detailed comparison of the state of the art cathode materials used in SOFCPOWER and Ikerlan SOFC technologies is presented. Anode supported SOFC cells developed at SOFCPOWER were used for standard comparison of both cathode materials (LSF and LSCF) through a Taguchi matrix. The individual effect of the operational parameters (temperature, current density, air flow, water vapor in cathode atmosphere) together with the influence of chromium have been evaluated along with the influence of cathode thickness and cathode sintering temperature. A detailed comparative analysis, using Impedance Spectroscopy, IV curves and Scanning Electron Microscopy will be presented.

9:00 AM

(ICACC-S3-033-2011) Effects of oxygen partial pressure on the sintering behavior of LSM – YSZ cathode

M. Mahapatra, P. Singh*, University of Connecticut, USA

Reaction between LSM cathode and YSZ electrolyte has been associated with the degradation of the electrical performance of solid oxide fuel cell (SOFC). Such interactions occur during the fabrication as well as operation of the cells. This presentation addresses the chemical stability issues encountered during the fabrication of the cell. La0.8Sr0.2 MnO3 and YSZ (8Y) powders were mixed and sintered at 1200-1400°C for 2-10 hr in controlled environment (PO2 = 0.21 to 10-6 atm). Extent of densification, surface morphology, and compound formation were studied using SEM, XRD, FIB, TEM and TGA-DSC techniques. Possible reaction mechanism, responsible for chemical interactions and morphological changes is proposed based on the thermo-chemical stability and the experimental results.

Electrolytes

Room: Coquina Salon E

Session Chairs: Tatsumi Ishihara, Kyushu University; Nguyen Minh, Consultant

10:00 AM

(ICACC-S3-035-2011) Novel and superior solid oxide fuel cell with 1 μm thick 8YSZ electrolyte layer

T. Van Gestel*, F. Han, H. Buchkremer, D. Stöver, Forschungszentrum Jülich, Germany

A solid oxide fuel cell (SOFC) with a thin-film 8YSZ electrolyte layer was developed and tested. This novel SOFC shows a similar multilayer set-up as other current anode-supported thin-film SOFC, with a Ni/8YSZ anode, a 8YSZ electrolyte layer and a LSCF cathode. To increase further the power density and lower the SOFC operating temperature, the thickness of the electrolyte layer was further reduced from around 10 μm to 1 μm, using a nano-particle deposition method. By using the novel electrolyte layer, the power output of our SOFC progressed to 2.7, 2.1 and 1.7 A/cm^2 at an operation temperature of 800, 700 and 650°C, respectively, and out-performs all similar cells reported to date in the literature. An important consideration is also that cost-effective dip-coating and spin-coating methods are used for the synthesis of the thin-film electrolyte and the scalability of the coating methods has been demonstrated by making prototypes with a dimension of 50 x 50 mm^2 and 100 x 100 mm^2. Further studies are currently devoted to the electrochemical characterization of the cells and first short stacks consisting of 4 cells have been made for long-term stability testing. In this paper, the preparation of the novel SOFC's is shown and their morphology is illustrated with high resolution SEM and TEM pictures. Further, the performance is demonstrated and the results of the ongoing stability tests are reported.

10:20 AM

(ICACC-S3-036-2011) Industrial-scale magnetron sputter deposition of YSZ and CGO thin films for SOFC applications

S. Sonderby*, Danish Technological Institute, Denmark; A. J. Nielsen, Aarhus University, Denmark; B. H. Christensen, K. P. Almtoft, L. P. Nielsen, Danish Technological Institute, Denmark; J. Bottiger, Aarhus University, Denmark; P. Eklund, Linkoping University, Sweden

This presentation focuses on synthesis and characterization of Y_2O_3-ZrO_2 (YSZ) and Gd_2O_3-doped CeO_2 (CGO) thin films as well as YSZ/CGO bi- and multilayer films for SOFC applications deposited in an industrial setup. All films are produced using a CemeCon CC800/9 Sinox coating unit applicable for medium scale production. The YSZ and CGO thin films were grown by reactive pulsed DC magnetron sputtering from $Zr_{0.84}Y_{0.16}$ and $Ce_{0.9}Gd_{0.1}$ targets, respectively. The substrates were traditional YSZ anodes and electrolytes in addition to Si wafers for easy characterization. We demonstrate homogenous deposition over large areas on substrates of sizes larger than 10 cm x 10 cm to satisfy industrial requirements. XRD, TEM and SEM characterization showed that dense films could be grown with a cubic fluorite crystal structure. On Si substrates, the texture of the YSZ films could be controlled through substrate bias voltage and temperature variations. Three regimes of different texture were observed at low, intermediate and high substrate bias voltages. The CGO films were highly textured, unless deposited at both low substrate bias and temperature. When depositing CGO or YSZ on poly-

crystalline YSZ anode substrates, local epitaxy on the individual grains in the substrate was seen. This is of technological importance for YSZ electrolytes and CGO barriers, as it may result in greatly improved adhesion.

10:40 AM

(ICACC-S3-037-2011) Defect equilibria, electrical properties, and thermo-chemical expansion of Pr doped ceria

S. Bishop*, J. Kim, W. Jung, Massachusetts Institute of Technology, USA; T. Stefanik, Nanocerox, USA; D. Chen, H. Tuller, Massachusetts Institute of Technology, USA

Many oxide mixed ionic electronic conductors (MIEC) can absorb or release oxygen above or below stoichiometry with changes in temperature and oxygen partial pressure (pO2), sometimes resulting in deleterious changes in their electrical and mechanical properties. When acceptor doped ceria solid oxide fuel cell (SOFC) electrolytes are exposed to a large pO2 gradient (air to fuel), they become MIECs, partially short circuiting the SOFC, as well as expanding (chemical expansion), resulting in stresses that can lead to mechanical failure. It is therefore important to measure these properties and develop a fundamental model to predict ways in which these effects can be mitigated as well as better understood. Pr doped ceria (PCO) is a particularly interesting oxide ion conductor to study because both Pr and Ce can change valence, meaning that as pO2 is decreased from high to low values, PCO transitions through an MIEC region to an ionic region and then back to an MIEC region while undergoing chemical expansion. In this work, experimental values for chemical expansion and electrical conductivity of bulk PCO samples and the modeling of these properties based on oxygen stoichiometry variations as a function of temperature and pO2 is presented. In addition, electrical properties of PCO thin films will also be presented.

11:00 AM

(ICACC-S3-038-2011) Circumventing Strontium Segregation in Strontium-doped La-Monazite Ceramics

M. Ng, J. C. Lucio-Vega, P. Morgan, M. L. Mecartney*, University of California, Irvine, USA

Monazite ($LaPO_4$) is a promising electrolyte material for intermediate temperature proton conducting fuel cells. Studies have shown that proton conduction improves with Sr-doping but higher doping levels results in second phase formation that draws Sr out of the material. In this study, ($La_{(1-x)}Sr_xPO_4$) powders were synthesized via solution precipitation coupled with low temperature humid sintering in an attempt deliberately to increase strontium-doping up to at least 10%. It was found that segregation of Sr rich material to triple grain junctions occurred only near the surface of the sample; this region can then be mechanically removed to produce single phase Sr-doped monazite bulk ceramic as verified by SEM and EDS. Proton conductivity measurements characterized by impedance spectroscopy will be reported for $La_{(1-x)}Sr_xPO_{4-x}(OH)_x$ (x = 0, 0.05, 0.10) ceramics.

11:20 AM

(ICACC-S3-039-2011) Materials for components of Solid Oxide Fuel Cells

A. K. Suri*, A. K. Sahu, D. Prakash, Bhabha Atomic Research Centre, India

The development of solid oxide fuel cell (SOFC) and related technologies in Bhabha Atomic Research Centre (BARC), India is linked to the utilization of the hydrogen produced in a Compact High Temperature Reactor (CHTR). One of the significant concerns of SOFC technology is the development of suitable materials for various components that perform synergistically with one another. An extensive R & D programme on materials for various components – cathode, electrolyte, anode and interconnect is currently being pursued. The candidate materials presently considered for these components are lanthanum strontium manganite (LSM), 8 mol % Y2O3 stabilized zirconia (YSZ), Ni-YSZ cermet and doped (Mg and Ca) lanthanum chromites (LCs) respectively. These materials have been synthesized by novel solution based techniques. The powder treatment conditions have been optimized to obtain sintered bodies with desired properties (density/porosity, CTE, electrical conductivity). Processing conditions have been optimized for fabrication of various components by different techniques such as extrusion, CIP, dip coating, EPD. Test cells in the integrated form using the materials developed have been fabricated and evaluated for electrical characteristics. The open circuit voltage and I–V characteristics of the cell have been studied.

S4: Armor Ceramics

Nondestructive Characterization

Room: Coquina Salon D
Session Chair: Lisa Prokurat Franks, TARDEC

8:00 AM

(ICACC-S4-031-2011) Nondestructive Evaluation of Armor Ceramics (Invited)

R. B. Thompson, L. Brasche*, Iowa State University, USA

The movement to engineered, ceramic-based armor has increased the need for advanced inspection techniques to assure that the fabrication has been conducted within the tolerances required to assure the desired ballistic properties. This talk will present a number of resulting nondestructive evaluation (NDE) considerations. The talk will first review the role of NDE at different stages in the product development cycle. Attention will then turn to a discussion of available NDE techniques for the assessment of the quality of individual components of armor systems such as the ceramic core, including relative advantages and disadvantages. NDE of armor systems, which places a different set of requirements on the inspection techniques, will then be discussed. As an example, a set of results obtained on composite encapsulated ceramic armor will be presented. Included will be a discussion of a general methodology used to optimize the inspection and results on a set of panels that were fabricated for ballistic studies. The talk will conclude with a consideration of possible future directions.

8:30 AM

(ICACC-S4-032-2011) Determination of Bulk Heterogeneity Size Distributions in Armor Grade SiC Through Acoustic Spectroscopy

A. Portune*, R. Haber, Rutgers University, USA

The mechanical properties and performance of armor grade ceramic materials are dependent upon microstructural uniformity. The presence of bulk heterogeneities may detriment performance in high strain rate applications by acting as stress concentrators from which cracks propagate. In this work, a series of dense sintered SiC materials were studied using acoustic spectroscopy in the 10-80MHz range to determine variations in the concentration and size distribution of solid bulk heterogeneities. Application of acoustic physics defining absorption and scattering losses enabled identification of peaks in the loss spectrum for boron carbide and carbonaceous inclusions. Curve fitting provided attributes of each peak which were used to predict the mean size and concentration of each secondary phase. Mechanical sectioning and microscopy corroborated predictions made from ultrasound testing within ±0.50μm. Extension of acoustic spectroscopy techniques to large sample areas provided maps of variances in the concentration and size distribution of heterogeneities throughout the SiC tiles.

8:50 AM

(ICACC-S4-033-2011) Ultrasonic Nondestructive Characterization and its Correlation to Alumina Microstructure

S. Bottiglieri*, Rutgers University, USA

Ultrasonic nondestructive evaluation is currently used to spatially locate heterogeneities within dense ceramics and measure the elastic properties of these materials. The use of acoustic spectroscopy in dense ceramics to measure heterogeneity size, grain size, and hardness has had little investigation. Understanding the acoustic interaction within a ceramic material and the causes of energy loss for different frequency regimes can lead to a predictive method of using acoustic spectroscopy to understand microstructural parameters. This research focuses on the development of acoustic spectroscopy as a tool for microstructural characterization in dense aluminum oxide. As part of this research specific alumina sample sets were fabricated to control and vary different microstructural features such as additive content and grain size. Independently controlling certain aspects of the alumina microstructure lead to a better understanding of how the microstructure causes energy loss over an acoustic attenuation coefficient spectrum.

9:10 AM

(ICACC-S4-034-2011) Low Velocity Impact Damage Characterization of Transparent Materials

R. E. Brennan*, W. H. Green, U.S. Army Research Laboratory, USA

Advanced transparent materials are utilized to improve protection efficiency for lightweight vehicles and warfighters in applications such as face shields, riot gear, and vehicle windows. If any damage occurs, the ability to withstand single or multiple hits from various threats could be compromised. While these issues are most likely to occur due to impacts from high velocity projectiles during combat, they may also be the result of low velocity impacts from collisions, severe environmental conditions, or foreign object debris. In this study, transparent materials will be tested by comparing baseline conditions to experimentally controlled damage states. Destructive testing including air gun and sphere impact testing will be used to simulate low velocity impacts in the field. Characterization of the damaged state will include visual inspection, cross-polarization, x-ray, and ultrasound techniques. The combination of destructive testing and characterization of the resulting damage can help to establish a damage acceptance criterion for transparent materials used in protective systems.

9:50 AM

(ICACC-S4-035-2011) Statistical Quantification and Sensitivity Prediction of Phased-Array Ultrasonic Data in Composite Ceramic Armor

J. Steckenrider*, Illinois College, USA; T. J. Meitzler, U.S. Army, USA; W. A. Ellingson, Argonne National Laboratory, USA; L. Prokurat Franks, U.S. Army, USA

A series of 16-inch square by 2-inch thick, multi-layered ceramic composite armor specimens, some of which had intentional design defects inserted between the layers, were inspected using a 128 element, 10MHz immersion phased array ultrasound system. To overcome some of the issues associated with the acoustic wave propagation in layered media, two digital signal processing methods (FFT and Wiener filtering) were employed. While previous work has been presented on the significant improvement in defect detection associated with these methods, this paper presents a detailed and quantitative statistical analysis of these results. This analysis suggests that these intentional defects were a) not detectable when the defect was in a particular configuration, b) readily detectable in all cases for alternate defect position configurations, and c) clearly identifiable in most cases for those configurations. However, even in the configuration where intentional defects were not detected (owing to inherent design issues in the armor structure), significant variation in interfacial quality was observed and quantified, and these results will also be presented.

10:10 AM

(ICACC-S4-036-2011) Comparison of Penetration Damage in Novel Mg Specimens via Computed Tomography

W. H. Green*, K. C. Cho, U.S. Army Research Laboratory, USA

X-ray computed tomography (XCT) has been shown to be an important non-destructive evaluation (NDE) technique for revealing the spatial distribution of ballistically-induced damage in metals, ceramics, and encapsulated ceramic structures. Previous and ongoing work in this area includes assessment of ballistically induced damage in relatively lightweight individual ceramic targets and ceramic armor panels. In this paper the ballistic damage in two novel Mg alloy samples was completely scanned and extensively evaluated using XCT 2-D and 3-D analysis. Features of the damage in the samples were compared and contrasted. Some features of the damage were correlated with physical processes of damage initiation and growth. XCT scans and analyses of damage in the samples will be shown and discussed. This will include virtual 3-D solid visualizations and some quantitative analysis of damage features.

10:30 AM

(ICACC-S4-037-2011) Application of a Miniaturized Portable Microwave Interference Scanning System for Nondestructive Testing of Composite Ceramic Armor

K. Schmidt*, J. Little, Evisive, Inc., USA; W. Ellingson, Argonne National Laboratory, USA; L. P. Franks, US Army RDC TARDEC, USA; W. Green, US Army Research Laboratory, USA

A microwave interferometry system has been miniaturized and configured for flexible field use to determine the "status" of composite ceramic armor. The system utilizes Evisive Scan microwave interference scanning technique and has been demonstrated to detect damage on composite ceramic test specimens as well as composite ceramic surrogates with engineered features. The microwave interference scanning technique has demonstrated detection of cracks, interior laminar features and variations in material properties such as density. 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. Other methods, including through-transmission x-ray, x-ray Computed Tomography, and destructive examination, have been used to corroborate the microwave data and establish quantitative performance. Test panels used in this work were provided by commercial manufacturers, the US Army Research Laboratory, US Army Tank-Automotive Research, Development and Engineering Center (TARDEC) and by the Ballistics Testing Station through Argonne National Laboratory. This paper will describe the system and present current results. This work is supported by US Army Tank-Automotive Research, Development and Engineering Center (TARDEC) and US Army Research Laboratory.

Multi-Scale Modeling I

Room: Coquina Salon D
Session Chair: Lisa Prokurat Franks, TARDEC

10:50 AM

(ICACC-S4-038-2011) Multiscale Modeling of Armor Ceramics: Focus on AlON (Invited)

G. A. Gazonas*, USARL, USA

This talk will outline a multiscale modeling effort for first-principles design of armor ceramics, with a focus on polycrystalline aluminum oxynitride (AlON), and the special computational challenges that are required for linking the vast spatiotemporal scales from the quantum

to the continuum. The computational bridge linking atomistic and continuum length scales is addressed through development of: 1) a first principles unit cell model to predict the anisotropic elastic properties of AlON, 2) a molecular dynamics model for the study of single crystal slip and twinning dynamics, 3) a single crystal anisotropic elastic-plastic model to account for crystal slip and twinning mechanisms, 4) a mesoscopic polycrystalline FE model that incorporates single crystal deformation kinematics, and explicitly includes microcracks at grain boundaries using cohesive interface laws that allow investigation of crack nucleation, growth, and coalescence, and 5) a continuum FE model with an algorithm for coarse-graining microcrack coalescence behavior at the mesoscale to the continuum scale in a consistent fashion.

11:20 AM

(ICACC-S4-039-2011) Atomic structure and elastic properties at high pressure of aluminum oxynitride in cubic phase

I. G. Batyrev*, B. M. Rice, G. A. Gazonas, J. W. McCauley, US Army Research Laboratory, USA

The atomic structure and elastic properties of aluminum oxynitride spinel (AlON) at high pressure (up to 40 GPa) have been calculated from first principles. We have assumed an "ideal" stoichiometry of cubic AlON with 35.7 mole % AlN using the constant anion model. The elastic constants were calculated from independent strains that were applied to a unit cell, parameterizing the total energy as a function of the strain and from a stress-strain relationship. The purpose of the calculations is to determine if the location and/or segregation of N atoms in the unit cell affects the elastic properties of AlON. At ambient conditions a clustered distribution of N atoms has ~ 1 eV per 55 atoms higher total energy than for a random distribution and slightly, but systematically lower elastic constants. The pressure dependence of C11, C12 and C44 for random and cluster distributions of N atoms was calculated in the range of 0-40 GPa by performing six finite distortions of the lattice and deriving the elastic constants from the strain-stress relationship. The calculated values of dC11/dP are in the range of 4.0-6.2 and for dC44/dP ~0.8-1.5. The estimates are in reasonable agreement with experimental measurements of polycrystalline AlON. The structure of AlON with random distribution of N atoms was specified by using of the evolutionary algorithm with permutation operators.

11:40 AM

(ICACC-S4-040-2011) First Principles Calculation of Stress Induced Amorphization in Boron Carbide

D. Taylor*, Army Research Laboratory, USA; T. Wright, Johns Hopkins University, USA; J. McCauley, Army Research Laboratory, USA

Recent work at the Army Research Laboratory and Johns Hopkins University has identified the formation of nanoscale sized intragranular amorphous bands which seemingly lead to a dramatic change in the dynamic impact fragmentation of B4C. Pressure induced amorphization has been observed in other materials (α-quartz) and has been examined through analysis of the Born stability criteria which impose restrictions on the relative magnitudes of the elastic constants of a stable crystal structure. In the most general representation, the crystal structure stability is characterized by an elastic constant tensor that is positive definite. When the tensor becomes singular, a topologic or geometric instability occurs and further increments of strain along the corresponding eigenvector will cause no change in incremental stress and amorphization may occur. Almost all research has concentrated on the effect of hydrostatic pressure, however in this work, we intend to facilitate the study of the effect of shear on amorphization by using a stress/strain representation for finite elastic response that takes account of the fundamental symmetries of the boron carbide crystal structure. Elastic constants resulting from ab initio quantum chemistry calculations will be presented and the implications of the pressure softening of the C44 modulus will be discussed.

S5: Next Generation Bioceramics jointly with S9: Porous Ceramics

Porous Bioceramics I (joint with Symposium 9)

Room: Ponce de Leon
Session Chairs: Donglu Shi, University of Cincinnati; Aldo Boccaccini, University of Erlangen-Nuremberg

8:00 AM

(ICACC-S5-001-2011) Development of Nano-Macro Porous Bioactive Glass for Biomedical Applications (Invited)

S. Wang, H. M. Moawad, Lehigh University, USA; Y. Vueva, IST/UTL, Portugal; A. Rashad, Alexandria University,, Egypt; M. Saad, Alexandria University,, Egypt; R. Almeida, IST/UTL, Portugal; M. Falk, Lehigh University, USA; M. Marei, Alexandria University,, Egypt; H. Jain*, Lehigh University, USA

There is increasing interest in biocompatible/bioactive porous glass or ceramic structures for various biomedical applications. For example, bioactive materials are needed for use as bone and dental scaffolds, resorbable structures can be useful for drug delivery, etc. For most cases, a range of interconnected pores is needed with size ranging from a few nm to 100s of microns. Often the nano and macro pores at the two ends, differing in size by five orders of magnitude, serve different purposes, and therefore their independent control is desired during fabrication. For instance, macro pores larger than 300 μm are needed for the infiltration of osteoblasts, vascularization, etc. within a bone scaffold, whereas nano pores of specific size may be needed to provide optimum resorption rate, supply nutrients, etc. In this presentation, we will review and compare various methods for the fabrication of nano-macro porous glass and glass-ceramic structures, especially focusing on the ones recently developed in our laboratories by exploiting spinodal decomposition for interconnectivity and multiscale phase separation / devitrification for the generation of appropriate size pores. Biocompatibility of the material is verified in-vitro by the formation of hydroxyapatite layer and observing the proliferation of MC3T3 bone precursor cells as well as by the in-vivo response in animal models.

8:30 AM

(ICACC-S5-002-2011) Preparation and Characterization of Porous Wollastonite-Hydroxyapatite Bioceramics from a Preceramic Polymer Filled with Nano-particles (Invited)

E. Bernardo*, P. Colombo, University of Padova, Italy; I. Cacciotti, A. Bianco, University of Rome "Tor Vergata", Italy; R. Bedini, P. Raffaella, Italian National Institute of Health, Italy; L. Treccani, K. Rezwan, University of Bremen, Germany

Wollastonite/hydroxyapatite ceramics have been successfully prepared by the heat treatment of a silicon resin with suitable fillers and thermally treated in air. CaCO3 nanoparticles, providing CaO upon decomposition, acted as "active" filler, whereas micro-, commercial or synthesised nano-hydroxyapatite particles acted as "passive" filler. The homogeneous distribution of CaO, at a quasi-molecular level, favoured the reaction with the silica derived from the polymer, at the relatively low temperature of 900°C, preventing the thermal decomposition of hydroxyapatite. Open-celled porous ceramics were easily prepared from mixtures of filler-containing silicone resin with sacrificial PMMA templates or by adopting fuse casting techniques. The pore size (in the range of 80-400 μm) and the open porosity percentage (40-50%) were evaluated by means of micro–computerized tomographic (μ-CT) analysis, reconstructing the three-dimensional images of the products. The biocompatibility and bioactivity of the produced ceramics was further assessed by in vitro tests using human osteoblast cells. Such materials find potential applications for bone restoration and bone tissue engineering.

9:00 AM

(ICACC-S5-003-2011) Bioactive Calcium Phosphates and their Use for Composite Scaffolds in Bone Tissue Engineering (Invited)

M. Wang*, The University of Hong Kong, Hong Kong

In developing biomaterials for human tissue repair, the research on bioceramics has a relatively long history and synthetic bioactive calcium phosphates (including apatites) have been extensively investigated over the past three decades. Bioactive calcium phosphates are viewed as materials for hard tissue replacement as they are perceived as non-biodegradable. The branch of bioactive calcium phosphates of bioceramics has matured and the continued research concerning these materials is mainly applications-oriented. Tissue engineering emerged as a promising means for treating tissue loss. It emphasizes on tissue regeneration, requiring the use of cells and the provision of a microenvironment for the cells to attach and proliferate, leading to new tissue formation. In scaffold-based tissue engineering, 3D porous scaffolds are a key requirement. Composite scaffolds containing bioactive calcium phosphates can be very useful for bone tissue engineering, utilizing the osteoconductivity of calcium phosphates. Biodegradable polymer-based composite scaffolds can be produced by: (1) incorporating bioceramic particles in the scaffold; or (2) coating a polymer scaffold with a thin layer of apatite. Using either approach, factors such as matrix polymer, bioceramic phase, polymer-bioceramic interaction, etc. must be considered in order for the tissue engineering strategy to be successful.

9:50 AM

(ICACC-S5-004-2011) Morphological Control of Freeze-Cast Ceramics with Different Compositions (Invited)

M. White*, R. Chen, Dalhousie University, Canada

The control of porosity in technical ceramics is very important because of its relationship to physical properties, such as toughness, strength, thermal conduction, etc. Furthermore, porous ceramics can form the basis for hybrid materials, including bioceramics. Here we report the results of freeze-cast preparations of porous ceramics with different morphologies and compositions controlled by the slurry materials and binder concentrations. Compositions investigated include Al2O3, TiO2 and zeolite Y. We are able to control the interior structures of the ceramics, allowing lamellar, reticulate or dendritic structures. Furthermore, the distance between lamellae could be adjusted from 2 to 20 μm. This synthetic method provides a new means to design the interior morphology for ceramics.

10:20 AM

(ICACC-S5-005-2011) Hydroxyapatite scaffolds for bone tissue engineering with controlled porosity and mechanical strength

V. M. Sglavo*, A. Madinelli, M. Piccinini, University of Trento, Italy; F. Bucciotti, Eurocoating spa, Italy

Hydroxyapatite (HA) macroporous scaffolds suitable for bone tissue engineering applications with controlled porosity and mechanical strength were realized and characterized in the present work. The foam replica method was employed for the production of the ceramic and processing conditions were varied in order to obtain materials with different porosity, macro-pores size and compressive strength. Porosity from 70 to 80% and strength from 0.5 to 2 MPa were obtained. An interconnected porous structure with pore sizes between 100 and 500 μm is obtained, this allowing cells penetration, tissue ingrowth and vascularization as required in bone tissue engineering.

10:40 AM

(ICACC-S5-006-2011) Nanocrystalline apatite coatings for porous bioceramics; role on bone osteogenesis (Invited)

H. Autefage, F. Briand-Mesange, A. Gomez-Brouchet, S. Palierne, J. Briot, University of Toulouse, France; S. Goncalves, Teknimed, France; S. Cazalbou, C. Combes, C. Drouet, A. Autefage, D. Mathon, P. Swider, C. C. Rey*, University of Toulouse, France

Nanocrystalline apatites coatings have been proposed to enhance the biological activity of prosthetic devices and bone substitute ceramics. Coatings with different characteristics can be obtained within the pores of porous calcium phosphate ceramics sintered at high temperature using different techniques. The physical-chemical characteristics of these coatings are compared and the biological efficiency of one of them was evaluated in vitro (osteoblast cell culture) and in vivo (implantation in sheep). Different surface structures and morphologies were obtained depending on the coating process. Nanocrystalline apatite coatings increased the specific surface area of the porous ceramics without altering strongly the network of interconnected macropores. Additional inter-crystalline nanosized pores were formed. The biocompatibility of the coated ceramics was demonstrated in cell culture experiments. In vivo implantations revealed that the coated ceramics promoted the formation of bone without any added growth factor. At 3 months after implantation, the nanocrystalline coating appears as efficient, regarding osteoinduction, as sintered ceramics loaded with a growth factor, rhBMP-2. This very strong and highly specific effect of a nanocrystalline apatite coating is discussed considering the proposed mechanisms of osteoinduction.

11:10 AM

(ICACC-S5-007-2011) Load bearing, biocompatible and bio absorbable porous scaffolds (Invited)

S. Mullens*, J. Luyten, VITO, Belgium

Bone tissue engineering with the help of porous scaffolds is an amazing technology for repairing large bone defects. Although the huge progress made in the last years, this procedure encounters many practical problems. In this contribution we focus only on the first step: the synthesis of a proper porous scaffold. In our powder processing group at VITO, we produce porous load bearing and bioresorbable porous scaffolds respectively in Ti6Al4V and CaP by gel casting and by a 3D fiber deposition method. The porous scaffolds manufactured by gel casting mimic the macro properties of trabecular bone (porosity, pore size range, strength, young modulus and ductility). To increase their bioactivity, the metal scaffolds were coated with CaP by a biomimetic precipitation technique. More recently, we give also attention to porous Mg with the aim to produce a scaffold having load bearing and bioresorbable properties. Processing such Mg scaffold is a big challenge due to the high reactivity of the material. In addition the high corrosion rate of the Mg in a physiological environment has to be decreased.

11:40 AM

(ICACC-S5-008-2011) Development of porous ceramics with bioactive properties

D. Koch*, L. Treccani, B. Müller, M. Pulkin, K. Rezwan, Univ. of Bremen, Germany

Calcium phosphate ceramics are excellent materials for biomedical applications especially when resorbability and bioactivity can be adjusted for enhanced cell growth on the surface of the components. In this work the freeze gelation process is used for manufacture of ceramic components when a water based slurry consisting of silica sol and hydroxyapatite powder is transformed via sol gel transition forced by freezing. After freezing and warming up to room temperature a rigid body with reasonable green strength is achieved and no freeze drying is necessary. When sintered for high strength additionally a phase transformation from silica and hydroxylapatite to tricalcium phosphate can be provoked resulting in good resorbability. In order to functionalize the surface and to enhance cell adhesion proteins as serum albumine, lysozyme or fibrinogene can be attached to the surface. Alternatively the proteins can be added directly to the ceramic slurry and distributed homogeneously. In this so-called one step process no sintering is possible after freezing and drying at room temperature, however proteins act as binder and enhance the green strength of the net shape structures. The cell tests show that the pore morphology induced by freezing and the protein containing microstructure leads to preferred cell growth.

S7: 5th International Symposium on Nanostructured Materials and Nanotechnology: Development and Applications

Nanomaterials for Photocatalysis, Solar Hydrogen and Thermoelectrics

Room: Coquina Salon C
Session Chairs: Mrinal Pai, Bhabha Atomic Research Centre; J. Morante, University of Barcelona

8:00 AM

(ICACC-S7-021-2011) Chemical Approaches to Functional Nanostructures: Growth, Applications and Devices

S. Mathur*, University of Cologne, Germany

Chemical design of inorganic materials deals with the transfer of short range chemical order, present in the molecular precursor state, to infinite correlation lengths in three dimensions. A generic chemical strategy based on the transformation of molecular precursors into functional inorganic nanostructures allows producing nanomaterials of different dimensions and morphologies with precisely controlled chemical composition and phase purity. The successful synthesis, modification and assembly of nanobuilding units such as nanocrystals, -wires and –tubes of different materials have demonstrated the importance of chemical influence in materials synthesis, and have generated great expectations for the future. Inorganic nanostructures inherit promises for substantial improvements in materials engineering mainly due to improved physical and mechanical properties resulting from the reduction of microstructural features by two to three orders of magnitude, when compared to current engineering materials. The chosen examples will include nanostructured functional films for hydrophobic, hydrophilic and barrier properties, application of superparamagnetic iron oxide nanoparticles for drug delivery applications, molecule-based synthesis of nanowires and 1D heterostructures for energy applications.

8:20 AM

(ICACC-S7-022-2011) Microwave-assisted fabrication of nanostructured α-Fe2O3 films for solar-driven hydrogen generation

B. Vaidhyanathan*, S. Saremi-Yarahmadi, Loughborough University, United Kingdom; U. Wijayantha, Loughborougu Univeristy, United Kingdom

It is demonstrated for the first time that significant enhancement of photoelectrochemical performance could be achieved by using microwave-assisted annealing for the fabrication of α-Fe2O3 thin films. Different types of Fe thin films were oxidized using both microwave and conventional heating techniques. Electrodeposited, undoped and Si-doped iron oxide samples showed that microwave-annealing resulted in superior structural and performance enhancements. The photocurrent densities obtained from microwave annealed samples are among the highest values reported for α-Fe2O3 photoelectrodes fabricated at low temperatures and short times; the highest photocurrent density at 0.55 V vs. VAg/AgCl, before the dark current onset, was 450 μA.cm-2 for the Si-doped films annealed at 270 °C for 15 minutes using microwave irradiation (and 180 μA.cm-2 at 0.23 V vs. VAg/AgCl) while conventional annealing at the same temperature resulted in samples with negligible (3 μA.cm-2) photoactivity. The improved performance is attributed to the lower processing temperatures and rapidity of the microwave method that help to retain the nanostructure of the thin films whilst restricting the grain growth to a minimum. The lower processing temperature requirements of the microwave process can also open up the possibility of fabricating hematite thin films on conducting, flexible, plastic electronic substrates.

8:40 AM

(ICACC-S7-023-2011) Synthesis and properties of the mesoporous ceria zirconia solid solutions: Improvement of oxygen storage capacity

S. Abdollahzadeh-Ghom, University of Barcelona, Spain; T. Andreu, IREC, Catalonia Institute for Energy Research, Spain; M. Epifani, Instituto per la Microelettronica e i Microsistemi, Italy; J. R. Morante*, University of Barcelona, Spain

Mesoporous phases of ceria and ceria-zirconia up to 50% of Zr have been synthesized using hard template method. The structures of the obtained metal oxides replicas correspond to the chosen structures of the KIT-6 and SBA-15 silica. This method allows obtaining materials with a uniform and homogenous porous size distribution as replica of the used nanotemplate. This structure facilitates the interaction with the gas molecules, their diffusivity inside the material and the porous size control. Obtained replicas were analyzed using a variety of characterization techniques. TEM results reveal successful formation of the expected structures which were also supported by BET measurements. Replicas obtained applying SBA-15 and KIT-6 nanotemplates present similar behavior although KIT-6 shows a slightly higher active surface 5% with values in the range of 125 m2/g after thermal annealing. XRD and Raman spectra confirm formation of solid solutions with cubic structure up to 20% of zirconium. Above 20% of zirconium, formation of tetragonal phase has been observed. Functionally, besides their high active surface, these ceria-zirconia solid solutions show an important improvement in their oxygen storage capacity (OSC). In comparison with the pure mesoporous ceria, an increment of more than 30 times in its OSC has been found due to the introduction of zirconium.

9:00 AM

(ICACC-S7-024-2011) Photocatalytic Activity of 3- and 4-Layered Aurivillius Oxides

V. L. Knox*, E. J. Nichols, T. A. Nedimeyer, M. Haluska, S. T. Misture, Alfred University, USA

Aurivillius oxides are comprised of $[Bi_2O_2]^{2+}$ layers interleaved between perovskite blocks. Aurivillius oxides are unique because the bismuth oxide layer can be replaced using an ion exchange process. In this study, 3- and 4-layer Aurivillius oxides, $Bi_2A_2B_2TiO_{12}$ and $Bi_2A_3B_2Ti_2O_{15}$ (A=Ca, Sr, Ba; B=Ta, Nb) have been synthesized using solid state synthesis methods. The phase pure compositions have band gaps within the UV region of the electromagnetic spectrum, 3.3-3.5eV. The powders were leached in acid to exchange the $[Bi_2O_2]^{2+}$ layer with protons, thus partially exfoliating the crystals. The structural change yields slight increase in band gap, of approximately 0.2eV. Photocatalytic activity was quantified using a methylene blue degradation technique. The ion-exchanged forms yield degradation rates that are about twice those of the unaltered forms; compared to the commercial standard of Degussa P25 (TiO_2) which degrades methylene blue within one hour.

9:20 AM

(ICACC-S7-026-2011) A Review on Indium Titanate Based Photocatalysts for Water Splitting Reaction (Invited)

M. R. Pai*, A. M. Banerjee, S. R. Bharadwaj, Bhabha Atomic Research Centre, India

In the search for efficient photocatalysts for hydrogen evolution via water splitting, several types of materials including TiO2, metal oxides, nitrides, sulphides, oxysulfides, oxynitrides, niobates, tantalates, and titanates, have been studied [1-3]. However, most of the photocatalysts studied are deficient either in activity or stability and the maximum energy conversion efficiency of water splitting achieved up to now is still far from the required efficiency for practical applications. Hence, the development of new and superior photocatalyst materials is still a major issue. The In2TiO5, was selected as a photocatalyst, as it is composed of the octahedral [TiO6] and [InO6] mo-

tifs, containing both early-transition metal (d0) and p-block metal (d10). [InO6] octahedra in the crystal structure are considered to favour the mobility of charge carriers and elevate the photocatalytic activity.

10:10 AM

(ICACC-S7-027-2011) Nanostructured Fe-TiO2 thin film modified by Zn-Fe2O3 for solar hydrogen generation

P. Sharma, P. Kumar, R. Shrivastav, S. Dass, V. R. Satsangi*, Dayalbagh Educational Institute, India

Nanostructured titanium dioxide (TiO2) has emerged as an attractive material for its use in photoelectrochemical cell (PEC) because of its easy access, chemical stability and favourable band edge position. The major impediment in the use of TiO2 as photoelectrode is its wide bandgap (~3.2 eV) which allows only 4% absorption of solar energy. Modification of the TiO2 with the low bandgap material, α-Fe2O3 is one of the proficient ways to extend its absorption edge in the visible region, thereby improving its overall visible light photoresponse. In this study, iron doped nanostructured TiO2 (Fe-TiO2) thin films prepared by the sol-gel process has been modified with spray pyrolytically deposited Zn-Fe2O3 to explore its application in photoelectrochemical cell. Photoresponse of the modified photoelectrodes in visible light illumination was obtained with varying thickness of overlayered iron oxide thin film. The modified photoelectrodes exhibited higher photocurrent and photovoltage values than those of pristine Fe-TiO2 thin films. Maximum photocurrent density of 690 μA/cm2 at 0.85 V/SCE was observed for modified thin film photoelectrode. To support and analyse PEC results XRD, AFM, UV-VIS spectroscopy of the samples were carried out.

10:30 AM

(ICACC-S7-028-2011) Effect of Manganese incorporation on Photo-Electro-Chemical Application of Nano-Structured ZnO for Solar-Hydrogen Generation

V. Sharma, P. Kumar, J. Shrivastava, A. Solanki, S. Upadhayay, N. Singh, V. R. Satsangi, S. Dass, R. Shrivastav*, Dayalbagh Educational Institute, India

On account of the high stability and appropriate aligned band edges, nanostructured ZnO has becomes a very promising material for photoelectrochemical splitting of water to generate hydrogen. However, ZnO is not an efficient absorber of solar energy because of its high band gap energy. Major efforts are therefore needed to lower its band gap without compromising other advantageous material characteristics. Further, the creative synthesis procedures/protocols that lead to bulk generation of such nano-structured material are also needed for real life applications. In this study, an attempt has been made to synthesize Manganese incorporated nano-structured ZnO thin films by sol-gel spin-coating process on conducting glass substrate. Prepared thin films were characterized for: (a) formed crystalline phase by XRD analysis, (b) band gap energy by spectrometric measurement and (c) surface topography by AFM analysis. Subsequently, these were used as working electrode in PEC cell in conjunction with a platinum counter electrode, saturated calomel reference electrode and 150 W Xenon Arc Light Source for illumination, and PEC current densities were recorded under varied conditions. AFM analysis indicated preferential growth of nanocrystallites along c-axis.

10:50 AM

(ICACC-S7-029-2011) Nanofiber Networks as Electrode Materials for Li Ion Batteries by Electrospinning

R. von Hagen, X. Song*, A. Lepscha, M. Büyükyazi, S. Mathur, University of Cologne, Germany

Due to their enhanced properties (e.g., cycling stability, short diffusion path length), nanostructured electrode materials are one key step leading to lithium ion batteries with high power and energy density as they are desired for 2nd generation applications such as electromobility. Therefore a low cost production and simple integration of these materials into the batteries assembly is needed. The electrospinning method offers a great potential in the design and production of anode/cathode materials such as nanofibers of complex structure and composition. The fiber networks could directly be used in batteries with no need of additional binder or carbon powder. By the judicious choice of precursor solutions in sol-gel type electrospinning and the calcination of the fiber networks under inert atmosphere, we are able to produce Si/Sn/C anodes and Li3V2(PO4)3 cathodes which showed superior electrochemical performance. The nanofibers further were characterized by SEM, HR-TEM and XRD before and after the electrochemical cycling. The electrochemical performance was depending on the morphological and compositional characteristics of the nanofibers, which could be controlled by the precursor solutions, spinning and calcination parameters.

11:10 AM

(ICACC-S7-030-2011) Functional and Thermoelectric Properties of Multiwalled Carbon Nanotube and Zirconia Composites

K. Ahmad*, Tsinghua University, Pakistan; P. Wei, Tsingha University, China

Carbon nanotubes (CNT) are promising additive due to their outstanding electrical, mechanical, and thermal properties and have spurred considerable activity in the development of multifunctional value-added ceramic nanocomposites. The incorporation of CNTs into the bulk ceramic matrix provides new opportunities to design thermoelectric nanocomposites for achieving high figure of merit. Zirconia (3Y-TZP) is a versatile key engineering ceramic for wide range of structural applications. In this work, zirconia composites with different contents of multiwalled carbon nanotubes (MWNTs) were fabricated by Spark Plasma Sintering. The electrical, mechanical, thermal and thermoelectric properties of the composites were scrutinized. Results have shown that the incorporation of low fractions of MWNTs can be used successfully to convert electrically insulating zirconia into electrically conducting composites through spanning networks of MWNTs. The thermal conductivity of the composites decrease with increase of MWNT contents, which suggests that interfacial thermal barrier play a key role in determining thermal properties. In case of mechanical properties, no prominent improvements have been observed. The composites also demonstrated interesting thermoelectric properties suggesting potential for use as a promising thermoelectric material.

S8: 5th International Symposium on Advanced Processing and Manufacturing Technologies for Structural and Multifunctional Materials and Systems (APMT) in honor of Professor Katsutoshi Komeya

Design-Oriented Manufacturing I

Room: Coquina Salon B
Session Chairs: Wayne Kaplan, Technion - Israel Institute of Technology; Junichi Tatami, Yokohama National University

8:30 AM

(ICACC-S8-033-2011) Microstructural Control of Ceramic Matrix Nanocomposites via Interface Complexions (Invited)

W. D. Kaplan*, G. Gluzer, M. Baram, Technion - Israel Institute of Technology, Israel

The existence of nanometer-thick intergranular films (IGFs) at metal-ceramic interfaces has been experimentally verified for a number of metal (Ni, Cu, Au) alumina systems. Detailed aberration corrected transmission electron microscopy has provided the microstructural features of the films, and experimental measurements of the interface energy has shown that the presence of an IGF reduces the interface energy and increases metal-alumina adhesion. These

measurements also indicate that IGFs are an equilibrium phenomenon, and can be classified as an interface complexion. In the present study controlled doping of metal-reinforced alumina matrix nanocomposites has been used to produce nanocomposites with and without IGFs. The mechanical properties and microstructural evolution of the nanocomposites, in particular the location of the metal particles within the alumina matrix, has been correlated with the presence of IGFs. The use of IGFs as a means to control the microstructure and properties of metal-reinforced nanocomposites will be discussed.

9:00 AM

(ICACC-S8-034-2011) Hyperbranched Boron-modified Polysilazane as a Novel Single-source Precursor for SiBCN Ceramic

J. Zou*, L. An, University of Central Florida, USA

A hyperbranched boron-modified polysilazane in which boron, silicon and nitrogen atoms are bonded in an alternating sequence was synthesized through a A2+B3 polycondensation reaction, in which A2 represents a difunctional monomer of N, N-bis(trimethylsilyl) methylamine and B3 represents a trifunctional monomer of (tris (dichloromethylsilylethyl)borane). The synthesis was characterized by means of FTIR and NMR spectroscopies. By controlling the A2 to B3 ratios, the obtained polymers ranges from low viscous liquid to highly cross-linked solid. The hyperbranched polymer can be facilely cross-linked at elevated temperature and the subsequent sintering in a nitrogen atmosphere produces an amorphous and stable SiBCN ceramic.

9:20 AM

(ICACC-S8-035-2011) Synthesis of SiCN Ceramics from Polyvinylsilazanes with Varied Amounts of Vinyl Group

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

Silicon-Carbon-Nitride ceramics are prepared from polyvinylsilazanes precursor with different amounts of vinyl groups, which are synthesized by reaction of dichloromethylsilane, dichloromethylvinylsilane, and hexamethyldisilazane at desired ratios. The synthesized polyvinylsilazanes are then characterized by FT-IR and NMR. The ceramics are investigated by solid state NMR and EPR. These results show the structures, compositions and properties of polymer-derived ceramics can be tailored by changing the structures and compositions of the precursors.

10:00 AM

(ICACC-S8-036-2011) Microstructure control of Si_3N_4 ceramics using nanocomposite particles prepared by dry mechanical treatment (Invited)

J. Tatami*, M. Noguchi, Yokohama National University, Japan; H. Nakano, Toyohashi University of Technology, Japan; T. Wakihara, K. Komeya, T. Meguro, Yokohama National University, Japan

Microstructure control is important to improve the property of ceramics. In this study, nanocomposite particles composed of Y_2O_3 and Al_2O_3 nanoparticles as sintering aids and submicron Si_3N_4 particles were prepared by dry mechanical treatment to control microstructure of Si_3N_4 ceramics. The purpose of this study is microstructure control of Si_3N_4 ceramics by using the nanocomposite particles. The nanocomposite particles were molded by uniaxial pressing and CIP-ping. The green body was fired at 1800^OC for 2h in $0.9MPaN_2$. In comparison, powder mixture prepared by conventional wet mixing process was used to make a sintered body. Specific surface area of the powder mixture prepared by dry mechanical treatment decrease with an increase in the applied power and treating time, which means that nanocomposite particles were formed by joining of nanoparticles and a submicron particle. β-Si_3N_4 grains in the Si_3N_4 ceramics fabricated using nanocposite particles prepared by dry mechanical treatment were more elongated than that by wet ball mixing process. the developed Si_3N_4 powder by dry mechanical treatment showed higher fracture toughness due to the more elongated β-Si_3N_4 grains.

10:20 AM

(ICACC-S8-037-2011) Fabrication of CNT dispersed Si_3N_4 ceramics by mechanical dry mixing technique

A. Hashimoto*, J. Tatami, T. Wakihara, K. Komeya, T. Meguro, Yokohama National University, Japan

Silicon nitiride (Si_3N_4) ceramics have excellent mechanical properties and chemical stability. They are applied to structural compornent such as bearing. We have focused an attention on the study to give electrical conductivity by dispersing carbon nanotubes (CNTs) into silicon nitride ceramics. In order to make better CNT dispersed Si_3N_4 ceramics, dipsersion process of CNTs is very important. In the wet mixing process, we have to control dispersant, dipsersion process and so on. There are many process parameters for optimization. We have reported that mechanical dry mixing technique is suitable for homogeneous mixing of nano- and submicron-sized particles. In this study, the CNT dispersed Si3N4 ceramics by using CNT- TiO_2 nanocomposite particles prepared by the mechanical dry mixing process. CNT- TiO_2 nanocomposite particles are prepared by the particle composer (NOBILTA NB-130 (Hosokawa Micron Ltd.)). CNT-TiO_2 nanocomposite particles were added to the silicon nitride and sintering aids by wet mixing process. The powder mixtures are molded into pellets and plates. The green bodies were densified by gas pressure sintering technique. The density and the electrical conductivity of the sintered body were measured and the microstructure of samples was observed by SEM. As a result, dense CNT-dispersed Si_3N_4 ceramics were obtained. It was observed that many CNTs remained in the Si_3N_4 ceramics.

10:40 AM

(ICACC-S8-038-2011) Electrically conductive CNT-dispersed Si_3N_4 ceramics having double percolation structure

Y. Sara*, T. Junichi, W. Toru, Y. Tomohiro, K. Katsutoshi, M. Takeshi, Yokohama National University, Japan; K. Katsutosi,

Electrically conductive Si_3N_4 ceramics by adding carbon nanotubes (CNTs) have been researched. In this study, we focused on the double percolation structure composed of two kinds of different percolation elements in order to control electrical conductivity of CNT-dispersed Si3N4 ceramics. Granules of Si_3N_4 powder with different amounts of CNTs (0~3.0wt%) were prepared. Two kinds of granules with and without CNTs were mixed in the dry condition with several compositions. The powder mixtures were sintered by spark plasma sintering technique to obtain fully dense CNT dispersed Si_3N_4 ceramics. Finally, the density and the electric conductivity of each sample were measured and the microstructure of the sample was observed by SEM. For comparison, single percolation sample was prepared using only granules with CNTs. The single percolation sample having 0.5wt% CNT was insulator because it was below percolation threshold. It was found that the percolation threshold of CNTs was 0.85vol% (0.63wt%) in the single percolation. On the other hand, the electrical conductivity of double percolation sample having 0.5wt% CNT was about five orders of magnitude more than that of 0.5wt% single percolation sample. Consequently, it was shown that the electrical conductivity of CNT dispersed Si_3N_4 was able to be controlled by double percolation.

11:00 AM

(ICACC-S8-039-2011) High Thermal Conductivity and High Strength Sintered Reaction - Bonded Silicon Nitride Ceramics Fabricated by using Low Si powder

D. Kusano*, S. Adachi, G. Tanabe, Japan Fine Ceramic Co. Ltd.,, Japan; H. Hyuga, Y. Zhou, K. Hirao, National Institute of Advanced Industrial Science & Technology (AIST, Japan

Recently silicon nitride has attracted much attention as a substrate material for power semiconductor devices because of its excellent mechanical properties and high intrinsic thermal conductivity. Our research group has indicated that a reaction bonding process fol-

lowed by post-sintering is the sensible approach for fabricating silicon nitride ceramics with both high thermal conductivity and high strength1) When employing high purity silicon raw powder, silicon nitride ceramics with high thermal conductivity (>100Wm-1K-1) and high bending strength (>700MPa) have been successfully fabricated by this process. However, high purity silicon powder was expensive, hence industrially unsuitable. In this investigation, the sintered reaction-bonded silicon nitrides were fabricated using low-cost silicon powders and the effects of characteristics of raw silicon powders on the microstructure, thermal and mechanical properties of sintered reaction-bonded silicon nitride ceramics were systematically investigated. It was found that the impurity oxygen in the raw silicon powder played an important role on the densification and material properties, in particular, thermal conductivity.

11:20 AM

(ICACC-S8-040-2011) Processing porous β-Si3N4 ceramics in an air atmosphere furnace (Invited)

A. Gandhi, K. P. Plucknett*, Dalhousie University, Canada

It has recently been demonstrated that both dense and porous β-Si3N4 ceramics can be prepared using an air-atmosphere sintering furnace. This approach requires the use of a protective α-Si3N4 powder bed around the sample during sintering. In this instance, a SiO2 oxide scale forms on the powder bed, minimizing potential oxidation of the samples within. In particular, it can be seen that processing porous materials presents a significant challenge in preventing significant oxidation, as fully connected internal porosity is an intrinsic feature of the material. In the present work it will be demonstrated that careful control of the heating rate can essentially prevent any oxidation of the samples. A range of rare-earth oxide additives have been examined using this approach, with samples sintered at temperatures up to 1750°C. Similarly, the extent of porosity can be varied through the use of fugitive filler materials, in this instance fine graphite particles, which are removed prior to sintering. The effects of processing conditions on the microstructure of porous β-Si3N4 will be discussed, including the effects of packing powder, heating rate, and crucible material.

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

Novel Processing I

Room: Coquina Salon H
Session Chairs: John Halloran, University of Michigan; Sylvain Dubois, Laboratoire de Physique des Matériaux

8:00 AM

(ICACC-S12-001-2011) Ultra-High Temperature Ceramic Coatings for Oxidation Protection of C-C Composites (Invited)

E. L. Corral*, University of Arizona, USA

The development of next generation hypersonic flight vehicles requires new thermal protection system (TPS) materials. The structures of these vehicles are primarily manufactured using carbon-carbon (C-C) composites that oxidize in air at low temperatures (> 500°C). Our TPS materials efforts focus on processing superior coatings of ZrB2, SiC, HfB2, and B4C in order to provide oxidation protection for C-C composites at temperatures greater than 2000 °C. Our approach uses precursors and sol-gel chemistry methods to create continuous and adherent ceramic coatings from infiltrated pre-ceramic precursors. Short duration high temperature testing using thermogravimetric analysis was used in order to determine baseline high temperature oxidation kinetics for uncoated and coated C-C composites, up to 1650 °C, in oxidizing environment. Our uncoated and UHTC infiltrated and coated C-C composites were also evaluated for ablation resistance, up to 2000 °C, in oxidizing environment, using an oxyacetylene torch test facility. Both high-temperature oxidation and ablation tests show that our coatings provide enhanced oxidation resistance at temperature over uncoated C-C composite systems and have exceptional potential for use as oxidation protection coatings.

8:30 AM

(ICACC-S12-002-2011) Multi-Stage Spark Plasma Sintering To Develop ZrB2-18wt%SiC-xwt%TiSi2 Composites With Better Properties

B. Basu, N. Gupta*, K. Reddy, K. Pavani, Indian Institute of Technology Kanpur, India

The ultra high-temperature ZrB2 Ceramic has received considerable attention due to its excellent combination of physiochemical properties, such as low density, high melting temperature and good thermal conductivity. The use of monolithic ZrB2 is limited for high temperature applications due to poor sinterability and modest oxidation resistance. In order to improve the sinterability and properties of these ZrB2 ceramic, several additives i.e., ceramics/metals are. Here we report the development of ZrB2-18wt%SiC-xwt%TiSi2 composites with uniform microstructure and superior mechanical properties, adopting multi-stage spark plasma sintering (SPS) route. ZrB2-18 wt%SiC-2.5wt%TiSi2 composition was found to be the most optimum one, exhibiting excellent combination of properties. Near full densification was achieved in multi-stage SPS (MSS) as opposed single-stage (SSS) spark plasma sintering route. The development of finer and uniform distribution microstructure of these additives in ZrB2 composites via multi-stage SPS led to an improvement in flexural strength (455MPa), fracture toughness (>6 MPam-1/2) and optimum higher hardness (~28 GPa) has been achieved.

8:50 AM

(ICACC-S12-003-2011) Spark Plasma Sintering of ZrB2-SiC-ZrC Ultra-High Temperature Ceramics

L. Stanciu*, A. Snyder, T. Hou, Purdue University, USA

We report on the results related to our efforts to understand the microstructure-composition-properties relationships in Zr(Hf)B2-SiC-ZrC UHTC sintered via Spark Plasma Sintering (SPS). ZrB2-SiC-ZrC composites with four different compositions were prepared via SPS at 1800 C. The microstructure and density of sintered samples were evaluated by using density measurements (Archimede's method) and Scanning Electron Microscopy (SEM). The room temperature mechanical properties were measured by a three point bending test and Rockwell A hardness measurements. The thermal conductivity of the samples was also determined. The highest density was obtained for the sample containing the smallest amount of SiC. On the other hand, the presence of a higher percentage of ZrC in the composite led to an increase in density. These trends were reversed for Rockwell hardness values, with an increase in this value with and increased amount of SiC present in the composite, and a decrease in the hardness value as the amount of ZrC increased. The thermal conductivity measurements showed that an increase in SiC content resulted in an increase in thermal conductivity.

9:10 AM

(ICACC-S12-004-2011) Properties and microstructures of Hf-Al-C ceramic and related composites

N. Hongqiang*, L. Fangzhi, L. Jingjing, W. Jingyang, Z. Yanchun, Institute of Metal Research, Chinese Academy of Sciences, China

Recently, Zr-Al-C and Hf-Al-C carbides have attracted lots of attention for their excellent performances, such as low density, high melting point, high degree of stiffness and toughness, good oxidation and thermal shock resistance, which endow these carbides as

potential high-temperature and ultrahigh-temperature materials. In this work, the crystal structure of ternary carbide HfAl4C4 has been successful determined by a combination of X-ray diffraction, transmission electron microscopy and first-principles calculations. And HfAl4C4 also shows relative high elastic stiffness. In addition, the Hf-Al-C/graphite composites were investigated and the results show better machinability, thermal shock resistance and high-temperature strength, which extend the applications of Hf-Al-C ceramic. The atom-scale microstructures of ternary carbide and related composites were also carried out by means of transmission electron microscopy and scanning transmission electron microscopy. These characterizations were powerful to understand the relative properties and display the relationship between the structure and properties.

Novel Processing II

Room: Coquina Salon H
Session Chairs: Per Eklund, Linkoping University; Anne Joulain, University of Poitiers - CNRS

9:50 AM

(ICACC-S12-005-2011) Low temperature growth of Cr2AlC and V2AlC thin films (Invited)

J. M. Schneider, M. to Baben*, Materials Chemistry, RWTH-Aachen University, Germany

Direct current and pulsed magnetron sputtering has been employed to grow Cr2AlC and V2AlC thin films. The effect of the substrate temperature on the phase formation has been investigated. Amorphous thin films were grown at room temperature and removed from the substrate to study the crystallization kinetics by differential scanning calorimetry (DSC) and X-ray diffraction. These data were compared to critical temperatures observed during vapor phase condensation of crystalline thin films with M2AlC stoichiometry. Significant differences with respect to the phase formation temperatures are observed. Additionally, significant differences of the phase formation temperatures for direct current and pulsed magnetron sputtered thin films are observed. These data support the conclusion that surface diffusion may be an important mechanism during structure evolution of MAX phase thin films grown at low substrate temperatures.

10:20 AM

(ICACC-S12-007-2011) Effects of Nb-dopant on oxidation behaviors of Ti3SiC2 at 1000-1300oC

L. Zheng*, L. Sun, J. Wang, M. Li, Y. Zhou, Institute of metal reseach, chinese academy of sciences, China

Ti3SiC2 is a member of the layered ternary compounds called Mn+1AXn phases, where M is a transition metal, A is an A-group element, and X is C or N. Recent interests in Ti3SiC2 were stimulated from its unique combination of the merits of both metals and ceramics, such as low density, high modulus and strength, good resistance to thermal shock and oxidation below 1100oC, high electrical and thermal conductivity, and easy machinability. However, the degradation of oxidation resistance and high temperature mechanical properties above 1100oC limits its widespread applications. To overcome these problems, a Nb-doped Ti3(Si0.95Al0.05)C2 solid solution (Ti0.98Nb0.02)3(Si0.95Al0.05)C2 was designed and synthesized to improve the high temperature oxidation resistance. Compared with Ti3(Si0.95Al0.05)C2, the oxidation resistance of (Ti0.98Nb0.02)3(Si0.95Al0.05)C2 was greatly enhanced, with the parabolic oxidation rate decreased by one to two orders of magnitude. The oxide scale formed on (Ti0.98Nb0.02)3(Si0.95Al0.05)C2 is much thinner and the grain sizes of the oxidation products are remarkably smaller than that formed on Ti3(Si0.95Al0.05)C2 under the same oxidation condition. It is expected that this work can highlight a new way to improve the oxidation resistance of MAX phases.

10:40 AM

(ICACC-S12-008-2011) Ti3AlC2/Al Composite Materials: From Synthesis to Mechanical Properties

W. Wang, G. Laplanche, G. Bei, V. Gauthier-Brunet, A. Joulain, J. Bonneville, S. Dubois*, Institut PPRIME, France

Ti3AlC2 MAX phase powders were first prepared at 1450°C for 2 hours. Thus, Ti3AlC2 powders were vibratory ball-milled from 15 to 60 minutes. From X-Ray Diffraction and Rietveld refinement; it is shown that Ti3AlC2 coherent domain size monotonically decreases down to 20 nm whereas microstrain increases as a function of milling time. Al-40 vol.% Ti3AlC2 powder mixtures were thoroughly mixed in a turbula and hot isostatically pressed under 1800 bars of argon at 550°C in order to synthesize dense Ti3AlC2/Al composite materials. Compression tests performed in the temperature range 293-773 K indicate that flow stress is strongly temperature dependent. A clear strengthening is observed for the Ti3AlC2/Al composite as compared with pure Al, such a strengthening is moreover comparable to the one obtained with AlCuFe quasiparticles as the reinforcement phase. Deformed microstructures are observed by Scanning Electron Microscopy. Finally, mechanical properties of the AlCuFe/Al and Ti3AlC2/Al composites will be compared and discussed.

11:00 AM

(ICACC-S12-009-2011) Novel synthesis method of ternary carbide powders

S. Lee*, B. An, H. Kim, KIMS, Republic of Korea

Synthesis of fine Al3BC3 and Al4SiC4 powder having sub-micrometer in size was attained by using spark plasma sintering (SPS) method was investigated. The ternary aluminum carbides were obtained when heating the stoichiometric mixture of aluminum, B4C, Si and carbon at 1250 – 1600oC in Ar using SPS. In contrast, the monolithic ternary powders could be synthesized after heating at 1750 – 1800oC for 2 h when using a conventional graphite furnace. The average particle size of the compound powders could be decreased more than 10 times by using novel SPS method (1 vs. 12 micrometer). The improvement of mold design in order to increase synthetic capacity per batch and to decrease synthetic temperature will be discussed.

S13: Advanced Ceramics and Composites for Nuclear Fusion Applications

Processing I

Room: Oceanview
Session Chair: Sasa Novak, J. Stefan Insitute

8:00 AM

(ICACC-S13-021-2011) Integrated R & D of SiC Matrix Ceramic Composites for Energy/Environmental Application (Invited)

A. Kohyama*, Y. Kohno, H. Kishimoto, K. Shimoda, J. Park, H. Jung, Y. Park, Muroran Insttute of Technology, Japan

OASIS at Muroran Institute of Technology is now intensively enforcing its efforts for industrialization of advanced SiC based composites by NITE (Nano Infiltration and Transient Eutectoid) method, which can provide near full-dense and highly crystallized SiC matrix for fiber/particle reinforced composites. . This paper provides the brief review of the activities at OASIS under the cooperation with IEST Co., Ltd, GUNZE Co., and many other industries. The near-net shaped preforms with the NITE green-sheets and prepreg-sheets are made into near-net shape components mainly by HP and Pseudo-HIP. Currently, the main applications are (1) energy, (2) environment, and (3) aero-space areas where complex and varying extreme service conditions are required to be satisfied. The application for nuclear fission/fusion energy expands from fuels, fuel pin, in-core components through intermediate heat exchanger to out of reactor energy conversion system components. The representing fuel components, fuel pins and thermal shield panels for fission reactors

and fusion reactors will be presented. In the case of near term utilization, SiC/SiC and/or C/SiC hybrid structures with metallic materials, such as steels, Ti alloys and other refractory metals, look realistic. For this reason many options for bonding and joining SiC/SiC and/or C/SiC with metallic materials have been investigated.

8:30 AM

(ICACC-S13-022-2011) Processing of advanced non-oxide ceramics for nuclear energy systems

A. K. Suri*, R. Fotedar, K. Nagaiyar, Bhabha Atomic Research Centre, India

Many non-oxide ceramics are listed for potential or actual use in nuclear energy systems for structural or as functional materials. The use of boron carbide for control and shielding purposes in both thermal and fast reactor cores is fairly well established. The neutron absorption characteristics of both constituents of binary alloys are utilized in compositions such as hafnium boride, europium boride while in alloys such as chromium boride and zirconium boride the high temperature stability of materials is key to their use. Silicon carbide has many advantages as structural material in high temperature fission reactors as well as in fusion systems. There are however issues such as fabrication, toughness and low surface heat capability, helium retention that need to be resolved for these materials. The present paper deals with issues of the preparation and processing of boron carbide, borides of refractory metals and rare earths, and silicon carbide. The conventional fabrication methods of sintering, hot pressing and newly developing methods such as spark plasma sintering have been covered along with results on the use of sinter additives to enhance densification and/or lower temperature needs. The properties of the materials in the as produced and processed conditions are also covered.

8:50 AM

(ICACC-S13-023-2011) Innovative Alumina Jig designed for high temperature annealing of TRISO coated particles

I. J. van Rooyen*, CSIR National Laser Centre, South Africa; J. Steyn, C. A. Smal, National Laser Centre, CSIR, South Africa; J. H. Neethling, Nelson Mandela Metropolitan University, South Africa

The design of a custom made alumina heat treatment jig resulted from the need to do various high temperature heat treatment studies on TRISO coated particles. High temperature annealing studies were undertaken by PBMR's Fuel Design group to test the design parameters of the CPs for application in very high temperature reactors. As the studies included various testing parameters, the jig was designed to specifically cater for the processing prior to and after heat treatment within this fixture and so that the traceability of the various test samples be kept at all times. This paper describes the innovative use of a Nd:YAG laser with a maximum average output power of 100W to fabricate this innovative alumina jig. The behaviour of this jig up to temperatures of 1600°C are discussed and although it is be expected that an alumina jig can easily withstand temperatures up to 1600°C and higher, the lessons learned during the handling of the small coated particles are of significant interest. Some characterization results using Scanning Electron Microscopy (SEM) are also described.

9:10 AM

(ICACC-S13-024-2011) Densification of SiC-matrix by hybrid process of EPD-PIP

A. Ivekovic*, G. Drazic, S. Novak, Jozef Stefan Institute, Slovenia

Silicon carbide (SiC) is considered as a promising material for high temperature structural applications in future fusion reactors, due to its unique intrinsic properties. To ensure sufficient fracture toughness and reliability of the material, SiC is proposed to be used in the form of continuous SiC-fiber-reinforced SiC composite (SiCf/SiC). Densification of the SiC-matrix within the composite is a very challenging task demanding a further investigation since the currently developed techniques do not meet the requirements. In this work the combination of electrophoretic deposition (EPD) and polymer infiltration and pyrolysis (PIP) was used for moderate-temperature densification of SiC-matrix. Due to the relatively high initial density of the deposits produced by EPD (62%) in comparison to other shaping techniques, the number of PIP cycles needed for densification was reduced. Density of the material was increased after each consecutive PIP cycle achieving 86.5% TD after six PIP cycles. Thermal conductivity of the deposits consolidated with PIP was significantly higher (> 40 W/mK after 3 PIP cycles) in comparison to the deposits sintered at low temperatures (1673 K) with the use of transient eutectoid (< 10 W/mK). Crystallinity of the sample was found to be the governing parameter for thermal properties of the material although porosity also influences the thermal properties of the material to some extent.

9:30 AM

(ICACC-S13-025-2011) Effects of Preform Densification on Performance of Near-Net Shaped NITE-SiC/SiC Composites

N. Nakazato*, Y. Kohno, H. Kishimoto, J. Park, H. Jung, A. Kohyama, Muroran Institute of Technology, Japan

SiC fiber-reinforced SiC matrix (SiC/SiC) composites are potential structural materials especially for advanced energy and aero-space systems, where SiC/SiC composites by Nano-Infiltration and Transient Eutectic-phase (NITE) method present the great attractiveness. One of the key fabrication methods for system components is the near-net shape technique. However, the large volume reduction in matrix and no reduction in fiber during the whole NITE process produce serious performance degradation of near net shaped components. Densification of slurry, green-sheet, prepreg-sheet and preform can be an effective option to improve the performance of near-net shaped NITE-SiC/SiC composites. This work cares for development of preform densification techniques and provides its effect on the performance of the final NITE-SiC/SiC products near-net shaped. The preforms were isostatically or uniaxially pressed to make dense preforms. The advantages of mid-process densification, that is to densify preforms and other elements, on performance of final NITE-SiC/SiC components near-net shaped will be presented in various aspects. Bending test results and baseline property measurements results will be also provided in details.

Processing II and Mechanical Properties

Room: Oceanview
Session Chair: Shaoming Dong, Shanghai Institute of Ceramics, Chinese Academy of Sciences

10:10 AM

(ICACC-S13-026-2011) Preparation of SiCf/SiC composites by SITE process (Invited)

S. Novak*, A. Ivekovic, G. Drazic, Jozef Stefan Institute, SFA Euratom-MHEST, Slovenia

The intrinsic properties of silicon carbide, such as high mechanical and thermal stability in combination with low neutron activation of pure SiC, make SiC-based composites good candidate materials for structural applications in future fusion reactors. To ensure sufficient fracture toughness and reliability of the material, SiC-fibre-reinforced SiC-composite is proposed as the most promising option. However, state-of-art techniques fail in preparation of the material fulfilling all the required properties and therefore, attempts have been made in development of various improved fabrication techniques in order to achieve a dense material without jeopardizing the advantageous properties of the pure SiC. With this aim, a new fabrication technique combining electrophoretic deposition principle and infiltration with densification aid was introduced. The so-called SITE processing route involves two steps: first, the SiC-fibre perform is infiltrated with charged SiC particles by aid of electric field that results in green bodies with high green densities, i.e. >62 % T.D. In the next step the green part is vacuum infiltrated either with a phosphate

based precursor for low-temperature sintering (SITE-A) or with a preceramic polymer (SITE-P) and densified at moderate temperatures (<1700 °C). The resulting materials are characterised with a low (< 5 W/mK) or high (>40 W/mK) thermal conductivity, respectively.

10:40 AM

(ICACC-S13-027-2011) Influence of stress induced damage on the thermal properties of ceramic matrix composites

J. L. Lamon*, J. El Yagoubi, CNRS, France; J. Batsale, TREFLE, France; M. Le Flem, CEA Saclay DEN, France

Ceramic matrix composites (CMC) are very attractive materials for structural applications at high temperatures. With a view to the development of the GENIV next generation of nuclear reactors, not only must the CMC be damage tolerant, but they must also allow thermal management. For this purpose heat transfers must be controlled even in the presence of damage. Damage consists in multiple cracks that form in the matrix and ultimately in the fibers, when the stresses exceed the proportional limit. Therefore the thermal conductivity dependence on applied load is a factor of primary importance for the design of CMC components. This original approach combines a model of matrix cracking with a model of heat transfer through an elementary cracked volume element containing a matrix crack and an interface crack. It was applied to 1D composites subject to tensile and thermal loading parallel to fiber direction in a previous paper. The present paper compares predictions to experimental results. During tensile monotonous loading, Hi-NicalonS/SiC minicomposites were heated using a laser beam while the thermal response was recorded using an Infrared camera. The diffusivity of minicomposites was estimated at various load steps using the Lock-in Thermography and Angstrom's model. Experimental results were found to be in good agreement with predictions.

11:00 AM

(ICACC-S13-028-2011) Tensile Property Evaluation of Unidirectional CVI SiC/SiC Minicomposites Reinforced with Near-Stoichiometric SiC Fibers

K. Ozawa*, Y. Katoh, E. Lara-Curzio, Oak Ridge National Laboratory, USA; T. Nozawa, Japan Atomic Energy Agency, Japan; L. L. Snead, Oak Ridge National Laboratory, USA

Silicon carbide (SiC) matrix composites are candidate structural materials for nuclear fusion and advanced fission energy applications. In order to design an optimum interphase for radiation service, the irradiation effects on fiber/matrix interfacial properties must be thoroughly and systematically understood. This study examines the effects of different fibers and interphases on tensile properties of non-irradiated advanced SiC/SiC composites. It is a preparatory step to the evaluation of irradiation effects. Unidirectional single-tow composites reinforced with near-stoichiometric SiC fibers were produced by the CVI process and the tensile properties evaluated at ambient temperature. The interphase was either a single pyrolytic carbon (PyC) layer or SiC/PyC multilayer. The ultimate tensile stress increased with the estimated interfacial sliding stress (τ) for Tyranno-SA3, experimental Sylramic and Sylramic-iBN but not for Hi-Nicalon Type-S (HNLS) composite. The HNLS composite seems to have achieved a high tensile strength due to very low τ, arising from the larger residual radial tensile stress and the smooth fiber surface. In contrast, the fracture behavior of the other composites may have been strongly affected by the clamping stress produced by the relatively rough fiber surfaces. The test results are explained by the influence of interphase thickness.

11:20 AM

(ICACC-S13-029-2011) Design Approaches for Nuclear Grade SiC/SiC for Gen IV Nuclear Applications

R. J. Shinavski*, Hyper-Therm HTC, Inc., USA

Silicon carbide matrix composite materials fabricated by chemical vapor infiltration with reinforcement from near-stoichiometric silicon carbide fibers (SiC/SiC) offer a great deal of promise for use in very high temperature reactors (VHTR) due to their elevated temperature mechanical properties. In particular SiC/SiC composites are well suited for Class 2 (high dose-high temperature) structural components such as the control rod sheath. Use of SiC/SiC provides a more radiation stable component with higher operating temperature capability. One of the longest tasks to be accomplished prior to the use of these composites for structural in-core applications is achieving ASME Boiler Code qualification. Before such a case can be made, the decision to qualify these materials using probabilistic methods versus a deterministic approach must be made. This work examines high temperature lifing data as a function of oxygen partial pressure with respect to both a probabilistic approach that the matrix remains uncracked and with a deterministic approach that assumes a precracked SiC matrix, and life predictions can deterministically be made based upon the performance of the reinforcing SiC fiber.

S14: Advanced Materials and Technologies for Rechargeable Batteries

Lithium Batteries and Beyond

Room: Coquina Salon F
Session Chairs: Stefan Adams, National University of Singapore; Laurence Croguennec, CNRS

8:30 AM

(ICACC-S14-027-2011) Advanced Ultra-high Energy Density Batteries based on Protected Lithium Metal Electrodes (PLEs) Stable to Air and Water (Invited)

S. Visco*, E. Nimon, L. De Jonghe, PolyPlus Battery Company, USA

The extremely high theoretical energy density of lithium-air and lithium-water couples have attracted the attention of battery researchers for decades. Unfortunately, the high reactivity of lithium metal with water made the practical realization of Li-Air and Li-Water batteries doubtful at best. In 2004 PolyPlus Battery Company announced the development of protected lithium electrodes based on multi-layer structures utilizing water-stable solid electrolytes with high Li+ conductivity. The invention of the PLE allowed for the 1st time, the practical development of Li-Water and Li-Air batteries with exceptional energy density. Due to the extremely low electronic conductivity of the solid electrolyte layer, the self-discharge rate for Li-Air and Li-Water batteries based on PLE technology is effectively zero. This is quite different from the behavior of conventional metal-air batteries which are typically plagued by corrosion and high rates of self-discharge. Furthermore, chemical isolation of the lithium electrode through PLE technology provides battery scientists with tremendous flexibility in the choice of solvents and electrolytes for the air electrode. PolyPlus has already demonstrated lithium-water batteries with specific energy of greater than 1300 Wh/kg, and lithium-air batteries with more than 800 Wh/kg. In this presentation we will describe a new generation of ultra-high energy density battery technologies based on PLE technology.

9:00 AM

(ICACC-S14-028-2011) Electrochemical and Thermal Investigation of Graphite Anode Materials for Li-ion Batteries

W. Lu*, C. Lopez, A. Jansen, D. Dees, Argonne National Lab, USA

As the most widely used anode material for lithium ion batteries, graphite has high reversible capacity (372 mAh/g with the stoichiometry of LiC6), good cycleability, and low cost. However, graphite operates at a potential very close to lithium metal. There is a great chance for lithium metal to deposit at the surface of the electrode. The lithium plating will not only detrimentally affect the electrochemical performance and cycle life, but also its thermal stability

of the lithium ion battery system. Lithium plating becomes a more profound issue when the lithium ion battery is used in hybrid electric vehicles, since the lithium ion battery undergoes high rate charge (regen) pulses and will need to operate at lower temperatures during a significant portion of its life. In this study, an intentionally overcharged graphite electrode was investigated using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The lithium plating effect on the morphologies and structure of the overcharged graphite electrode was analyzed and its impact on cell performance will be discussed. In addition, the thermal properties of the graphite anode are characterized using isothermal Micro-Calorimetry (IMC) and Differential Scanning Calorimetry (DSC). The impact of graphite morphology on its thermal stability is discussed.

9:20 AM

(ICACC-S14-030-2011) Development of High Performance Lithium/Sulfur Rechargeable Battery (Invited)

K. Kim*, H. Ahn, J. Ahn, Y. Choi, H. Ryu, G. Cho, Gyeongsang National University, Republic of Korea

Lithium/sulfur battery is very attractive redox couple for a next generation lithium battery because of its high theoretical specific capacity of 1675mAh/g-sulfur, assuming complete reaction to form the product Li2S. Besides, elemental sulfur as cathode active material is very cheap, abundant, and nontoxic material. Despite of those advantages, lithium/sulfur battery is difficult to commercialize due to low sulfur utilization and poor cycle performance. To solve the problems, we prepared sulfur cathode containing nano Al2O3 to prevent the dissolution of lithium polysulfides (Li2Sn, n≥4) into liquid electrolyte. Also, multi-walled carbon nanotubes (MWNTs) and carbon nanofibers (CNFs) were added into sulfur cathode to provide good electrical contact and electronically conducting network. Test cells to evaluate electrochemical properties were assembled in a stainless-steel case (Swagelok®) by stacking a lithium foil, a separator containing liquid electrolyte, and a sulfur cathode in turn. Charge/discharge tests were carried out with galvanostatic method using WBCS3000 battery cycler. As a result, sulfur cathode containing MWNTs showed the best cycle performance until the 150th cycle.

10:10 AM

(ICACC-S14-031-2011) Silicon-Based Composite Anode Materials for Lithium-Ion Battery

T. Yoon, Dong-A University, Republic of Korea; H. H. Kung, Northwestern University, USA; J. Lee*, Dong-A University, Republic of Korea

The rechargeable Li ion batteries (LIBs) have attracted a great deal of interests as an enabling technology for energy storage devices for electrical vehicles, load-leveling of stationary power generation, and renewable wind and solar power applications. Their energy and power densities, cost and cycling life have to be much improved for practical applications. One area of active research is to replace graphite as the energy storage component in the anode with materials of higher storage capacities. Because silicon possesses the highest theoretical energy density among common elements, cheap, and easy to handle, it is attractive candidate and a focus of investigations. Its use as lithium-ion battery anode, however, is hindered by poor cycling stability due to electrode pulverization caused by mechanical stresses during cycling. In this study, strategies have been developed to prepare highly dispersed Si nanoparticles in nanostructured carbons, e.g., Si nanoparticles encapsulated in a mesoporous carbon and carbon microspheres, and Si nanoparticles dispersed in the inter-layers of graphene sheets which are exfoliated from graphite. These novel materials showed very high power capabilities as well as stable cycling performances as anodes for Li-ion battery. The results of using these composites as anode for a Li-ion battery, the charge/discharge behavior and cycling performances will be presented.

10:30 AM

(ICACC-S14-032-2011) Three Dimensional Construction of Electrodes - Open Door to High Capacity Lithium Batteries

J. Prochazka*, L. Kavan, M. Zukalova, JHI, Czech Republic; J. Postler, HE3DA, Inc., Czech Republic

The thin-film lithium battery technology has made a significant progress in the past ten years and in many aspects it has reached the theoretical possibilities. While the thin-film battery is nearly optimized, the capacity limits of lithium accumulators can be further extended by an original construction of 3-D electrodes. The 3-D design with electrodes several millimeters thick allows new features that have not been used in the battery industry yet. 3-D concept of the accumulator not only increases capacity of the individual cell but also significantly reduces size of the assembled modules. Construction of prototypes and their electrochemical performance will be demonstrated.

10:50 AM

(ICACC-S14-033-2011) Sodium-beta Rechargeable Battery Technology Development

G. Tao*, N. Weber, Materials and Systems Research Inc., USA

Extraterrestrial exploration activities, particularly for long-duration missions, require high-performance and highly-specialized rechargeable batteries. Battery energy capacity is of paramount importance for missions. The batteries may also be called upon to operate in an extreme atmosphere imposing unique challenges on battery reliability and safety. Particularly, Venus has an extremely dense, CO2-rich atmosphere with a surface temperature over 450C. Thus it is desirable to develop a cost-effective rechargeable battery possessing high specific energy and capable of operating at temperatures at or above Venus surface temperature. While a number of state-of-the-art battery technologies have been developed and demonstrated high performance (specific energy/power, cycle life), certain restrictions place severe limitations on deployment to environments like the Venus. An advanced rechargeable battery, which was built upon a sodium-ion conducting beta" alumina solid electrolyte (BASE) and a metal salt, was developed at MSRI and demonstrated robust performance meeting the temperature extremes needs at a lab-cell level. In this talk, the battery development and results will be presented, along with performance optimization. In addition, BASEs fabricated by MSRI's unique vapor phase process will be discussed to demonstrate controlling electrolyte wall thickness and merits of high resistance to moisture and CO2 attack.

11:10 AM

(ICACC-S14-034-2011) How Green is Battery Recycling? (Invited)

L. Gaines*, I. Belharouak, A. Burnham, J. Sullivan, Argonne National Laboratory, USA

Our previous work compared lifecycle energy use and emissions of criteria pollutants and greenhouse gases per unit distance traveled for several types of conventional and hybrid vehicles. The results indicated that moving a car with electricity generally provides the lowest impacts. In this paper, we focus our attention on the lithium-ion batteries that will store that electricity (until something better is developed). We ask how impacts from these batteries can be minimized. This paper will compare existing and proposed recycling processes for lithium-ion batteries to each other and to production from raw materials, on the basis of energy and other resource use, as well as potentially-harmful emissions. Although few have been produced to date and the chemistry(ies) to be used is (are) not yet decided, work is underway to develop the best processes to recycle these batteries when they are no longer usable in vehicles. Secondary use of the batteries, such as for stationary storage of wind energy by utilities, could delay return of material for recycling, possibly increasing the demand for virgin material and requiring recycling process modifications. We will discuss the trade-offs and implications of the different end-of-life options.

S1: Mechanical Behavior and Performance of Ceramics & Composites

Environmental Effects of Ceramics and Composites

Room: Coquina Salon A
Session Chair: Randall Hay, AFRL

1:30 PM

(ICACC-S1-043-2011) Kinetics of Passive and Active Oxidation of Hi-Nicalon-S SiC Fibers: Relationships between SiO2 Scale Thickness, Crystallization, Residual Stress, Fiber Strength, and Fiber Microstructure

R. Hay*, G. Fair, AFRL, USA; P. Mogilevsky, UES, Inc., USA; R. Bouffioux, New Mexico Tech., USA; A. Hart, J. Clark, U. Cincinnati, USA

Relationships between Hi-Nicalon-S SiC strength, thickness and crystallinity of the SiO2 scale, and oxidation temperature, time, residual stress and pO2 were characterized. Passive oxidation kinetics were determined from 700° to 1400°C by TEM of oxidized fiber cross-sections, and modeled using Deal-Grove kinetics. Fiber tensile strength distributions were measured using 30 single filament tensile tests.Residual and growth stresses in scales were calculated from oxidation volume expansion and CTE mismatches. Strength increased by ~10% for fibers with scales less than 100 nm thick, but decreased with scale thickness for scales thicker than ~100 nm. The decrease in fiber strength after passive oxidation correlates with the extent to which the SiO2 scale has crystallized, and the resulting change in scale residual stress from compressive to tensile. Cracks form in crystallized scales both during oxidation and during cool-down. Strength after active oxidation is most severely degraded at oxygen partial pressures where active oxidation is most rapid, and correlates microstructurally with open porosity filled with small graphitic flakes.

1:50 PM

(ICACC-S1-044-2011) Fatigue of Hi-NICALON/HyprSiC Ceramic Matrix Composite at 1200°C in Air and in Steam

J. Delapasse, M. Ruggles-Wrenn*, Air Force Institute of Technology, USA; A. Chamberlain, J. Lane, T. Cook, Rolls-Royce Corporation, USA

The fatigue behavior of a Hi-Nicalon/SiC ceramic composite was investigated at 1200°C in laboratory air and in steam environment. The composite consisted of an oxidation inhibited HyprSiC matrix reinforced with laminated woven Hi-Nicalon fibers. Fiber preforms had pyrolytic carbon fiber coating with boron carbide overlay applied and were then densified with CVI HyprSiC. Tension-tension fatigue behavior was studied for fatigue stresses between 100 and 140 MPa in air and in steam. Fatigue limit (based on a run-out condition of 200000 cycles) was 100 MPa in air and in steam. Presence of steam had little effect on fatigue performance for $\sigma_{max} \leq 130$ MPa, but decreased cyclic life by 42% for $\sigma_{max}=140$ MPa. Specimens that achieved run-out were tested in tension to failure to characterize the retained tensile properties. The material retained 100% of its tensile strength. Modulus of 12% was observed. Composite microstructure, as well as damage and failure mechanisms were investigated.

2:10 PM

(ICACC-S1-045-2011) Fatigue behavior of CMC under constant load at intermediate temperatures

J. L. Lamon*, R. Maurin, M. R'Mili, G. Fantozzi, P. Reynaud, N. Godin, CNRS, France

Self-healing ceramic matrix composites, like the SiC/[Si-B-C] composites, are designed for long-term use at intermediate temperatures, with a view to aeronautical applications. Thus, lifetime predictions become an important issue. The objective of this work was to investigate the fatigue behavior under constant load at intermediate temperatures under air. The fatigue behaviour of self-healing composite is analysed using the tensile deformation curves under constant load and features of unloading-reloading cycles at successive time steps. The deformation curves describe the macroscopic behavior, whereas the loops reflect constituent damage, through variations of mean elastic modulus, loop area or residual strains. Features of the deformation curves were correlated to interface degradation through changes in the shape of the hysteresis loops (internal friction, width at mid stress), which allowed the phenomena driving composite behavior to be identified. Two regimes were observed: first a non linear regime of deformations when oxidation activated degradation of interfaces and slow crack growth in fibers operate both, and a second domain of linear deformation when crack healing is effective so that slow crack growth is limited. A micromechanical analysis is done to model the evolution of deformations with time. Finally, implications for lifetime predictions are discussed.

2:30 PM

(ICACC-S1-046-2011) Creep Behavior of Polycrystalline YAG at 1300°C in Air and in Steam

C. Armani, M. Ruggles-Wrenn*, Air Force Institute of Technology, USA; R. Hay, Air Force Research Laboratory, USA; H. Lee, K. Keller, UES Inc., USA; G. Fair, Air Force Research Laboratory, USA; T. Parthasarathy, UES Inc., USA

The compressive creep behavior of polycrystalline yttrium aluminum garnet (YAG, Y3Al5O12) with ~ 2-3 μm grain size was investigated at 1300°C in air and in steam. Extremely high-purity (99.999%) polycrystalline YAG specimens prepared with and without silica as a sintering aid were tested in this study. Testing of YAG specimens both with and without silica dopant allowed discrimination of the creep mechanisms intrinsic to YAG from extrinsic mechanisms due to the presence of silica. Compressive creep behavior was examined for creep stresses in the -50 to -200 MPa range. Minimum creep rate was reached in all tests. The presence of silica had a beneficial effect on creep of polycrystalline YAG in both air and steam. Creep rate magnitudes in specimens with silica dopant were $< 3x10^{-7}$ s^{-1}, while those in specimens without the silica dopant reached $1x10^{-6}$ s^{-1}. Steam had no effect on creep of specimens with silica dopant, and negligible effect on creep of specimens without silica dopant.

3:10 PM

(ICACC-S1-047-2011) Static fatigue of fiber bundles under constant deformation

J. L. Lamon*, M. R'Mili, CNRS, France

Delayed failure of fibers is an important issue for the use of composites in severe conditions, since the resistance of fibers controls composite load carrying capacity. Glass and ceramic fibers are sensitive to slow crack growth when subjected to a constant load in environment containing water or oxygen at room or high temperature. Today, the determination of slow crack growth constants uses a time consuming procedure with a lot of long-term fatigue tests. These tests are always conducted under a constant load. This technique presents several shortcomings. Furthermore, the determination of slow crack growth constants and statistical distributions of fiber lifetime data is biased for several reasons. The present paper proposes a most powerful approach based on static fatigue tests under constant deformation. A single test provides several hundreds of rupture time data. It is demonstrated that unbiased slow crack growth parameters and pertinent statistical distributions of filament lifetimes are obtained. The exact equation for probability-time-stress-size relation is established. The approach is assessed on model E-glass fibers. Static fatigue tests under constant deformation were carried out on bundles of glass fibres immersed in water environment. Slow crack growth constants and statistical distributions of fiber lifetime data were extracted. Satisfactory lifetime predictions were obtained.

3:30 PM

(ICACC-S1-048-2011) Creep Behavior of Nextel™610 and Nextel™720 Fiber Tows at Elevated Temperatures in Air and in Steam

C. Armani, M. Ruggles-Wrenn*, Air Force Institute of Technology, USA; G. Fair, Air Force Laboratory, USA

The creep behavior of polycrystalline oxide fibers was investigated at temperatures up to 1200°C in air and in steam. Nextel™610 polycrys-

talline fibers are high-purity alumina. Nextel™720 polycrystalline fibers contain two phases: mullite and alumina. Tensile creep behavior was examined for creep stresses in the 100-500 MPa range. These fibers were tested in bundles consisting of approximately 400 fibers, as supplied by the manufacturer. Primary and secondary creep regimes were observed in all tests. The presence of steam accelerated creep rates and reduced creep lifetimes of both Nextel™610 and Nextel™720 fiber bundles. At 1100 °C the secondary creep rates of Nextel™610 in steam were nearly an order of magnitude higher than those in air. At 1200 °C the secondary creep rates of Nextel™720 in steam were also about an order of magnitude higher than those in air. For Nextel™610 at 1100°C, creep run-out (set to 100 h) was achieved at 100 MPa in air and in steam. For Nextel™720 at 1200°C, creep run-out was achieved at 200 MPa in air and at 100 MPa in steam. Dramatic decrease in creep lifetimes of both Nextel™610 and Nextel™720 fiber tows at higher creep stress levels in steam is attributed to environmentally-assisted subcritical crack growth. The damage and failure mechanisms were also investigated.

Characterization

Room: Coquina Salon A
Session Chair: Waltraud Kriven, University of Illinois at Urbana-Champaign

3:50 PM

(ICACC-S1-049-2011) Phase Transformations in the Cadmia-Telluria-Tungstate System

E. Ersundu, W. M. Kriven*, University of Illinois at Urbana-Champaign, USA

The cadmia-telluria-tungstate system has several phase transformations which will be studied by hot stage optical microscopy, XRD and thermal analyses.

4:10 PM

(ICACC-S1-050-2011) X-ray studies of Phase Transformations in Tantalum Pentoxide

P. Sarin*, R. P. Haggerty, J. L. Bell, Z. D. Apostolov, W. M. Kriven, R. P. Haggerty, University of Illinois at Urbana-Champaign, USA

Tantalum pentoxide (Ta_2O_5) has useful dielectric, optical, catalytic, and chemical properties. Crystalline Ta_2O_5 exists in two distinct structural forms. The low-temperature-stable, orthorhombic phase (L-Ta_2O_5) transforms into the high temperature- stable phase (H-Ta_2O_5) above ~1360 °C. With sufficiently slow cooling rates, H-Ta_2O_5 transforms back into L-Ta_2O_5. However, the prototypic H-Ta_2O_5 phase cannot be retained at room-temperature even by cooling at rates >50 °C/s. In this research phase transformations of Ta_2O_5 were studied in-situ at high temperatures by synchrotron X-ray diffraction and total X-ray scattering (PDF). Powder samples were heated up to 1500 °C in air and the crystal structure changes were simultaneously recorded, both while heating and cooling. Results will be presented to interpret the phase transformations observed in Ta_2O_5, and the role of the oxygen sublattice will also be discussed. It is anticipated that these studies will provide insight into the structure-property relations in Ta_2O_5, and guide further development of this material system.

4:30 PM

(ICACC-S1-051-2011) In Situ Studies of Phase Transformations in Ta2O5 and DyNbO4 by Hot Stage Microscopy

D. R. Lowry*, P. Sarin, W. M. Kriven, University of Illinois Urbana-Champaign, USA

To complement our in situ high temperature synchrotron studies of the tantula (Ta2O5) and dysprosium niobate (DyNbO4) systems, we have conducted in situ hot stage optical microscopy studies. Using a transmitted and reflected polarized light Carl Zeiss microscope equipped with a Linkam hot stage capable of reaching 1500°C in air. The evolution of the microstructure was followed during densification, grain growth, and phase transformation. Tantula is unusual in that it exhibits exaggerated grain growth accompanying its orthorhombic to monoclinic transformation at 1360°C on heating. This behavior which is reminiscent of the Hedvall effect was recorded using time lapse imaging in both transmitted and reflected polarized light. For comparison the monoclinic to tetragonal phase transformation in DyNbO4 which is an example of a second order ferroelastic system was studied at 842°C.

4:50 PM

(ICACC-S1-052-2011) Fracture Surface Characterization of Multilayer Ceramic –Polymer Composites

P. A. Robinson*, C. A. Wilson, J. J. Mecholsky, University of Florida, USA

It has been demonstrated that laminates of hydroxyapatite (HA) and polysulfone (PSu) disks show an increase in fracture toughness over HA alone. The fracture surfaces of bars and disks were analyzed using quantitative fractography, Raman spectroscopy and fractal analysis to determine mechanisms of failure. Important parameters in the toughness and strength of these laminates are outer layer thickness, interface bonding integrity, and porosity. Suggestions for optimizing the strength and toughness of these laminates will be discussed.

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

Coatings to Resist Wear, Erosion and Tribological Loadings

Room: Coquina Salon G
Session Chairs: Irene Spitsberg, Kennametal, Inc.; Oyelayo Ajayi, Argonne National Laboratory

1:30 PM

(ICACC-S2-042-2011) Development of Coating Technology Platforms for Wear Component Applications (Invited)

S. Brahmandam*, I. Spitsberg, D. Siddle, Kennametal Inc., USA

The global economic pressures and escalating energy costs create increasing demands on performance of engineered components used in various wear related applications. Surface engineering is an important tool to reach these objectives, especially because of its potential to significantly improve performance without changing structural properties of the substrate. To enable timely and effective development of new products, it is critical to establish smart approaches for leveraging, re-engineering and enhancing the existing technologies to make them suitable for new applications. This paper discusses the engineering challenges and systematic methodology for developing new thin coating platforms for wear resistant components starting with the current state of the art in metal cutting coating. The methodology is based on understanding fundamental limitations of currently available coatings with respect to the new application area, and developing approaches for modeling, testing and evaluation.

2:00 PM

(ICACC-S2-043-2011) Superhard, Ultra-Thick Nanocomposite Coatings and their Practical Applications (Invited)

R. Wei*, Southwest Research Institute, USA

SwRI has been conducting research on and developing deposition technologies for obtaining super-hard, ultra-thick nitride-based nanocomposite coatings for industrial applications. SwRI utilizes

its Plasma Enhanced Magnetron Sputtering (PEMS) techninology and has deposited TiSiCN-based coatings up to 500 µm thick. Using various microstructural characterization techniques, it has been observed that the TiSiCN coatings consists of nano-crystalline TiN, TiC0.3N0.7, and TiC0.7N0.3 about 4-10 nm in size in an amorphous SiCxNy matrix. The coatings with the Si concentration of 1-5 at% exhibit the highest hardness of up to 50 GPa. These coatings show high resistance to erosion, abrasion, sliding wear, and cavation erosion under various severe environments. The research also indicates these coatings are "tougher" than single-phased, crystalline ceramics. The higher toughness is essential in increasing the erosion resistance. These coatings have been applied to protect aero engine compressor blades, steam turbine blades, helicopter rotor blade section, components for oil/gas exploration, components for food grinders, and various cutting tools for metal machining. In this presentation, practical applications of the technology will be emphasized.

2:30 PM

(ICACC-S2-044-2011) Ceramic / Metal - Polymer Multilayer Coatings for Tribological Applications under Dry Sliding Conditions (Invited)

A. Rempp*, R. Gadow, A. Killinger, IFKB University of Stuttgart, Germany; P. Guth, M. Widmann, Wittenstein Bastian GmbH, Germany

The combination of thermally sprayed hard metal or oxide ceramic coatings with a polymer based top coat leads to bi or multilayered coating systems with tailored functionalities concerning wear resistance, friction, adhesion and wetting behaviour or specific electrical properties. This type of coatings is successfully inserted in numerous industrial applications. The basic concept is to combine the wear resistance and friction behaviour of the basic hard coating with the tribological or chemical abilities of the polymer top coat suitable for the respective application. This paper gives an overview of different types of recently developed multilayer coatings and their application in power transmission under dry sliding conditions. To evaluate the capability of these coatings, steel substrates were coated with oxide ceramics, metal alloys and hard metals by high velocity flame spraying (HVOF) and high velocity suspension flame spraying (HVSFS). After a grinding process several types of sliding lacquers are applied by air spraying on the coated specimens. Different sliding lacquers based on polyamide-imide filled with solid lubricants e.g. MoS2, PTFE or graphite were tested under various loads and sliding conditions. Wear resistance and friction coefficients of combined coatings were determined under dry sliding conditions using a twin disc test-bed.

3:20 PM

(ICACC-S2-045-2011) Application of HVOF and HVSFS for High Performance Cylinder Liner Coatings (Invited)

A. Manzat*, R. Gadow, A. Killinger, IFKB University of Stuttgart, Germany

Rising demands for low emissions automotive engines require a significant decrease in fuel consumption and internal friction. One approach to achieve this goal is the development of highly loaded and downsized internal combustion engines. This accentuates the need for highly wear resistant materials. In addition, the deployment of bio-fuels requires corrosion resistant materials. New technologies for the processing and application of advanced materials for improved tribofunctional coatings for internal combustion engines are described. These coatings contribute to reduce the frictional losses and improve the wear and corrosion resistance much needed. HVOF-sprayed metallic (Fe, FeCrMo) and cermetic (Cr3C2/NiCr, n-WC/Co) and HVSFS-sprayed ceramic (TiO2/TiC) coatings will be presented. The HVSFS process represents a novel method for the direct processing of nanoscale materials which opens new application fields even for established materials since the nanoscale structure can show improved properties compared to the respective standard coatings. Selected test results of the novel coatings compared to state-of-the-art materials will also be presented.

3:50 PM

(ICACC-S2-046-2011) Comparison of tribological and nanomechanical behavior of different diamond-like-carbon (DLC) coatings

N. Demas*, A. Navratil, Argonne National Laboratory, USA; I. Shareef, Bradley University, USA; O. Ajayi, Argonne National Laboratory, USA

Diamond-like-carbon (DLC) coatings are increasingly being used for tribological applications. There are currently available different variants of DLC coatings deposited using different methods and with different compositions, microstructure and properties. In this work, tribological performance of two types of DLC coatings, namely hydrogenated amorphous carbon (a-C:H) and a metal-doped amorphous (a-C:H:Me+a-C:H) DLC coatings deposited on hardened 4118 steel substrates were studied under reciprocating ball-on-flat contact configuration. Tests were conducted under both dry and oil lubricated conditions. In dry sliding contact, the a-C:H exhibited initial friction coefficients higher than 0.2 but decreased with time during the test a steady-state value of 0.2. The a-C:H:Me+a-C:H coating had an initial friction coefficient that was lower than 0.2, but a gradual increase during the test duration to a final value of about 0.18. Under lubricated conditions, the a-C:H exhibited a nearly constant friction coefficient of 0.1 while for the a-C:H:Me+a-C:H coating the friction coefficient showed a gradual decrease from initial value of 0.1 to about 0.08. The a-C:H:Me+a-C:H coating has higher nanohardness than the a-C:H and their nanomechanical response was also different with the latter showing nearly perfectly elastic behavior.

4:10 PM

(ICACC-S2-047-2011) Effect of Substrate Hardness on the Mechanical Properties of PVD Coatings

I. Shareef, Bradley University, USA; O. Ajayi*, N. Demas, Argonne National Laboratory, USA

Hard thin films coatings are extensively used for protection of surfaces from corrosion, friction, wear, yielding, and fatigue. In many engineering applications of thin film coatings, the substrate sometimes carries a significant percentage of the applied load. Most of the hardness values reported in the literature represent the composite hardness of the coating and substrate when the measurement is done on the macro and micro scale. For a given indentation load, the thinner the coating, higher is the influence of substrate hardness on the measured composite hardness. This paper presents results of investigation of hardness behavior of five different commercially available coatings: TiN, TiCN, CrN, AlTiN and Tribo Bond 40 deposited on 4118 steel substrate with three different substrate hardnesses. Surface roughness, Rockwell hardness, Vickers micro-hardness, Nano Indentation (for nano-hardness and elastic modulus), and Calo wear test were conducted. Mathematical models were developed using the rule mixture to determine the true hardness of the coating from the micro-hardness measurements. Results of the model were compared with the coating hardness measured by Nano-indentation techniques. Good correlation was found between the two hardenesses.

4:30 PM

(ICACC-S2-048-2011) Multilayer Coatings for Anti-Corrosion Applications

L. Lin, C. Qu, R. Kasica, Q. Fang, R. Miller, E. Pierce, E. McCarty, J. Fan, D. Edwards, G. Wynick, X. Wang*, Alfred University, USA

Magnesium alloy parts are being utilized to reduce the weight of a vehicle in light-weight vehicle designs. However, when magnesium

parts are fastened with carbon steel bolts, galvanic corrosions will occur unless the steel fasteners are isolated from the magnesium parts. In order to reduce the galvanic corrosions, aluminum oxide and silicon nitride thin film coatings are being considered as the anti-corrosion barrier layer materials. Each thin film material coated on a carbon steel plate has being individually evaluated by the EIS measurement. For example, the impedance modulus of silicon nitride varies as the function of the film thickness, varying from 20 nm to 850 nm. In this paper, we report new results on the multilayer coatings, including silicon nitride and aluminum oxide. After a multilayer coating is applied to a 1050 carbon steel disc, the galvanic current is obtained. Using the lowest current value as the criterion, a candidate multilayer stacking design is then selected for the coating on the carbon steel bolts. The coated bolts are subsequently evaluated by a salt spray testing method. To correlate the anti-corrosion behavior with the materials and mechanical properties, the samples are measured via SEM/EDS, nano-indentation, and nano-scratching measurements.

4:50 PM

(ICACC-S2-049-2011) Processing and Tribological Properties of MoN/Cu Coatings

K. Pappacena*, D. Singh, O. Ajayi, J. Routbort, O. Eryilmaz, Argonne National Laboratory, USA

The use of hard thin film coatings to improve surface tribological performance of machine element components in sliding and rolling contact is continuously increasing. However, there is a need to establish a reliable connection between coating structure and tribological performance. In this study, MoN/Cu coatings of three compositions were deposited on steel substrates to correlate compositional variables resulting from processing to tribological properties. The usefulness and durability of these coatings, particularly for engine-related applications, is strongly dependent on their adhesion and tribological behaviors. Scratch testing was performed to measure coating adhesion energy, and wear rate was determined using a high frequency reciprocating rig. It was observed that coatings with lower copper content performed better in the wear test and exhibited higher coating adhesion energy. At relatively low contact load, abrasion and polishing were the dominant wear mechanisms for coatings with little or no copper, whereas greater copper content showed a higher degree of delamination and fracture. This transition in wear mechanisms is indicative of differences in coating properties and structure. Since coating processing variables affect the tribological properties of these MoN coatings, processing parameters can be used to optimize coating composition for enhanced tribological performance.

5:10 PM

(ICACC-S2-050-2011) Properties of SiAlON and SiZrON Coatings Deposited by Reactive Magnetron Co-Sputtering

M. Byrne, T. Bremm, R. J. Lad*, University of Maine, USA

Oxynitride ceramics combine the oxidation resistance of oxides with the toughness of nitrides, and their multi-component stoichiometry allows for a very large parameter space that can be tailored to yield a variety of specific structures and properties. In this study, SiAlON and SiZrON thin film coatings up to 1 micrometer thick were synthesized using RF reactive co-sputtering of sputtering of Si+Al or Si+Zr targets in $Ar/O_2/N_2$ process gas on both silica and sapphire substrates. For deposition at substrate temperatures up to 600°C, both SiAlON and SiZrON films are amorphous. Post-deposition annealing up to 1000°C in vacuum causes negligible stochiometry changes and the coatings remain amorphous. Annealing treatments at 1000°C in air cause surface oxidation and nitrogen loss in the films. The oxidized SiAlON films remain amorphous, whereas in the case of SiZrON films, ZrO_2 nano-precipitates form within in an amorphous film matrix as determined by X-ray diffraction. Determination of the nano-wear coefficients of the coatings as measured by AFM scratch testing with a diamond probe indicated that SiAlON films are more wear resistant than the SiZrON films. The high hardness and wear resistance of these oxynitride films make them attractive as passivation coatings for a variety of high temperature applications.

S3: 8th International Symposium on Solid Oxide Fuel Cells (SOFC): Materials, Science and Technology

Fuel Reforming

Room: Coquina Salon E

Session Chairs: Toshio Suzuki, National Institute of Advanced Industrial Science and Technology; S. (Elango) Elangovan, Ceramatec, Inc.

1:30 PM

(ICACC-S3-041-2011) Carbon dioxide reforming of methane for solid oxide fuel cells (Invited)

M. Kawano*, H. Yoshida, K. Hashino, T. Inagaki, The Kansai Electric Power Co., Inc., Japan

Solid oxide fuel cells (SOFCs) with Ni-ceria-based oxide anode are developed by The Kansai Electric Power Co., Inc. Fuel flexibility is one of the advantages of SOFC. For example, biogas containing methane and carbon dioxide is one of the candidates as a fuel for SOFC. In this study, power generation utilizing carbon dioxide reforming of methane was carried out to clarify the biogas fueled SOFCs. Lanthanum gallate compounds, Ni-ceria-based oxide cermet, and samarium cobaltite compounds were selected as an electrolyte, an anode, and a cathode, respectively. Mixture of methane and carbon dioxide were supplied to the anode. Air was supplied to the cathode. The gaseous composition of the fuel and I-V characteristics at 750, 700, 650°C were measured under various conditions. The results of the measurement of gaseous composition at the anode and I-V performance indicated that methane was effectively reformed at the anode at 750°C, resulting in the stable SOFC performance. On the other hand, it was also indicated that methane was insufficiently reformed at the anode at 700 and 650°C, resulting in the relatively low SOFC performance. It was concluded that carbon dioxide reforming attained sufficient level of conversion for SOFC power generation at 750°C, while it gave insufficient level of conversion at 700 and 650°C.

2:00 PM

(ICACC-S3-042-2011) Reforming of Liquid Hydrocarbon Fuels Using Non-thermal Plasma Reactor

S. Elangovan*, J. Hartvigsen, P. Czernichowski, L. Frost, Ceramatec, Inc., USA

Ceramatec has previously established in laboratory work that plasma reformer can successfully reform high sulfur logistic fuels. Since the reformer uses a non-thermal plasma to catalyze the reforming, the energy required is very low (less than 2% of the heating value of the input stream for the plasma assuming a 50% efficient fuel cell). In addition since the plasma acts as the catalyst the reformer is completely sulfur tolerant. The reformer is also not sensitive to the choice of input fuels and can be adjusted to the fuel selected by simple control changes. Thus, the reformer provides fuel flexibility. The catalytic action of the plasma also provides a highly compact and robust system. The reformer can be operated in partial oxidation as well as autothermal steam reformation modes to enable both cold start and high efficiency operation. The same reformer design also successfully reformed a number of other fuels such as NATO F76, conventional diesel, low sulfur diesel, Syntroleum S8, and JP10. An overview of plasma reformer development will be presented.

Electrochemical/Mechanical/Thermal Performance

Room: Coquina Salon E
Session Chairs: S. (Elango) Elangovan, Ceramatec, Inc.; Toshio Suzuki, National Institute of Advanced Industrial Science and Technology

2:20 PM

(ICACC-S3-043-2011) Development of A Functional Layer for Direct Use of Hydrocarbon Fuel using Microtubular Solid-Oxide Fuel Cells

T. Suzuki*, T. Yamaguchi, K. Hamamoto, Y. Fujishiro, M. Awano, National Institute of Advanced Industrial Science and Technology, Japan; N. Sammes, Colorado School of Mines, USA

Microtubular solid-oxide fuel cells (MT-SOFCs) have shown to be one of ideal shapes for obtaining high volumetric power density and high robustness which make them attractive to use for many application uses such as auxiliary power units and potable power devices. Because SOFCs are operated at high temperatures, typically in excess of 700 oC, direct use of hydrocarbon fuel becomes possible, which minimizes the system size as well as reducing the cost. It is, however, difficult to utilize direct reforming of hydrocarbon fuel when the operating temperature is below 600 oC, which is the target for intermediate temperature SOFCs. Here, we report a new concept of an SOFC utilizing a functional layer on the surface of an anode, for the direct reformation of a hydrocarbon fuel using a micro-tubular design. Preparation of the functional layer is cost-effective and the layer can consist of any catalyst including, for example, pure-ceria (CeO2). The cell with a CeO2 functional layer displays practical cell performance below 500 oC using methane-water mixture as the fuel gas, and shows enhanced performance compared to systems without a functional layer.

2:40 PM

(ICACC-S3-044-2011) Development of a standard SOFC test fixture for materials and processing evaluation

Y. Chou*, E. T. Thomsen, J. P. Choi, W. E. Voldrich, J. W. Stevenson, Pacific Northwest National Laboratory, USA

Button cells are widely used for materials development for solid oxide fuel cells. However, the too simplistic geometry, flow pattern, and small sizes often limit the interpretation of the results from these tests. Pacific Northwest National Laboratory (PNNL) has been leading the task for DOE's SECA program in developing a "standard" stack test fixture to bridge the gap between button cells and real-sized industrial stacks. In this presentation, we'll demonstrate our Gen2 design with focus on short stack tests with 3 cells. The materials, coatings, and seal systems will be described. Typical data of OCV, impedance, and IV sweep will be reported. Post-mortem analysis will also be presented.

3:20 PM

(ICACC-S3-045-2011) Enhanced Densification of the Ceria Interlayer in Solid Oxide Fuel Cells

J. Hardy, Z. Lu*, J. W. Templeton, J. W. Stevenson, Pacific Northwest National Laboratory, USA

A ceria interlayer is often employed between the perovskite cathode and the yttria-stabilized zirconia (YSZ) electrolyte in a solid oxide fuel cell (SOFC) as a barrier to the formation of electrically-resistive strontium zirconate that would otherwise form due to reaction at their interface during cathode sintering and cell operation. A fully dense pulsed laser deposited (PLD) samaria-doped ceria (SDC) interlayer was utilized in a cell and found to exhibit significantly superior performance to cells with the typical porous screenprinted SDC interlayer. Therefore, an effort was undertaken to achieve enhanced density in screenprinted SDC interlayers without increasing the sintering temperature above 1200°C to avoid interdiffusion and reaction between the YSZ and SDC layers. Dilatometry and microscopy were used to determine the effects of average particle size, cation doping, and ink formulation on the sinterability of SDC. A significant increase in the density of screenprinted SDC interlayers was achieved through a combination of cation doping of the SDC and optimization of the screenprint ink formulation. The impact of the improved density on cell performance will be discussed.

3:40 PM

(ICACC-S3-047-2011) Thermo-mechanical Properties of Scandia and Ceria Doped Zirconia Electrolyte Material for SOFCs

N. Orlovskaya, University of Central Florida, USA; W. Lim, M. Tanjea, Texas A&M University, USA; J. Kuebler, EMPA, Swaziland; M. Radovic*, Texas A&M University, USA

Thermo-mechanical properties of Scandia and Ceria doped Zirconia (SCZ) - Sc0.1Ce0.01ZrO2 – an electrolyte material for intermediate temperature solid oxide fuel cells has been studied. They include coefficient of thermal expansion (CTE), elastic moduli, storage and loss moduli, bending strength, fracture toughness and from room temperature up to 1000 oC. A slight increase in the CTE with temperature was observed at ≈ 500 oC. It was also found that elastic moduli, fracture toughness, and strength of SCZ decrease by ~40 % within a narrow temperature range from 400-600 oC, after which they all increase gradually up to 1000 oC. Observed changes in thermo-mechanical properties are related to the structure of the defects and their ordering, and are discussed in more details in this paper.

4:00 PM

(ICACC-S3-048-2011) Mechanical and Electrical Properties of Porous Ni-YSZ for Anode-Supported SOFC Application

A. R. Ballal*, Visvesvaraya National Institute of Technology, India; S. N. Malhotra, P. Gopalan, Indian Institute of Technology Bombay, India; D. Prakash, P. Sinha, B. P. Sharma, Bhabha Atomic Research Center Vashi Complex, India

Nickel/yttria-stabilized-zirconia (Ni-YSZ) cermet is a popular anode material for SOFC. The anode microstructure plays a vital role in performance of the anode-supported SOFC. It is required to have porous structure with good networking of Ni and YSZ grains. The porosity helps the diffusion of fuel gas but affects the mechanical property of the anode. Hence, the porosity level needs to be optimized to obtain both, good mechanical property as well as electrical conductivity. In the present study, Ni-YSZ cermet was prepared by reducing anode precursor, NiO-YSZ in hydrogen. NiO was synthesized by glycine-nitrate process. NiO was mixed with YSZ in various proportions so that the Ni content in the cermet is 40, 50, and 60 vol%. Pore former, graphite, was added upto 15 wt% to obtain the required porosity. The compacts of resulting mixtures were sintered at 1350 and 1400 °C in air to get NiO-YSZ precursors with varying porosity levels. The dynamic modulus of elasticity for NiO-YSZ and Ni-YSZ was measured using Impulse excitation technique following the ASTM standard. Electrical conductivity of Ni-YSZ was measured upto 800 °C in hydrogen by four-probe method. The modulus of elasticity reduced linearly with porosity level. The electrical conductivity was found to increase upto a certain porosity level and then decrease. Highest electronic conductivity values obtained were around 10^4 S/cm.

4:20 PM

(ICACC-S3-049-2011) Transient Thermal Stress Analysis of Planar-SOFC PEN Structure under Realistic Temperature Field

G. Iqbal, S. Pakalapati, H. Guo, I. Celik, B. Kang*, West Virginia University, USA

Positive/electrolyte/negative (PEN) assembly is the electrochemically active composite structure of a solid oxide fuel cell (SOFC). The thermal stress in this structure may arise due to coefficient of thermal expansion mismatch between its layers, temperature gradient and physical boundary conditions. The aim of this study is to characterize the thermal stress distribution in the PEN structure from room to the op-

erating temperature under realistic temperature profile in a co-flow configuration. Thermal stresses are determined by incorporating temperature fields, obtained from an in-house developed thermo-electrochemical model, into finite element analysis (FEA) model. To determine the critical location of stress concentration, maximum principal stresses (MPS) are calculated from room to the operating temperature. Under operating conditions, the peak MPS occur in the anode material at the anode/electrolyte interface whereas cathode and electrolyte layers experience highest MPS near the air inlet region. The stress discontinuities across the interfaces are due to the different material properties. The knowledge obtained from transient stress analysis can be used established control parameters during cell operation.

S4: Armor Ceramics

Multi-Scale Modeling II

Room: Coquina Salon D
Session Chair: Raymond Brennan, U.S. Army Research Laboratory

1:30 PM

(ICACC-S4-041-2011) Moldeling amorphization in boron carbide under uniaxial compression

W. Ching*, S. Aryal, University of Missouri-Kansas City, USA

Boron carbide (B4C) is a strong protection material of light-weight used mainly in military applications. In spite of more than 40 years of research and development, its full potential has not been realized. The main problem is that B4C undergoes amorphization under uniaxial compression and losses its strength when stress exceeds the Hiognoit elastic limit (HEL) of about 22GPa. The microscopic mechanism of amorphization of B4C under high velocity impact is not fully understood and the ways and means to avoid such weakening are not available. The mechanical properties and the deformation behavior of B4C under pressure are related to its unique interatomic bonding. We report a detailed ab initio simulation of B4C under compression and decompression using a large supercell of 180 atoms up to a strain of 50% in the axial direction (z-direction). Abrupt amorphization was observed at strain between 0.23 and 0.24 corresponding to a sudden shift in the bonding of the chain atoms to highly deformed icosahedrons and the bending of the C-B-C chain. Upon unloading to the original volume, the material remains amorphous showing the transformation process is irreversible. We further explore the possibility of mitigating or extending the pressure at amorphization by various means such as N incorporation.

1:50 PM

(ICACC-S4-042-2011) Length Scale Effects on the Dynamic Failure Strengths of Brittle Materials

N. Daphalapurkar*, K. T. Ramesh, L. Graham-Brady, The Johns Hopkins University, USA

Brittle materials with very high strengths have low toughness and are very sensitive to flaws (e.g. processing-related flaws in ceramics). These flaw-size distributions lead to variability in the failure strength of the material. Often, scaled down versions of sample sizes are used in the laboratory experiments along with some form of volumetric-Weibull scaling function, to predict the failure strengths at a larger scale. However, such approaches fail to address the physical processes that control failure, and questions remain open in regards to applying the same scaling laws to predict the dynamic failure strengths. In this work, we establish a theoretical model and perform simulations incorporating explicit pre-existing flaw size distributions. Failure processes are explicitly simulated to estimate the macroscopic variability in failure strength. This methodology will ultimately assist in the development of improved high-strength ceramics through microstructural design and processing design.

2:10 PM

(ICACC-S4-043-2011) A Scaled Model Describing the Rate-Dependent Compressive Strength of Brittle Materials

J. Kimberley*, G. Hu, K. T. Ramesh, The Johns Hopkins University, USA

A universal relationship is developed that describes the rate-dependent compressive strength of brittle solids based on the micromechanics of the growth of brittle cracks from populations of initial flaws. The model captures the dynamics of interacting and rapidly growing cracks. The fundamental time and length scales involved in the problem are used to develop expressions for a characteristic stress and a characteristic strain rate in terms of material and microstructural properties. Scaling experimental and simulation results by the characteristic stress and strain rate collapses the data to a single curve in failure stress–strain rate space. This curve represents the universal response, which captures both the relatively constant failure stress at low rates as well as the dramatic increase in strength observed as the applied strain rate increases above the transition rate. The resulting model for the universal response compares well with experimental data for ceramics and geologic materials, indicating that the model has adequately captured the physics of compressive failure for a wide range of materials.

Manufacturing

Room: Coquina Salon D
Session Chair: Raymond Brennan, U.S. Army Research Laboratory

2:30 PM

(ICACC-S4-044-2011) Improving Radio Frequency Lamination Method for Armor Panels

S. M. Allan*, M. Fall, H. Shulman, Ceralink Inc, USA

Radio Frequency (RF) Lamination is a new technology that shows promise for eliminating the need for autoclaving for transparent armor. The technology has been used to laminate single-pane glass laminates in less than 1 minute, and multilayer transparent armor panels (3.8 cm thick) in just five minutes. Optical and V-50 ballistic testing of RF laminated ballistic windows confirm that properties and performance meet the specification criteria required for armor windows. Demonstrations to date have shown equivalent performance for thermoplastic polyurethane (TPU) laminated windows. Recently, lamination of polyvinyl butyrate (PVB)-bonded windows has been studied with a focus on producing environmentally stable laminates. Laminates were studied using accelerated aging tests, mechanical performance testing, and non-destructive evaluations of adhesion bonding strength. Results of PVB-laminate progress and performance will be presented.

2:50 PM

(ICACC-S4-045-2011) Manufacture of Armor Tiles and Modules by Encapsulating Ceramic with Aluminum and Aluminum Metal Matrix Composites

J. P. Sorensen*, R. Adams, CPS TECHNOLOGIES CORP, USA

CPS Technologies is the largest producer in the world of aluminum Metal Matrix Composite lids and baseplates for thermal management of electronics. We ship tens of thousands of parts per week for use by OEM's such as Motorola, Cisco, HP, Infineon, BMW and Mercedes. With the help of the US Army we applied this same technology to the manufacture of fully encapsulated ceramic armor. We have made individual encapsulated tiles as well as modules containing many tiles (up to 17 x 32 inches and up to 4 inches thick). This presentation will explain the process, the material choices for each layer of the armor system, and the manufacturing capacity (size and quantity).

3:30 PM

(ICACC-S4-046-2011) Chemical Interactions and Effect of Impurities in Transparent Polycrystalline Magnesium Aluminate Spinel Hot Pressed with LiF

M. Rubat du Merac*, I. Reimanis, C. Smith, Colorado School of Mines, USA; H. Kleebe, Technical University of Darmsdadt, Germany

Transparent polycrystalline magnesium aluminate spinel (MgAl2O4) has potential application as infrared missile windows, transparent armor, and scratch-resistant windows for consumer goods. Lithium fluoride (LiF) is used as a sintering aid during hot-pressing to achieve a fully dense, transparent material. However, the sintering kinetics of spinel and role of LiF are still not fully understood. In this regard, transparent spinel samples have been hot pressed using different powders and under varying conditions and characterized with optical microscopy, SEM and TEM. Results indicate that processing parameters, LiF doping, and impurity content markedly influence microstructure. Impurities are found to play a key role during sintering, forming second phases, hindering densification, causing abnormal grain growth, and ultimately reducing transparency. Analysis with LA-ICP-MS/OES, IR spectroscopy, STA-MS, and modeling with thermodynamic software reveal the chemical evolution of species during sintering and indicate that LiF acts as a cleanser, removing impurities and allowing sintering to complete density. A discussion of this new work will be presented.

3:50 PM

(ICACC-S4-047-2011) Large Area, High Volume Transparent Spinel Composite Ballistic Protection

J. Kutsch*, Technology Assessment & Transfer, Inc., USA

Technology Assessment & Transfer Inc., along with ArmorLine Corporation has developed the ability to fabricate optically clear transparent spinel windows larger and in greater volumes than any other company. They can incorporate these windows into laminates that defeat a large variety of ballistic projectiles at substantial weight and thickness improvements compared to traditional glass solutions. With TA&T as it's research arm, procedures & equipment have been developed at ArmorLine to fabricate spinel plates up to 12x12" in very large volumes (1000s) as well as very large area plates, 30" x 50" x 0.5". Research continues to investigate the properties and advantages of ArmorLine transparent spinel armor composites through the characterization of overall thickness, areal density and both single shot and multi-hit ballistic performance. Spinel (MgAl2O4) optical ceramic is a transparent polycrystalline ceramic whose combination of high hardness, light weight and broadband optical properties make it a leading candidate for stringent optical applications and transparent armor. Its transmission range spans from 0.19 um to 6.0 um and exceeds that of single crystal sapphire and ALONTM.

4:10 PM

(ICACC-S4-048-2011) Transparent Armor for the New Standard in Battlefield Performance

J. J. Carberry*, K. T. Leighton, SCHOTT Diamondview Armor Products, LLC, USA; D. W. Templeton, U.S. Army, USA

ATPD 2352 revision P was issued last year to create a new standard for transparent armor, aimed at improving battlefield performance, maintenance costs, equipment survivability, and general durability based on data collected from performance of transparent armor in the battlefield. DiamondView Armor Products (DAP), later acquired by SCHOTT North America, invented, developed and commercialized a transparent armor specifically focused on satisfying all of these specification's requirements. In the lead up to winning sole source supply of window armor for the MATV last year, DAP undertook a Cooperative Research and Development Agreement with TARDEC which resulted in DAP and TARDEC evaluating DAP's armor to all the metrics of ATPD 2352 rev P and now R. In this paper we will report on this and follow on work. We will: a) Explain the requirements of ATPD 2352 and the challenges they present from a materials properties, armor performance, lifetime testing, transparency, durability and environmental perspective; b) We will present data, analysis, and preliminary modeling showing the materials and performance proprieties of a variety of materials to highlight how and why SCHOTT DAP's zero CTE, discontinuously nano-reinforced glass system was able to pass all the requirements of ATPD 2352, including ballistic, environmental, and optical, many never successfully mastered in transparent armor before.

4:30 PM

(ICACC-S4-049-2011) Hybrid Monolithic Ceramic/Ceramic Matrix Composites; from Turbine Airfoils to Armor

J. E. Holowczak*, C. E. Bird, R. A. Barth, W. K. Tredway, United Technologies Research Center, USA

An overview and brief history of the development and testing of hybrid monolithic ceramic - fiber reinforced ceramic matrix composites (CMCs) will be given. These material systems were originally developed as an approach to providing improved foreign object damage resistance for monolithic ceramic turbine engine hot section components. Charpy impact testing was used to demonstrate a 25x increase in energy absorption for hybrid ceramic/CMCs compared to monolithic ceramics alone More recently, hybrid ceramic/CMCs have undergone development for ballistic armor. These include both helicopter armor and body armor applications. Helicopter efforts have included the development, fabrication and successful demonstration of combination structural panel/armor components. Highlights from this effort will be discussed. Efforts in body armor development have examined several types of monolithic ceramic/CMC combinations. Early efforts in gas gun impact and ballistic evaluation will be provided and basic theories of why hybrid ceramic/CMCs appear to provide benefits will be discussed. This work has been supported in part by the U.S. Army Aviation Applied Technology Directorate (Contract no. W911W6-06-2-0001), the Army Research Laboratory (Contract no. W991QX-C-0077), and United Technologies Corporation.

4:50 PM

(ICACC-S4-050-2011) Characterization of Residual Stresses in SiC Based Tiles

B. S. Munn*, K. Li, Oakland University, USA; J. Zheng, K. Masters, US Army, USA

Many manufacturing operations can induce residual stresses in components. These residual stresses can influence in-service component performance. Therefore, it is important to be able to effectively characterize any induced residual stresses in finished components. One common technique for measuring residual stresses is the hole drilling method. This has been a simple yet effective method for measuring residual stresses in metal components for almost twenty years. However, this method has yet to be established as a reliable technique for measuring residual stresses in advanced ceramic components. This paper first establishes the hole drilling method as a reliable technique to measure residual stresses in a silicon-carbide (SiC) substrate. The hole drilling method is then used to determine residual stress characteristics in a series of SiC tiles of varying thicknesses. The residual stresses are first identified for type (compressive or tensile) and then, analyzed to identify any trends that may exist between the tiles tested. In general, the residual stresses were determined to be tensile in nature and to exist at or near the tile surface. These residual stresses decreased rapidly away from the tile surface. The residual stresses were also found to vary in magnitude based on tile thickness.

S5: Next Generation Bioceramics jointly with S9: Porous Ceramics

Porous Bioceramics II (joint with Symposium 9)

Room: Ponce de Leon
Session Chairs: Himanshu Jain, Lehigh University; Dietmar Koch, Univ. of Bremen

1:00 PM

(ICACC-S5-009-2011) Polymer Ceramic Composites for Engineering Tissue-Tissue Interface (Invited)
H. Lu*, Columbia University, USA

The seamless integration of bone with soft tissues such as tendons and ligaments is critical for synchronized musculoskeletal motion. These soft tissues connect to bone through a fibrocartilaginous interface, which further divides into noncalcified and calcified regions. Reestablishment of this complex interface post injury is essential for integrative repair of biological and synthetic soft tissue grafts. Adapting a biomimetic approach, we have designed stratified scaffold based on biodegradable polymers and polymer-ceramic composites for the regeneration of the multi-tissue transition between soft tissue and bone. Optimization of the polymer-ceramic composites, especially in terms of mineral content for interface regeneration and osteointegration both in vitro and in vivo will be presented. In addition to promoting integrative soft tissue repair, by bridging distinct types of tissue, interface tissue engineering will be instrumental for the clinical translation of integrated musculoskeletal tissue systems with biomimetic complexity and functionality.

1:30 PM

(ICACC-S5-010-2011) Unveiling the Deformation and Toughening Mechanisms of Nacre (Invited)
X. Li*, University of South Carolina, USA

Nacre is a natural nanocomposite with superior mechanical strength and toughness. What is the secret recipe that Mother Nature uses to fabricate nacre? What roles do the nanoscale structures play in the inelasticity and toughening of nacre? Can we learn from this to produce nacre-like nanocomposites? The recent discovery of nanoparticles in nacre is summarized, and the role that these nanoparticles play in nacre's toughness is 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. Stacking fault and dislocation formation together with deformation twinning were found to play an important role in the plastic deformation of individual nanoparticles. This talk also presents future challenges in the study of nacre's nanoscale structure and mechanical properties.

2:00 PM

(ICACC-S5-011-2011) Nanostrucutred Ceramics: Potential, Challenges and Opportunities for Implant Applications (Invited)
R. Bizios*, UTSA, USA

The need (1) for biomaterials with properties similar to those of physiological tissues (most of them characterized by nanometer range surface grain sizes), and (2) for elucidating the conditions that maximize specific functions of cells pertinent to new tissue formation in the human body has motivated the study of nanostructured materials (i.e., materials with grain sizes less than 100 nm in at least one dimension) for prosthetic, implant devices. Nanostructured materials have an advantage for implant applications because they promote protein interactions from surrounding biological tissues and fluids and thus mediate subsequent cell responses which are select, specific and different than those observed in conjunction with conventional materials of the same chemistry. In order to design and fabricate the next generation of nanostructured biomaterials, however, pertinent material structures and properties, material synthesis and preparation methodologies, as well as the mechanisms of biomolecular interactions with nanophase material surfaces must be identified and elucidated. Moreover, the biocompatibility of nanoparticles must be definitively established. Biomaterials, which reliably and predictably promote specific interactions of biomolecules leading to subsequent functions of select mammalian cells and controlling new tissue formation, have the potential of major clinical impact.

2:30 PM

(ICACC-S5-012-2011) Poly(ethylene glycol) conjugated nano-graphene oxide for photo-dynamic therapy (Invited)
H. Dong, Z. Zhao, H. Wen, Y. Li, A. Shen, P. Frank, C. Lin, Tongji University, China; D. Shi*, University of Cincinnati, USA

A novel methoxy-poly(ethylene glycol) modified nano-graphene oxide (NGO-mPEG) was designed and synthesized as a pho-tosensitizer (PS) carrier for photodynamic therapy of cancer. NGO with size below 200 nm was prepared by a modified Hum-mers method. NGO was observed by AFM to exhibit a structure with single-layer graphene oxide sheets down to a few nano-meters in height. Hydrophilic mPEG conjugation of NGO (NGO-mPEG) was found to enhance solubility in cell culture me-dium. No obvious cytotoxicity of the NGO-mPEG was observed towards MCF-7 carcinoma cell line. Zinc phthalocyanine (ZnPc), a photosensitizer for photodynamic therapy, was loaded in the NGO-PEG through π-π stacking and hydrophobic in-teraction, with the drug loading efficiency up to 14 wt%. Importantly, hydrophobic ZnPc was internalized in MCF-7 cells, ex-hibiting a pronounced phototoxicity in the cells under Xe light irradiation. The results of study indicate a great potential of NGO-mPEG for photodynamic therapy of cancer.

3:20 PM

(ICACC-S5-013-2011) Structural investigation of nanosized carbonated hydroxyapatites (Invited)
F. Babonneau*, Y. Wang, N. Nassif, T. Azais, C. Bonhomme, Université Pierre et Marie Curie-Paris6 / CNRS, France; S. Hayakawa, A. Osaka, Okayama University, Japan

Biological apatites, one of the main constituents of bones and hard tissues in mammals refer to poorly crystallized non-stoichiometric carbonate-containing hydroxyapatites (CAp). CAp is also found in pathological calcifications, such as kidney stones, and growth of CAp can be promoted by bioactive synthetic materials used as implants. In all these examples that relate to the growth of nanocrystalline substituted apatites in contact with biological tissues and/or fluids, a precise description of the mineral phase is complex due to the extreme tunability of the apatite structure. In the present study, two synthetic methods to prepare CAp nanoparticles have been used. The first one is a classical neutralization method leading to well crystalline nanoparticles. The second method is more original. It is based on a diffusion method suitable to mineralize collagen matrices. All these CAp samples have been fully characterized via X-ray diffraction, TEM observations, FTIR and multinuclear NMR to determine the phase composition, degree of crystallinity and substitution sites.

3:40 PM

(ICACC-S5-014-2011) Ceramic Nanosensor and Breath Analyzer for Point-of-Care Diagnostics (Invited)
P. Gouma*, SUNY Stony Brook, USA

The detection and monitoring of gases in exhaled human breath up to date has been limited by the lack of appropriate materials and technologies that could rapidly and selectively identify the presence and monitor the concentration of trace levels of specific analytes-biomarkers. We present novel metal oxide-based nanosensors that are highly specific to biomarkers such as ammonia, nitric oxide, isoprene, acetone and ethane gases in breath-simulating environments at low part-per-billion concentrations. The design of a MEMS-based handheld breath analyzer for gas detection in exhaled human breath is described and examples are given for urea monitoring and diabetes detection. Semiconducting ceramics are presented as suitable sensor

materials for easy and affordable noninvasive diagnostics for diabetes, cancer, asthma etc.

4:00 PM

(ICACC-S5-015-2011) Hollow Hydroxyapatite Microspheres for Controlled Delivery of Proteins

M. N. Rahaman*, H. Fu, D. E. Day, Missouri University of Science and Technology, USA

Hollow hydroxyapatite (HA) microspheres were prepared by reacting solid microspheres of lithium–calcium–borate glass (106–150 microns) for 2 days in K_2HPO_4 solution (0.02 M; 37°C), and evaluated as a controlled delivery device for a model protein, bovine serum albumin (BSA). Biocompatible HA microspheres with a hollow core diameter equal to 0.6 the external diameter, high surface area (≈100 m2/g), and a mesoporous shell wall (pore size ≈15 nm) were formed using this method. After loading the hollow HA microspheres with a solution of BSA, release of the BSA into a medium of phosphate-buffered saline (PBS) initially increased linearly with time, but almost ceased after 24-48 hours. Modification of the BSA release kinetics was achieved by manipulating the microstructure of the as-prepared HA microspheres using a controlled heat treatment (1-24 h at 600°C-900°C). Sustained release of BSA was achieved over more than 14 days for HA microspheres heated for 5 h at 600°C. The potential application of these hollow HA microspheres as a device for controlled local delivery of protein growth factors and drugs is discussed.

4:20 PM

(ICACC-S5-016-2011) Hierarchical Structure and Deformation Mechanisms of Bone (Invited)

W. Wagermaier*, M. Kerschnitzki, Max Planck Institute of Colloids and Interfaces, Germany; H. S. Gupta, Queen Mary, University of London, United Kingdom; P. Fratzl, Max Planck Institute of Colloids and Interfaces, Germany

Bone is a hierarchically structured fiber composite made of collagen fibrils, reinforced by embedded mineral nanoparticles. The structure of bone on the micron and nanometer scale has substantial influence on the macroscopic mechanical properties of bone. A detailed knowledge of the structure at different length scales, i.e. structural arrangements of cellular, organic and mineral phases in bone, and the investigation of structure-function relations in bone are relevant for materials science as well as for biological and medical science. The mineralized collagen fibrils are interwoven in various ways, depending on the function of the respective bone. We investigated the extent to which the organization of the collagen matrix is controlled by the cellular network found in various bone tissues using different microscopy methods. We find that the formation of a highly oriented collagen matrix requires an alignment of bone forming cells on a substrate layer. Deformation of bone depends on a cooperative mechanism at different levels of structural hierarchy, which we investigated by combining in-situ tensile tests with x-ray diffraction. It was shown that mineral particles and collagen fibrils take up only a fraction of the overall strain in bone, while the remaining strain is taken up by shearing. This cooperative mechanism shields the brittle mineral phase from the largest applied stresses and maintains bone integrity.

4:50 PM

(ICACC-S5-017-2011) High surface area nano-macro porous bioactive glass scaffold for hard tissue engineering

S. Wang*, H. Jain, Lehigh University, USA

Formation of three-dimensional (3D) nano-porous bone scaffolds with sufficiently large macro pores (≥300 μm) remains a challenge in spite of several methods reported in literature. This combination of interconnected multimodal porosity is required for tissue ingrowth and for the concurrent degradation of implanted structure. We report a new technique for fabricating superior high surface area, nanomacroporous bioactive glass scaffold, which combines the sol–gel process and polymer sponge replication method. The formation of 3D structure is demonstrated in 70mol% SiO2 – 30mol% CaO glass composition as an example, which is uniform across the sample. It consists of open, interconnected macropores with size from 300 to 600 μm, as desired for tissue ingrowth. At the same time, coexisting nanopores provide high-specific surface area (> 100 m2/g), which is needed for enhancing the structure's degradation rate. Furthermore, we demonstrate that by mixing xerogel powders with different surface area, we are able to change surface area of the scaffold, which pave a way for tailoring the degradation rate of bioscaffolds desired for various future biomedical related needs. Thus, these bioscaffolds hold promise for applications in hard tissue engineering.

5:10 PM

(ICACC-S5-018-2011) A Simple Method to Synthesize "Naproxen-Layered Double Hydroxides" Nanohybrid

S. Azimi*, M. Solati-Hashjin, P. Khoshakhlagh, A. Darvish, Amirkabir University of Technology, Islamic Republic of Iran

In the recent years, physicians and pharmacists have focused on drug release and controlled release mechanisms of NSAIDs. Excessive drug prescription, repetitious intake as a result of inadequate efficiency of drugs along with serious side effects particularly gastrointestinal complications are some of deficiencies of traditional NSAID formulations which are expected to be rectified by novel drug delivery systems' utilization. Layered Double Hydroxides (LDHs) have attracted a great deal of attention due to their ability of carrying anions recently. In this project it has been attempted to synthesize a nanohybrid of Naproxen-LDH via a simple coprecipitation method and evaluate the capability of this system to improve release properties in order to decrease its side effects. This simple-inexpensive method has been proved to be able to form Naproxen-LDH hybrid quite easily. Furthermore, the results show a significant improvement in the drug's solubility and indicate sustained-release over time.

5:30 PM

(ICACC-S5-019-2011) Nanoscale Study of Hydrothermally Precipitated Hydroxyapatite and Ag-Doped Hydroxyapatite Coatings

K. Zeytin*, H. Kizil, C. Ergun, Istanbul Technical University, Turkey; M. Cuberes, University of Castilla-La Mancha, Spain

The present study shows the preparation steps of hydroxyapatite (HAP) and Ag-doped HAP coatings via Ca-EDTA decomposition method. Atomic Force Microscopy (AFM) and Ultrasonic Force Microscopy (UFM) were used to obtain information about the nanoscale structure and elasticity of the prepared samples. The topography is characterized by crystalline 200-800 nm in diameter grains, with HAP hexagonal basal terraces delimited by steps and facetted surfaces. Facets on the crytallites are expected to result from energy minimization, as in the process of pit formation when HAP is dissolved. UFM images of individual HAP grains did not exhibit significant variations in elastic contrast, suggesting that the HAP nanocrystals form free from structural defects. Nevertheless, scattered grains with a distinct UFM contrast were also observed, presumably corresponding to a Ca-Phosphate phase different from HAP. Remarkably, AFM and UFM images recorded on pure HAP and Ag-doped HAP coatings were indistinguishible, and AFM/UFM provided no clue to discern the incorporation of Ag in the HAP matrix. Our data may help understanding the mechanical response of the coatings, and the way those interacts with cells in biological process.

S7: 5th International Symposium on Nanostructured Materials and Nanotechnology: Development and Applications

Nanotubes, Nanorods, Nanowires and Other One-dimensional Structures

Room: Coquina Salon C
Session Chairs: Francisco Hernandez-Ramirez, Catalonia Institute for Energy Research; Gurpreet Singh, Kansas State Univ.

1:30 PM

(ICACC-S7-034-2011) Formation and Surface Modification of Tin Oxide Nanowire Based Heterostructures for Device Applications (Invited)

J. Pan, M. Hoffmann, R. Mueller, H. Shen*, S. Mathur, University of Cologne, Germany; J. Prades, F. Hernandez-Ramirez, University of Barcelona, Spain

We present here the synthesis, structure and properties of tin oxide nanowires based heterostructures (SnO2@SnO2, SnO2@VOx and SnO2@CdS) obtained by two-step CVD growth and chemcial bath deposition. The SnO2 nanowires with contact angle (CA) of 3o exhibited superhydrophilic property, whereas the CA of SnO2@SnO2 heterostrucutres increased to 133o. Reversible surface wettability of SnO2@SnO2 heterostructure was observed by alternation of UV irradiation, dark storage and O2 annealing. In comparison to pure SnO2 NWs, gas sensing experiments on SnO2@VOx nanostructures showed higher sensitivity and selectivity for gases at lower operating temperature and exhibited improved transducing response towards changing gas atmospheres which is attributed to the additive VOx inducing a local surface depletion area which strongly influenced the density of conducting electrons in ambient and analytic gas atmospheres. SnO2@CdS heterostructures had a remarkably enhancement in photoconductivity than non-coated SnO2 nanowires due to the electrons transfer from CdS into SnO2.The UV-Vis and photoconductivity spectra revealed that the absorption edge of SnO2 nanowires and SnO2@CdS heterostructures locate at 350 nm and 540 nm, respectively indicating the expanding of optical absorption form UV to visible light due to the decoration of CdS on SnO2 surface.

2:00 PM

(ICACC-S7-032-2011) Synthesis, Characterization and Testing of Polymer-derived Ceramic Composite Nanowires (Invited)

G. Singh*, Kansas State Univ., USA

Carbon based nanomaterials such as graphene, carbon nanotubes and nanohorns have been a topic of intense research in the last few years due to their well defined geometry and mechanical properties. More recently, carbon containing polymer-derived ceramics such as SiCN and Si(B)CN have found applications in ultra-high temperature applications (~1300 C). Our research group is interested in exploiting the unique properties of both these materials to develop next generation of micro-nanocomposites for mechanical engineering related applications, particularly force sensors and high power laser thermal detector coatings. This presentation will focus on: (a) synthesis and characterization of SiCN/MWCNT "shell/core" nanowires in which MWCNT forms the core and (b) scanning electron microscope (SEM) and focused ion beam (FIB) microscope based 3-D nano-manipulation techniques that we have been developing for mechanical testing of these nanowires.

2:30 PM

(ICACC-S7-033-2011) Investigating optical, electrical and structural properties of laterally grown heterojunctions of ZnO nanowires on GaN substrate (Invited)

B. Nikoobakht*, National Institute of Standards and Technology, USA

Previously we reported a surface-directed vapor-liquid-solid growth method for lateral growth of zinc oxide (ZnO) nanowires on substrates such as a-plane sapphire. Extending the planar growth of ZnO on gallium nitride (GaN) results in formation of high quality n-p heterojunctions. This growth technique allows site selective formation of micron- to centimeter-size arrays of nanowire heterojunctions in which nanowires are connected to ZnO back backbones with a controlled hierarchy. In this presentation, using electron microscopy (HRTEM), we will examine the crystal structure of the n-p heterojunctions along their two dimensions, i.e., along the length of the NWs (normal to the m-planes of GaN) and along the width of the NWs (a-direction of GaN). From both perspectives, HRTEM data show an epitaxial heterojunction and a nearly coherent interface without defects such as threading dislocations known in III-V family and their corresponding electro-optical devices. In examining numerous heterojunctions, we typically observe two emissions, i.e., a UV emission under forward bias and an orange emission at 640 nm under forward bias. However, under forward bias we have observed sharp Gaussian emissions centered at 720 nm or 900 nm. A model will be proposed to explain the observed emissions while the Fermi energy is varied.

3:20 PM

(ICACC-S7-031-2011) Synthesis and characterization of 0D and 1D functional oxide nanostructures (Invited)

F. Rosei*, Université du Québec, Canada

1D nanowires and nanotubes have attracted interest because of their unusual electronic, optical and mechanical properties, for possible use in electronics, sensing and solar energy conversion. Multiple hetero-nanostructures are a promising new class of materials due to their multifunctional character and the possibility of effectively coupling different properties, offering significant advantages over single component systems. However, synthesis from distinct materials is challenging due to the lattice mismatch and the difficulty in balancing two growth processes with different microscopic mechanisms and reaction rates. Here we focus on multiple heterostructures of ferroelectric/ semiconductor nanostructures. We demonstrate multiple NaNbO3 nanoplates created inside hollow Nb2O5 nanotubes, forming a novel class of multiple ferroelectric (NaNbO3)/semiconductor (Nb2O5) heterostructures. The semiconductive properties of the host Nb2O5 nanotubes allow for switching of electrical conductivity by an external electric field, even though ferroelectric NaNbO3 nanoplates are attached to the inner surface of nanotubes, showing great potential for the fabrication of memory and other multifunctional ferroelectric/semiconductor devices. Finally, we report on the near IR photoresponse of upconverting nanocrystals.

3:50 PM

(ICACC-S7-035-2011) Hydrothermal growth of patterned ZnO nanorods

M. Ladanov*, G. Matthews, M. Ram, A. Kumar, University of South Florida, USA

Recently, ZnO nanostructures have attracted a great deal of interest due to their optical, piezoelectric, electrical and biocompatible properties, and have been used in solar cells, nanogenerators, sensors and biosensors. ZnO nanowires have shown interesting properties in combination with biological system. Apart from their electrical and optical properties, ZnO nanostructures could be used for the mechanical reinforcement of existing biomimetic scaffolds such as collagen and/or other biodegradable polymers. One of the major complications in device development is how to grow ZnO nanowires in well aligned and patterned films with predefined geometrical shape and aspect ratio. Controlled growth is required to achieve optimal density of nanowires and to produce a defined geometric structure for incorporation in the device. Under his work, we have presented a method by which vertically aligned ZnO nanowires could be grown in defined patterns on the surfaces without the use of resists. We have used a hydrothermal method with growth modifiers to fabricate ZnO nanorods on a substrate that was pre-patterned with a seeding solution by means of microcontact lithography. This method has produced vertically aligned ZnO nanorods of predefined shape and size

with pattern resolution high enough for the production of rows of single nanorods. The nanorods were characterized by SEM, FTIR, Raman, TEM, and XRD techniques, respectively.

4:10 PM

(ICACC-S7-036-2011) Preparation and properties of flat (3-carboxypropyl)-ferrocene nanotubes

Q. Wu*, Tongji University, China

A novel nanotube composed metallocene molecule, (3-carboxypropyl)-ferrocene flat nanotube, was first reported, which was prepared by a new method of ulrrasonic-pH-controlling-reprecipition. The scanning electron microscope (SEM) shows the nanotubes have a length of 20~30 μm, and a thickness of 0.2~3 μm. X-ray diffraction patterns of the products indicate that they keep the original bulk materials crystal structure. The optical properties of the products are characterized by FT-IR spectrometer and UV spectrometer, and they display quantum size effect. Compare to bulk materials, the as-obtained products gives a new UV absorption spectra peak in 256 nm. A possible "sheets exfoliating/rolling" mechanism is also proposed. The as-obtained nanotubes would have wide applications in the field of catalyst, drug delivery.

4:30 PM

(ICACC-S7-037-2011) Surface Ionization Gas Sensors based on Individual Metal Oxide Nanowires

F. Hernandez-Ramirez*, Catalonia Institute for Energy Research, Spain; J. Prades, University of Barcelona, Spain; A. Hackner, EADS, Spain; J. Morante, Catalonia Institute for Energy Research, Spain; G. Mueller, EADS, Spain; S. Mathur, University of Cologne, Germany

Since Seiyama et al. discovered that the electrical conductivity of metal oxides is dramatically changed by the presence of reactive gases in air; these materials have been intensively used as gas sensors due to their low cost and high compatibility with microelectronic processing. Commonly, the detection mechanism of these devices is based on resistive measurements (RES) that are explained in terms of surface combustion processes, in which ionosorbed oxygen is removed from the metal oxide surface and in which electrons, initially trapped on surface oxygen ions, are re-emitted into the conduction band thus generating a sensor signal. Nevertheless, this detection method provides poor selectivity since the surface combustion process happens with a whole variety of potential analyte gases. On the other hand, surface ionization (SI) gas detection is an alternative technique that involves ions formed by the adsorption of analyte molecules on heated solid surfaces, ion emission into the adjacent gas ambient and ion collection at a counter electrode positioned opposite to the emitter surface. The foundations of this technology were studied in the past by Zandberg, Rasulev and Morrison, and recently it was demonstrated that their principles could be applied to SnO2 thin-films (emitter surface), which is the most widely employed material in the fabrication of resistive metal oxide gas sensors.

4:50 PM

(ICACC-S7-038-2011) Microwave Irradiation of Ruthenium on Undoped and N-Doped Carbon Nanotubes

L. F. Mabena*, S. Sinha Ray, Council for Scientific and Industrial Research, South Africa; N. Coville, University of the Witwatersrand, South Africa

The dispersion of a metal on a support is still largely based on conventional catalyst preparation techniques, such as wet impregnation followed by chemical reduction. These approaches often lack good control of particle size and morphology, which are factors that influence the catalytic activity. Also, these processes can be time consuming since they include multiple steps such as long ageing, drying and calcination of the samples. Hence, there is an interest in using more alternative techniques such as microwave irradiation. In this presentation results obtained on a simple modern microwave irradiation method to prepare Ruthenium (Ru) nanoparticles on carbon nanotubes (CNTs) is reported. The undoped as well as N-doped CNTs prepared under the same environment are used as support. Ethylene glycol was used at 200oC to release the formaldehyde which reduces RuCl3. X-ray diffraction, high resolution transmission electron microscopy (HR-TEM) and temperature programmed reduction techniques were used to characterise the Ru/CNT. The results show that the microwave assisted method allows synthesis to be achieved using shorter reaction times, reduced energy consumption and better yields. The results of HR-TEM show a better and well of metals dispersion on the N-CNTs.

S8: 5th International Symposium on Advanced Processing and Manufacturing Technologies for Structural and Multifunctional Materials and Systems (APMT) in honor of Professor Katsutoshi Komeya

Design-Oriented Manufacturing II

Room: Coquina Salon B

Session Chairs: Yigal Blum, SRI International; Michael Halbig, US Army Research Laboratory

1:30 PM

(ICACC-S8-041-2011) Affordable Ceramic Matrix Composites with Enhanced Design and Size Capabilities (Invited)

Y. Blum*, SRI International, USA

One major drawback that inhibits wide usage of fiber-reinforced ceramic composites is the excessive high cost associated with very expensive starting materials, processes (including slow CVI or multiple step infiltration cycles) and capital equipment. The presentation will discuss approaches to lower costs of starting materials, simplify fabrication techniques, reduce the number of matrix infiltration cycles, and/or use less capital and energy intensive processing equipment. The discussed concepts are based on the use of preceramic polymers and their modifications, slurry formulations with selected fillers, and in-situ chemistry. Combinations of these approaches are aimed at minimizing the high cost and simultaneously allowing the manufacturing of larger scale and production volumes of CMC in general and oxide/oxide composites in particular.

2:00 PM

(ICACC-S8-042-2011) Criticality of technologically strategic functional metals

A. Reller*, University of Augsburg, Germany

Most of the relevant technologies depend on the properties and functionalities of metals, metal alloys or metal compounds. In the last two to three decades the spectrum of metals being implemented in technical devices has increased enormously. However, the deposits and the production of many of the metal resources are scarce and, therefore, risks for future developments arise. The determination of the criticality of strategic metals is a useful concept for validating their potentials and risks. This concept is based on criteria like scarcity, functionality, economic measures, dissipation, ecologic issues, geo-political deoendencies, social conflict potentials, etc. Results of studies on communication, energy and mobility technologies are presented.

2:20 PM

(ICACC-S8-043-2011) DHS Advanced and High Performance Materials Database

G. Fischman*, Future Strategy Solutions, USA

A new database developed for the Department of Homeland Security needs to be populated. It focuses on advanced and high-performance materials that will relate to the DHS Infrastructure and Geophysical Division. This database has the potential of helping develop connections between the advanced structural materials communities and possible funding and commercialization opportunities.

2:40 PM

(ICACC-S8-044-2011) Synthesis of SiAlON phosphors by the reduction-nitridation method

T. Suehiro*, Tohoku University, Japan

In recent years, highly covalent Si_3N_4-based oxynitrides (SiAlONs) have been developed as an important family of phosphor host materials due to their great potentials for white LED applications. Generally, SiAlON-based nitride phosphors are synthesized from Si_3N_4, AlN, and other constituent metal oxide or nitride raw powders at ~1600 - 2000 °C, followed by the postsynthesis grinding step to pulverize crude reaction products. This obvious low manufacturability is a major obstacle to their widespread use in LED applications, triggering the intense investigations for developing more sophisticated processing techniques. In this regard, we have developed the gas-reduction—nitridation (GRN) method, which enables direct synthesis of SiAlON fine powder phosphors from the multicomponent oxide system. Successful GRN syntheses of various novel SiAlON phosphors possessing promising applicability for white LEDs have been demonstrated in the current work.

3:20 PM

(ICACC-S8-045-2011) Fabrication and Characterization of Brazed Joints for SiC-Metallic Systems Utilizing Refractory Metals

B. P. Coddington*, R. Asthana, University of Wisconsin-Stout, USA; M. C. Halbig, US Army Research Laboratory, USA; M. Singh, Ohio Aerospace Institute, USA

Metal to ceramic joining plays a key role for the integration of ceramics into many nuclear, ground and aero based technologies. In order to facilitate these technologies, the active metal brazing of silicon carbide (CVD β-SiC, 1.1 mm thick, and hot-pressed α-SiC, 3 mm thick) to the refractory metals molybdenum and tungsten using active braze alloys was studied. The joint microstructure, composition, and microhardness were evaluated by optical microscopy (OM), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and Knoop hardness testing. The braze alloys, Cusil-ABA, Ticusil and Copper-ABA, all formed sound joints with excellent wetting and chemical bonding with the SiC substrate. Despite the close thermal expansion match between the metal substrates and SiC, hairline cracks formed in α-SiC while β-SiC showed no signs of residjavascript:setNextPage('ABSTRACT_CAT_PRES');ual stress cracking. The use of ductile interlayers to reduce the effect from residual stresses was investigated and joints formed with copper as an interlayer produced crack free systems utilizing both CVD and hot-pressed SiC.

3:40 PM

(ICACC-S8-046-2011) Joining of Silicon Nitride Long Pipe by Local Heating

M. Hotta*, N. Kondo, H. Hyuga, H. Kita, National Institute of Advanced Industrial Science and Technology (AIST), Japan

In order to use ceramics as large components for manufacturing plant, it is necessary to establish technology that solves the problems of high cost of production and mechanical reliability of components. Joining of ceramics, including Si3N4, is important technique for producing large or complex ceramic components, improving reliability of ceramic parts and repairing damaged ceramic parts. For joining of the large components, local heating is cost-effective fabrication, because large-scaled furnace that places the whole components is not required. In this study, joint of Si3N4 long pipe was prepared by local heating. The specimen was liquid-phase sintered Si3N4 with Y2O3 and Al2O3 additives. The size of the specimen was 28 mm in diameter and 1000 mm in length. Joining was achieved by heating near the joint area with horizontal electric furnace at mechanical pressure of up to 5 MPa in nitrogen atmosphere. The microstructure of the joint and bulk regions was observed by SEM. The flexural strength was measured by four-point bending strength. This research was supported by METI and NEDO, Japan, as part of the Project "Innovative Development of Ceramics Production Technology for Energy Saving".

4:00 PM

(ICACC-S8-047-2011) Ceramic Joining by Microwave Local Heating

N. Kondo*, H. Hyuga, M. Hotta, H. Kita, K. Hirao, National Institute of Advanced Industrial Science and Technology (AIST), Japan

Joining is one of the important techniques for fabricating large scaled and/or complicated shaped ceramic components. In usual case, whole parts are put into a furnace and heated for joining. However, large furnace is needed for this procedure to join large components. Local heating is a potential technique to solve this problem. Microwave absorption for heating is depending on material specifics. This means that local heating can be achieved by using an appropriate combination of materials. For joining, heating is only required near the joint. Thus, microwave heating is a potential technique to achieve local heating. Here, a combination of silicon nitride (poor microwave absorber at low temperatures), alumina fiberboard insulator (poor microwave absorber), and silicon carbide susceptor (microwave absorber) was tried. Glass was placed at joint. Local heating was actualized by microwave radiation. The joint was heated up to 1500C, and silicon nitride parts were successfully joined.. (Research supported by METI and NEDO, Japan, as part of the Project "Development of innovative ceramics manufacturing technologies for energy saving.")

4:20 PM

(ICACC-S8-048-2011) Interface Engineered Diamond Coatings for Dry Machining

H. Gomez*, University of South Florida, USA; K. Chou, The University of Alabama, USA; X. Xiao, M. Lukitsch, General Motors, USA; A. Kumar, University of South Florida, USA

In this study, adherent diamond on WC-Co (6%) turning inserts was deposited under different surface pretreatments including chemical etchings, heat treatment and Cr/CrN/Cr interlayer to overcome the adhesion issues associate with the detrimental effect of cobalt and to reconstruct the surface in order to promote an interlocking behavior between the diamond film and the substrate. Scanning electron microscopy (SEM), energy dispersed spectroscopy (EDS), and X-Ray diffraction techniques were used to characterize the morphology, cobalt content and nature of the substrate surfaces after each pretreatment; optical interferometry was utilized to characterize the surface roughness. With the aim to evaluate the initial diamond film adhesion, Rockwell hardness tests were performed on the surface to measure the resulting film delamination and fracture patterns. Finally, dry machining performance tests for all diamond coated turning inserts were performed on an aluminum alloy A390 H3. Correlations between the initial Rockwell indentation and tool life were established. Despite the apparent increasing in adhesion reported for Cr/CrN/Cr interlayers, samples under Rockwell indentaion tests, no significant tool life was achieved for the interlayered samples during dry machining; however, superlative adhesion for chemical treated samples was achieved compared with diamond coated turning inserts found in the market.

4:40 PM

(ICACC-S8-049-2011) Tin Oxide-Based Ceramics for Sputtering Targets

E. Medvedovski*, C. J. Szepesi, O. Yankov, Umicore Thin Film Products, USA

Dense tin oxide-based ceramic semiconductors may have a high potential for sputtering targets manufacturing due to their low cost and starting materials availability comparing with indium oxide-based ceramics. Until the present time, these ceramics were unavailable in the market because of lower sinterability and rather high electrical resistivity. Umicore Thin Film Products (Providence, RI) has developed the ceramic compositions and manufacturing process of uniform microcrystalline tin oxide-based ceramics achieving density up to

99.5% of TD and physical properties, which are adequate for DC magnetron sputtering. The obtained materials may be prospective for thin films manufacturing for optoelectronic applications, solar cells, e.g. for transparent coatings with high corrosion resistance, and for thermoelectrics.

S10: Thermal Management Materials and Technologies

Nano Heat Transfer Fluids and Thermal Energy Storage

Room: Coquina Salon F
Session Chairs: Andrew Gyekenyesi, Ohio Aerospace Institute; Mrityunjay Singh, Ohio Aerospace Institute

1:40 PM

(ICACC-S10-001-2011) Enhanced Viscosity of Aqueous Silica Nanofluids

B. Jo, D. Banerjee*, Texas A&M University, USA

The viscosity of water-based silica (SiO_2) nanofluids was measured using a parallel-disk rotational rheometer. The silica nanoparticles had a nominal diameter of ~10 nm. The mass concentration of the silica nanoparticles was varied in this study from 0.1 -20%. Each nanofluid sample was sonicated in an ultra-sonication bath for the same duration. Environmental temperature was varied by a convection oven within the test section to investigate the variation viscosity of the aqueous silica nanofluids as a function of temperature. The viscosity measurements were carried performed by increasing the shear rate. The pH of the nanofluids were maintained at a fixed value for each sample. The results show that the viscosity of the nanofluids follow a shear thinning behavior where the viscosity decreased as the shear rates were increased. This feature was more significant at higher temperatures. The viscosity of the nanofluids with the same pH value was found to increase with increase in the concentration of the nanoparticles.

2:00 PM

(ICACC-S10-002-2011) Engineering the Heat Transfer Nanofluids: The Efficiency Approach

E. V. Timofeeva*, W. Yu, D. M. France, D. Singh, J. L. Routbort, Argonne National Laboratory, USA

The heat transfer performance of any fluid results from the combination of thermo-physical properties such as thermal conductivity, viscosity, heat capacity and density. Introduction of nanoparticles to the base fluid affects all these properties. Heat capacity and density depend only on the concentration of the solid phase in the fluid and are unrelated to nanoparticle morphology (size, shape etc.). However both thermal conductivity and viscosity are largely determined by the shape and size of the solid particles constituting the nanofluid systems. The talk will report on the progress in the establishing the relationship between the size and shape of nanoparticles to macroscopic system parameters and the use of those parameters for estimating the overall heat transfer efficiency. The base fluid and the temperature effects on the nanofluid heat transfer efficiency will also be covered.

2:20 PM

(ICACC-S10-003-2011) Enhancement of Heat Capacity of Molten Salt Eutectics Using Inorganic Nanoparticles for Solar Thermal Energy Applications

D. Banerjee, D. Shin*, Texas A&M University, USA

Thermal energy storage using phase change materials have been widely investigated for concentrating solar power applications. The system efficiency in concentrating solar power applications is affected significantly by the storage temperature, while 70% of the total cost of solar power arises from the material costs of the thermal storage devices. Hence, increasing the operating temperature and decreasing the size of the storage materials can reduce the cost of solar energy. Molten salts (such as carbonate eutectics) have melting points between 200°C and 600°C and are stable up to 600°C. They are also reasonably cheap and environmentally safe. However, the specific heat of the molten salts are low (< 2 J/gK) compared to other conventional thermal storage materials. In this study, silica and magnesia nanoparticles were doped in various carbonate and chloride eutectic mixtures of Ba, Na, Ca, Li and K. Specific heat measurements were performed using a differential scanning calorimeter. The specific heat of the eutectics in both solid and liquid phase were enhanced dramatically (greater than ~ 6% - 20%) on addition of nanoparticles of silica and magnesia, at only 1-1.5% mass concentrations. Materials characterization studies showed that the nanoparticles induced nano-scale phase transformations in the solvent phase.

2:40 PM

(ICACC-S10-004-2011) Enhancement of Heat Capacity of Nitrate Salts Using Mica Nanoparticles

S. Jung*, D. Banerjee, Texas A&M University, USA

The specific heat of the solid phase of nitrate salt eutectic (KNO_3: $NaNO_3$ in 60:40 molar ratio) was observed to be enhanced on addition of minute concentration of mica nano-particles. The measurements were performed using a differential scanning calorimeter (DSC). The specific heat measurements were performed for a temperature range of 160-200°C which was chosen to be below the melting point of nitrate salt. The experiments were performed for different mass concentrations of mica nano-particles, which ranged from 0.5% to 2%. The specific heat capacity of the nitrate eutectic in the solid phase was found to be enhanced by as much as 20% on addition of the mica nanoparticles. The implication of these results are in reduced cost of solar thermal energy due to the reduction in material costs for thermal energy storage. Thermal energy storage and the associated material costs are the most dominant factors that contribute to the total cost of solar thermal energy. Hence, application of these mica nanoparticles to nitrate salts can be quite effective in reducing the cost of solar thermal energy since nitrate salt eutectics are typically used as conventional materials for solar thermal energy storage.

3:20 PM

(ICACC-S10-005-2011) Power Required to Pump Ceramic-Based Nanofluids

J. Routbort*, D. Singh, W. Yu, R. K. Smith, E. Timofeeva, Argonne National Laboratory, USA

It has been demonstrated that nanofluids can have enhanced thermal conductivities when compared to the base fluid. However, adding nanoparticles to a fluid increases the viscosity. Therefore, the power to pump the nanofluid in a heat exchanger system will increase. Hence any additional heat removal resulting from the enhanced heat transfer coefficient might be offset by an increase in parasitic energy losses resulting from increased pumping power. We have measured the torque required to pump several ceramic–based nanofluids in the turbulent flow region using an automotive water pump. The nanofluids were a 2.2 vol.% SiC (170 nm) in a 50-50 mixture of ethylene glycol and water and a 0.5 to 4.0 vol.% alumina (40 nm) in water. The SiC was supplied by Saint Gobain while the Al2O3 was supplied by Sasol. The increased pumping power is in good agreement with theoretical calculations based on the pressure drop, volumetric flow rate, fluid density and viscosity. Work supported by the Office of Vehicle Technologies and the Industrial Technology Programs of the U.S. Department of Energy under contract number DE-AC02-06CH11357 at Argonne National Laboratory, managed by the University of Chicago Argonne LLC.

3:40 PM

(ICACC-S10-006-2011) Thermal energy storage nanocapsules

R. Rodriguez*, M. Garcia de Cortazar, Inasmet-Tecnalia, Spain

New sources for more efficient, ecologically friendly and cost effective ways to capture and store energy are been investigated. Phase change

materials (PCMs) appear as a real alternative in thermal energy storage technology because they can absorb or release a large quantity of latent heat when they change phase from solid to liquid state or vice versa. However, in order to hold the liquid phase and to protect PCMs from the influence of outstanding environment, recently these materials have been microencapsulated. Nevertheless, one of the major drawbacks of microcapsules latent energy storage technique is low PCM thermal conductivity. An alternative to avoid this low thermal conductivity is PCM nanoencapsulation. Their nano scale particle size generates huge surface-volume ratio and thus increases the specific heat transfer area. Therefore, the objective of this study was to develop thermal energy storage nanocapsules containing paraffin wax as phase change material. Nanocapsules were synthesized by batch miniemulsion polymerizations. To understand and enhance heat storage capacity the influence of paraffin wax/methyl methacrylate ratio on polymerization kinetics, particle morphology, phase change properties and thermal stability was investigated. It was observed that the latent heat capacity increases as the content of encapsulated paraffin wax increases. In addition, the encapsulated PCMs were thermally stable.

4:00 PM

(ICACC-S10-007-2011) 3-Dimensional Modeling of Graphitic Foam Heat Sink

K. Alam*, A. Bradu, Ohio University, USA

Recent advances in integrated circuits and aerospace systems have led to the generation of high heat fluxes which require very efficient heat dissipation. Highly conductive graphitic foams are being considered for such heat sink applications. In this paper, a heat sink design based on flow through graphitic carbon foam is investigated by numerical simulation using the FLUENT software. This analysis is based on a true 3D model of the foam, which is obtained through x-ray tomography carried out at the Air Force Research Laboratory (AFRL, WPAFB, Ohio). A solid model of the foam heat sink is then developed by reconstructing the surface from the x-ray images and simulation of coolant flow through the foam. The results of the numerical simulation show a large enhancement of heat transfer due the flow through the pores of the graphitic foam.

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

New Materials

Room: Coquina Salon H
Session Chairs: Martin Magnuson, IFM; Yanchun Zhou, Aerospace Research Institute of Materials & Processing Technology

1:30 PM

(ICACC-S12-010-2011) Synthesis, microstructure and mechanical properties of Ti3Sn(1-x)AlxC2 MAX phase solid solutions

G. Bei, V. Gauthier-Brunet, C. Tromas, S. Dubois*, Laboratoire de Physique des Matériaux, France, Institut PPRIME, France

Ti3Sn(1-x)AlxC2 MAX phase solid solutions have been successfully synthesized from different reactant mixtures. It is shown that 312 solid solutions is likely formed from reaction between TiC and 211 solid solution. Rietveld refinement allows to carefully characterize the structure and the ocathedra and trigonal prims distortion parameters as a function of the Al content. It is shown that, for both Ti3SnC2 and Ti3AlC2, hexagonal unit cell is strongly distorted. Nevertheless, [Ti6C] octahedra are mainly distorted in Ti3SnC2 whereas [Ti6Sn(1-x)Alx] trigonal prisms are mainly distorted in Ti3AlC2. Nanoindentation experiments allows to determine hardness and elastic modulus of some Ti3Sn(1-x)AlxC2 solid solutions. It is demonstrated that solid solution hardening is not operative in this system. Elastic modulus sligthly increases with Al content ; such an increase may be attributed to the Ti-Al stiffer bonds present in Ti3AlC2 than the Ti-Sn bonds in Ti3SnC2. Finally, Young's modulus of the Ti3Sn0.2Al0.8C2 solid solutions is shown to slightly vary with temperature in the range 20-450°C.

1:50 PM

(ICACC-S12-011-2011) (Ti0.5Nb0.5)5AlC4: A New Layered Compound Belonging to MAX Phases

L. Zheng*, J. Wang, X. Lu, F. Li, J. Wang, Y. Zhou, Institute of Metal Research, Chinese Academy of Sciences, China

The Mn+1AXn phases (also called the MAX phases), where M is an early transition metal, A is an A group element, X is C and/or N, are layered carbides or nitrides. This family of materials has attracted the attention of material scientists, physicists, and chemists due to their combination of excellent properties of both metals and ceramics, including good thermal and electrical conductivity, resistant to thermal shock, machinable, and damage tolerant, low density, high elastic stiffness, being refractory and resistant to high temperature oxidation. Up to now, more than fifty M2AX, six M3AX2, and seven M4AX3 compounds have been determined. In addition, Ta6AlC5 and Ti7SnC6 were also reported. However, no M5AX4 phases have been found so far. To explore new MAX phases, Ti-Nb-Al-C quaternary system was selected in this work, and a new layered compound, (Ti0.5Nb0.5)5AlC4, was discovered. Experimentally, it was synthesized by reactive hot pressing of Ti, Nb, Al, and C powders. The crystal structure was determined by the combination of X-ray diffraction and transmission electron microscopy (TEM) analyses, which is consisting of a 5(Ti, Nb)-C bond chain linked by a Al layer. It is the first and unique MAX phase with n = 4 discovered so far. The discovery of this new phase (Nb0.5Ti0.5)5AlC4 not only injects new vitality into the family of MAX phases, but also enriches the knowledge of this family of materials.

2:10 PM

(ICACC-S12-012-2011) Novel insights into the mechanical properties and deformation behavior of MAX phase materials (Invited)

C. Tromas*, A. Guitton, A. Joulain, L. Thilly, P. Villechaise, V. Gauthier-Brunet, S. Dubois, Institut Pprime, CNRS - Université de Poitiers - ENSMA, France

In this study, the elementary deformation mechanisms of MAX phase polycrystals (Ti_3SnC_2, Ti_3AlC_2, Ti_2AlN, Ti_4AlN_3) have been studied in terms of individual dislocations. Due to the macroscopic brittleness of the samples, mechanical testing has been performed under confining pressure. In a macroscopic approach, compression tests have been performed in a Paterson press, under gaseous hydrostatic pressure. In a microscopic approach, plastic deformation has been locally introduced in single crystals by nanoindentation, the confining pressure being ensured by the surrounding material. The stress field generated by this technique offers areas in compression, tension or shear, and reaches locally very high values. This is thus an interesting method to probe all the possible slip systems. The dislocation structures have been then determined by Atomic Force Microscopy (AFM) through the observation of slip lines induced by the emergence and propagation of the dislocations. The local crystallographic orientations have been determined by Electron Back Scattered Diffraction (EBSD) to reveal the local crystal rotation and to identify the slip systems associated to the slip lines. Complex dislocation behaviors, including dislocations out of the basal plane, associated to more conventional kink bands formation have been observed.

2:40 PM

(ICACC-S12-013-2011) Synthesis of $Ti_2Al(C_xN_{(1-x)})_y$ carbonitrides MAX phases

T. Cabioch*, University of Poitiers, France; P. Eklund, Linkoping University, Sweden; V. Mauchamp, M. Jaouen, University of Poitiers, France

The milling, cold compaction and thermal annealing (4h-1400°C-Ar flow) of Ti, TiC, Al and AlN powders were achieved to produce

$Ti_2Al(C_xN_{(1-x)})_y$ compounds with x=0; 0.25; 0.5; 0.75;1 and 0.7≤y≤1. XRD analysis, SEM observations combined with X-Ray microanalysis revealed the formation of the almost pure carbonitride MAX Phase $Ti_2AlC_xN_{(1-x)}$ for y=1 whereas an increasing amount of intermetallics (TiAl, Ti_3Al) was characterized for lower values of y. On the basis of Rietveld refinement of the XRD spectra and EELS analysis it is possible to conclude that substoichiometry in carbon and/or nitrogen can be obtained in the carbonitrides and nitrides whereas only stoichiometric compounds are obtained fore pure carbides. The a cell parameter and the volume of the unit cell vary linearly with x. On the contrary, c cell parameters values from the carbonitrides are lower than that of the pure carbide or nitride. Furthermore, a detailed study of the XRD spectra clearly indicates the occurrence of microstrains in all the carbonitrides.

Novel Characterization

Room: Coquina Salon H
Session Chairs: Erica Corral, University of Arizona; Christophe Tromas, Institut Pprime

3:20 PM

(ICACC-S12-014-2011) Non-Contact Creep Characterization of ZrB2-SiC Composites with the Electromagnetic Mechanical Apparatus (Invited)

S. Gangireddy, J. W. Halloran*, University of Michigan, USA; Z. N. Wing, Advanced Ceramics Manufacturing Inc., USA

The creep behavior of electrically conductive ultra-high temperature ceramics can be characterized with no physical contact in the hot zone using thin ribbon specimens which are self-heated with a DC current and mechanically loaded with electromagnetic Lorenz forces generated by a magnetic flux density. We describe the design and implementation of a second generation Electromagnetic Mechanical Apparatus (EMMA-2), which uses a variable magnetic field to apply stress, continuous non-contact to measure deflection, and operation in a controlled atmosphere. Theoretical models are presented for mechanical stress and temperature, as related to specimen geometry, electrical current, magnetic flux density, and combined with creep models behavior to predict the accessible range of temperature and stress. Creep measurements are presented for a series of ZrB2-SiC composites at temperatures in the range of 1500-1800oC.

3:50 PM

(ICACC-S12-015-2011) Stress measurement of $Zr^{11}B_2$/SiC composites using neutron diffraction and Raman spectroscopy

J. Watts*, G. Hilmas, W. Fahrenholtz, Missouri University of Science and Technology, USA

Previous research at Missouri S&T has demonstrated that 10 to 30 volume percent SiC particulate additions to ZrB_2 affect the strength, fracture toughness, thermal shock resistance, and hardness among other properties. These effects are in part due to the stresses generated in and around the dispersed SiC particles upon cooling from the processing temperature. Raman spectroscopy has been used to measure the compressive residual stress in SiC particles on the surface of the composite. Neutron diffraction was performed on a composite sample in order to measure residual stresses in both the $Zr^{11}B_2$ matrix as well as the dispersed SiC phase. Samples of the composite materials, as well as pure $Zr^{11}B_2$ and SiC powders, were heated to ~1800 °C. Neutron diffraction patterns were obtained at regular intervals upon cooling from 1800°C back to room temperature. Residual stress in the composite was calculated by comparing the lattice spacings of $Zr^{11}B_2$ and SiC in the composite to those of the individual powders. The point at which the composite lattice parameters started to deviate from those of the powders upon cooling was also determined, providing the temperature at which stresses start to accumulate. The stress values calculated from neutron diffraction and Raman spectroscopy were also compared.

4:10 PM

(ICACC-S12-016-2011) Anisotropy in the electronic structure of Ti3SiC2 probed by x-ray emission spectroscopy in comparison to ab initio calculations (Invited)

M. Magnuson*, IFM, Sweden; P. Eklund, L. Hultman, Linköping University, Sweden

The anisotropy of the electronic structure and chemical bonding of Mn+1AXn-phases has been explored at Linköping University using bulk-sensitive and element selective x-ray fluorescence spectroscopy. For example, the anisotropy in the electronic structure of an epitaxially grown film of Ti3SiC2 was investigated and compared to amorphous silicon. The differences between the in-plane and out-of-plane bonding at the internal interfaces of the nanolaminates was investigated in detail by angle-resolved precision measurements. The Ti L, C K and Si L1, L2,3 emission spectra of Ti3SiC2 are compared with first-principles density-functional theory including core-to-valence dipole transition matrix elements. Strongly hybridized spectral shapes are detected for Si imbedded in Ti3SiC2. The anisotropy of the electronic structure and chemical bonding is discussed in relation to the various hybridization regions and macroscopic properties such as conductivity, elasticity and thermopower.

4:40 PM

(ICACC-S12-017-2011) Macroscopic deformation mechanisms of MAX phases investigated by Transmission Electron Microscopy and In-Situ Neutron Diffraction

A. Guitton, G. Bei, A. Joulain*, L. Thilly, C. Tromas, University of Poitiers, France

The macroscopic deformation mechanisms of two MAX systems (Ti-Al-C and Ti-Al-N) are investigated by complementary methods. First, compression tests under gaseous hydrostatic pressure are performed and followed by post-mortem transmission electron microscopy (TEM) analysis. Plastic deformation at room temperature (RT) under a strain rate of 2 10^(-5) s^(-1) is achieved without fracture of the sample. The surface deformation morphology is studied with SEM and exhibits the early stage of Kink Bands (KB) formation. The deformation microstructure observed by TEM shows a large density of dislocations with various configurations: dislocation walls, pile-ups, interactions, sources (partial or perfect). Second, in-situ compression under neutrons experiments are performed at RT, i.e. monotonous and cyclic compression at low strain rate to monitor the evolution of the elastic strains of the different grain families and the storage of dislocations, via diffraction peak profiles analysis. All these results are combined to gain insight into the origin of the brittle-to-ductile transition of the MAX phases and their peculiar deformation modes.

S13: Advanced Ceramics and Composites for Nuclear Fusion Applications

Composite Materials for Fusion Energy

Room: Oceanview
Session Chair: Akira Kohyama, Muroran Insttute of Technology

1:30 PM

(ICACC-S13-030-2011) Carbon-carbon composites and tungsten for high heat flux components in future fusion reactors - a comparative analysis (Invited)

G. Pintsuk*, Forschungszentrum Juelich, Germany

Carbon-carbon (C/C) composites and tungsten are potential plasma facing materials for further application towards commercial fusion reactors. While both materials have their advantages the cons need to be addressed to judge on the materials suitability. Besides well known tritium retention issues for C/C composites it's the ability of the materials to withstand thermal and neutron loads that plays a decisive role. Under transient thermal loads C/C composites suffer from the erosion of fibers oriented parallel to the loaded surface due to local overheating and related thermal stresses. The amount of erosion

thereby increases with increasing base temperature which is influenced by steady state heat loads (P = 10-20 MW/m2) but also by the degradation of thermal conductivity of carbon based materials under neutron irradiation resulting in even lower erosion thresholds. While carbon erosion has minor influence on the plasma performance, the latter is threatened by tungsten melt erosion. Therefore any material damage favoring high-Z plasma contaminations has to be minimized. This comprises the setup of minimum temperatures to avoid brittle crack formation and power density thresholds to reduce the risk of high cycle thermal fatigue damage. Both, minimum temperatures and power density thresholds are negatively influenced by recrystallization and neutron irradiation.

2:00 PM

(ICACC-S13-031-2011) Qualification of carbon-carbon composites as an armour material for the ITER divertor

J. Linke*, T. Loewenhoff, G. Pintsuk, M. Roedig, C. Thomser, Research Center Juelich, Germany

To qualify and characterize plasma facing material in future thermonuclear fusion reactors, extensive mechanical and thermo-physical analyses were performed on a number of different 3-directional C/C composites with different fiber architecture. To demonstrate the high heat flux performance under all ITER relevant loading scenarios, thermal fatigue and thermal shock experiments in electron beam test facilities were carried out to determine the threshold values for the initiation of irreversible damage to the plasma facing materials and to the joints. In particular under very short transients, C/C composites shows the tendency to disintegrate due to brittle destruction of the matrix; in addition, fibers which are aligned perpendicular to the heat flux direction show rather substantial erosion rates up to 1 μm per ELM event (1 MJ/m2). Special attention is being paid to ELM-simulation experiments with high cycle numbers. To evaluate the acceptability of a C/C armoured divertor in a nuclear environment (e.g. during the D-T-phase of ITER), different material grades and small scale components were irradiated to fluences ≤ 1 dpa. Post irradiation examination of these test samples gave evidence of a substantial degradation of the thermal conductivity, i.e. a reduction of the heat removal efficiency of C/C based modules, and an increase in material erosion.

2:20 PM

(ICACC-S13-032-2011) SiC materials for fusion reactor

J. Narciso*, J. M. Molina, USA

The development of structural materials to produce the components facing the plasma in fusion reactor is one of the key problems in fusion technology. Among the advanced material under considerations for the first wall and breeder blanket, SiC based composites offers the greatest potential. In this work, an experimental procedure for manufacturing SiC materials with homogeneous properties from different carbon sources is described. The proper selection of the carbon materials plays a mayor role in the final properties of the SiC. The strict control of the Beta-phase formation could be determined if the materials it is useful or not to be used in plasma reactor

2:40 PM

(ICACC-S13-033-2011) SiC/SiC Composite Structures for Flow Channel Inserts

R. J. Shinavski*, A. M. Goetz, Hyper-Therm HTC, Inc., USA; G. E. Youngblood, Pacific Northwest National Laboratory, USA

Silicon carbide fiber-reinforced silicon carbide matrix composites are believed to have stability under high flux irradiation, high mechanical strength at temperature, damage tolerance/toughness and compatibility with Pb-Li to meet the requirements for fabricating a flow channel insert that protects the ferritic steel structure in the blanket module of a fusion reactor. These composites must also possess a low electrical and thermal conductivity to minimize magnetohydrodynamic pressure drop and to prevent thermal coupling of the Pb-Li to the steel structure, respectively. This work examines means of manipulating the electrical and thermal conductivities of SiC/SiC composites such that the low conductivity goals are achieved without sacrificing the high strength and damage tolerance of the composite. Electrical conductivities were modified through manipulations of the fiber coating process, while engineering of the composite as a structure was identified as an efficient means to obtain the desired thermal properties. Such a combined approach is most suitable for proposed flow channel insert designs that separate the electrical and thermal requirements of the insert. Mechanical, thermal, and electrical properties of SiC/SiC will be presented.

Ceramic Composites for Nuclear Applications

Room: Oceanview
Session Chair: Jacques Lamon, CNRS

3:20 PM

(ICACC-S13-034-2011) SiC-based Composites Potential for Applications in Advanced Nuclear Energy (Invited)

S. Dong*, B. Lu, Z. Wang, H. Zhou, L. Gao, P. He, Shanghai Institute of Ceramics, Chinese Academy of Sciences, China

Silicon carbide (SiC)-based ceramic-matrix composites (CMC), which consist of a SiC-based matrix reinforced with either carbon or SiC fibers and be referred to as C/SiC and SiC/SiC composites, have been studied for nuclear energy applications for more than a decade. The potential for these materials have been widely discussed and is now understood to be (1) the ability to operate in temperature regimes much higher than for metallic alloys, (2) an inherent low level of long-lived radioisotopes that reduces the radiological burden of the structure, and (3) perceived tolerance against neutron irradiation up to high temperatures. This present work reviews the recent progress in development, characterization, and irradiation effect studies of SiC-based CMC for nuclear energy applications. The remaining general and specific technical issues for SiC-based CMC development for nuclear energy applications are also identified.

3:50 PM

(ICACC-S13-035-2011) Influence of fibres surface roughness on mechanical behaviour of minicomposites SiC/SiC based on Hi-Nicalon S and SA3 reinforcement

C. Sauder*, CEA, France; J. Lamon, INSA, France

Owning to recent progress in the fabrication of stoichiometric fibers and their stability under neutron irradiation, SiC/SiC composites are candidate for nuclear applications as structural material for fuel containment in Gas Fast Reactor (GFR). For these applications, mechanical properties (deformation capability) and resistance to neutron irradiation are key factors. It is well known that a high fibre surface roughness leads to a high interfacial frictional shear stress, and so, a low ductility composite. In this work, the natural surface roughness of Hi-Nicalon S fibre has been raised to a level similar to that of Tyranno SA3 fibre. SiC matrix minicomposites were made with treated tows. Then, the tensile behaviour of SA3 and Hi-Nicalon S reinforced minicomposites (with various types of interface and surface roughness) has been investigated. Microstructure analyses were performed in order to determine fibre pullout length lp, crack spacing distance at saturation ds and interfacial shear stress. Features of the stress-strain behaviour are discussed with respect to minicomposite interface type and surface roughness characteristics.

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(ICACC-S13-036-2011) Refractory Enhanced SiC Composites for Reactor Applications

J. Steinbeck*, D. Stebbins, F. S. Lauten, Physical Sciences Inc., USA

Physical Sciences Inc. is currently investigating the use of refractory enhanced carbon fiber reinforced silicon carbide composites (Cf/SiC)

for use in next generation nuclear systems. A series of aging, oxidation and erosion tests were performed to determine the viability of Cf/SiC materials for nuclear applications. Composite specimens were fabricated using the polymer impregnation and pyrolysis (PIP) process. Samples were held at 1000°C in helium to mimic the anticipated thermal environment in a next generation nuclear system for 3000 hours. The flexure strength and thermal conductivity of the most successful composite formulation were seen to remain constant over the duration of the aging experiments at 280 MPa and 30 W/m-K, respectively. Less than 1% mass loss was measured throughout the 3000 hour test period. Rapid oxidation testing was performed to 1400°C in air and was shown to degrade the flexure strength of aged specimens by less than 20%. A helium erosion study was performed using a MIDJet plasma torch that enables a hot (1000°C), high speed (> 100 m/s) flow of moderate pressure (8 Torr) helium over test specimens. Initial results show that the flexure strength of the specimens were unaffected by the helium flow. The results of the study indicate that PIP processed Cf/SiC materials may have a role in future nuclear systems and warrant further study.

4:30 PM

(ICACC-S13-037-2011) New Mechanical Test Standards for Carbon-Carbon and SiC-SiC Composites in the Very High Temperature Reactor (VHTR) Project

S. T. Gonczy*, Gateway Materials Technology, USA; Y. Katoh, Oak Ridge National Laboratory, USA

The U.S. Department of Energy has selected the Very High Temperature Reactor (VHTR) to demonstrate the use of nuclear power for electricity and hydrogen production without greenhouse gas emission. The VHTR design is a helium-cooled, graphite moderated, thermal neutron spectrum reactor with a helium outlet temperatures >800°C and off-normal core temperatures > 1200°C, well beyond the capability of current metal alloys. Ceramic matrix composites (CMC) are being developed for the control rod systems in the reactor core. The CMCs consist of high strength carbon-carbon and SiC-SiC composites, providing high temperature strength, damage tolerance, corrosion resistance, and long-term radiation durability. These nuclear-qualified CMCs will require new geometry-specific mechanical test standards to support material development, property data bases, design codes, and component specifications, as well as NRC regulations on nuclear design approval, certification, and licensing. These new standards are being developed in a DOE–ASTM C28 project with broad industrial participation. This paper will report on the current status of applicable mechanical test standards, the need for new standards, a 5-year standards development plan, and progress on the first priority test standards – tensile and shear strength of tubes.

4:50 PM

(ICACC-S13-048-2011) Active and passive oxidation of CVD-SiC under HTGR operating condition

C. Kim*, Korea Institute of Science and Technology, Republic of Korea; Y. Katoh, Oak Ridge National Laboratory, USA

As a potential HTGR and Fusion material CVD-SiC is attractive in that it is free of Boron which captures neutron during nuclear reaction. CVD-SiC can be applied to a nuclear reactor as a matrix material for a SiC/SiC composite component. High temperature and oxidizing impurities during HTGR operation can change the property of CVD-SiC by either active oxidation or passive oxidation. In order to understand oxidation behavior CVD-SiC oxidation system is set up with atmospheric oxygen concentration and flow rate control system connected to a tube furnace. Passive or active oxidation regions are determined by comprehensive interpretation of weight change, microstructure,and elemental analysis. Theoretical studies and experimental results are compared and possible reasons for the deviation between two results are discussed. Projected transition criteria for high pressure application will be predicted based on the discussed factors.

Poster Session B

Room: Ocean Center

(ICACC-FS1-P075-2011) Correlation between Water Loss and Chemical Composition in Aged Alkaline Activated Metakaolin Based Geopolymers

M. Lizcano*, A. Gonzalez Elizondo, M. Radovic, Texas A&M University, USA

The weight changes in geopolymers during and after curing have been investigated. Samples were prepared by mixing metakaolin precursor with alkaline silicate solutions having molar ratios of SiO2/A2O3 ranging from 2.5 to 5 and H2O/(SiO2 +Al2O3) ranging from 2 to 4. The samples were cured at 60 oC for 24 hours in two environmental conditions and then aged at room temperature. Weight measurements were taken regularly. The results show that even after curing for 24 hours, the samples continue to lose water for many days in the air at room temperature. Additionally, a difference in weight change was noted between the two environmental conditions after the curing regime. An increase in weight loss with increasing H2O/(SiO2+Al2O3) ratios from the initial mixture of the sample was also noted. A correlation between SiO2/Al2O3 ratio and weight loss has been observed. The results of this investigation suggest that the curing process may continue longer than previously realized and changes in weight are related to SiO2/Al2O3 ratios. It was also found that the H2O/(SiO2+Al2O3) ratio in initial mixture affects significantly density of the sample after complete curing and again in the air.

(ICACC-FS1-P076-2011) Mechanical Properties of Na and K Activated Metakaolin-Based Geopolymers

M. Lizcano*, H. Kim, M. Radovic, Texas A&M University, USA

The aim of this study is to establish relationship between structural and mechanical properties of geopolymers, GPs, with different chemical compositions. The metakaolin-based geopolymers were prepared by mechanically mixing metakaolin and alkaline silicate aqueous solutions to obtain samples with Si/Al atomic ratios from 1.25 to 2.5 with Na/Al or K/Al atomic ratios equal to 1. Geopolymer samples were cured in a laboratory oven at 80 oC for 24 and 48 hours under ambient pressure in sealed conditions. Structural characterization of the samples with different chemical compositions was carried out using X-Ray Diffraction (XRD), Nuclear Magnetic-Resonance (NMR) spectroscopy and Scanning Electron Microscopy (SEM). The mechanical characterization included micro-indentation, Vickers indentation, fracture toughness measurement, as well as compressive testing. It was found that structure and mechanical properties of GPs depends on their chemical composition. The Na-GPs with ratio Si/Al = 1.5 had the highest Young's modulus and hardness. The K-GPs with Si/Al = 2 had the second highest value for Young's modulus. The highest compressive strength was found for samples cured for 48 hours for Na-GPS followed by K-GPs with Si/Al = 1.5. The K-GPs have a higher apparent density and fracture toughness than Na-GPs. The results of mechanical testing are linked to structural properties of processed geopolymers.

(ICACC-FS1-P077-2011) Effect of Granulated Blast Furnace Slag Addition on Structure, Pore Architecture, and Strength Properties of Geopolymers

T. Metroke, J. Eichler*, Universal Technology Corporation, USA; M. V. Henley, M. I. Hammons, Air Force Research Laboratory, USA

Geopolymers were prepared from mixtures of metakaolin (MK) or fly ash (FA) and granulated blast furnace slag (GBFS) in various physical states (wet, dry, dry–milled, and rehydrated–milled). The effect of GBFS slag preparation method and hydration level on the compressive strength, gel chemistry, and porosity characteristics of the resulting geopolymers were determined. For MK–GBFS materials, highest compressive strengths were observed upon incorporation of milled GBFS, where smaller particle size facilitates calcium release. For FA–GBFS materials, maximum calcium incorporation was observed when milled GBFS was used, though compressive strength for these materials was lower than for the FA-based binder. As compared to dry

and dry–milled slag, wet and rehydrated–milled slags produced materials exhibiting higher compressive strength.

(ICACC-FS1-P078-2011) Blended Fly Ash Geopolymers

G. M. Canfield*, Oak Ridge Institute for Science and Education, USA; N. Brown, D. Nagler, Air Force Research Laboratory, USA; T. Metroke, Universal Technology Corporation, USA; M. V. Henley, Air Force Research Laboratory, USA

Geopolymers were synthesized by blending Class F fly ash with a commercially available mixture of Class C/F fly ash. Optimum curing conditions were determined for selected blends. The effects of charge-balancing cation (Na, K) and calcium incorporation on the synthesis, set-up time, and compressive strength were determined as a function of increasing Class C/F content and increasing alkalinity. Data from strength measurements and initial structural studies using infrared analysis suggest the possible coexistence of both geopolymer and calcium silicate hydrate phases within the sample matrix. Elemental analysis using X-ray fluorescence and further structural analysis including SEM and X-ray diffraction are planned to assist in elucidation of these phases.

(ICACC-FS1-P079-2011) Use of Carbon Dioxide-Treated Zeolites in the Carbonation of Portland Cement Paste

S. W. Morefield*, M. E. Marcano,, R. Moser, C. A. Weiss, P. G. Malone, US Army ERDC-CERL, USA

Carbonation is a natural process that occurs in cement-based systems whereby CO2 reacts with calcium phases to form calcite (calcium carbonate). Carbonation in these systems has the effect of improving the physical properties of the material. This study investigated the introduction of CO2 into cement-based systems through the incorporation of zeolites during the production of the cement paste samples used in this test program. Zeolites are well known to be able to absorb distinct types of gases including CO2 because of its micro-porous structure. In this study, the effect of carbonated synthetic zeolites MS-4A, MS-5A and MS-13X as a cement replacement (at levels 0%, 10%, 15%, 20% and 25%) on the physical properties of cement pastes were investigated. Compressive strength results at early ages (1, 3 and 7 day) indicate that for the three kinds of zeolite-cement paste mixtures the optimum level of substitution was 15%. At 1 day zeolite-containing mixtures (especially those with smaller particle sizes) showed a higher compressive strength compared to the control mixtures. After 3 days the control mixtures showed higher compressive strengths than those at all levels of replacements. The presence of calcite was observed as early as 1 day using X-ray diffraction analysis.

(ICACC-FS1-P080-2011) Stabilization of Un-sufaced Roads over Volcanic Gravel Materials Using Geopolymer Technology

M. Sykes, P. Allison, P. Bly, D. Bailey, S. W. Morefield*, C. A. Weiss, P. G. Malone, US Army ERDC-CERL, USA

Stabilizing fine and coarse glassy volcanic aggregate for vehicular traffic is a challenge due to the fine-grained fraction produced on the road surface. Traffic over volcanic gravels produces a fine-ground glassy dust that generates a suspended, abrasive, dust plume in the air as each vehicle passes. A new technology developed from soil, which is currently classified as geopolymer technology, is being investigated as a solution to the problem. Preliminary work with this type of road in Hawaii indicates the problem can be handled by modifying conventional lime stabilization to raise the pH of the treated surface materials and activate additional glassy additives that can react with and contribute to cementation reactions that occur in the glassy aggregate. Initial work indicates that the addition of as little as 6% (wt.) each of ground metallurgical slag, fly ash, calcium hydroxide, and sodium carbonate to the wetted aggregate can produce a cementation reaction that allows a graded mixture of the volcanic aggregate to achieve strength in excess of 6.4 MPa in as little as seven days. X-ray diffraction patterns from the cemented materials suggest the major cementing material is a calcium silicate hydrate gel. Anothite present in the original volcanic material was unaltered, although examination of the volcanic glass indicated extensive surface etching.

(ICACC-FS1-P155-2011) Geopolymer materials prepared from LiOH

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Geopolymer materials were prepared directly by a mixing of metakaolinite, lithium hydroxide, water and filler; the content of which varied from 10 – 90 wt%, and Li/Al ~ 1.5. Geopolymer materials were characterized by DTA, RTG and SEM methods. The geopolymer materials are extremely porous, exhibiting homogenous nanostructured matrix and relatively low values of water extracted portions.

(ICACC-FS2-P081-2011) Metal-ceramic composites: optimal microstructure design for different loading cases

R. Piat*, Y. Sinchuk, Karlsruhe Institute of Technology, Germany

The aim of the presented studies is to determine the microstructure of metal-ceramic composite with minimal compliance. To achieve this, firstly the micromechanical model for calculation of the effective mechanical properties of the lamellar single domain is developed. Verification of this model was provided by comparison with results of the FE calculations for the real microstructure obtained from metallographic images and experimental measurements by ultrasonic technique. Secondly, the FE model of the macroscopic specimen under different loading cases was created. 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 ceramics in the domain. Solution of the optimization problem is carried out for prescribed volume of the ceramics in the whole specimen. Resulting optimal microstructures were obtained for different geometries of the specimen and different loading cases

(ICACC-FS2-P082-2011) Ab initio computations of the electronic, mechanical, and thermal properties of ultra high temperature ceramics (UHTC) ZrB2 and HfB2

J. W. Lawson*, C. W. Bauschlicher, NASA Ames Research Center, USA; M. S. Daw, Clemson University, USA

Refractory materials such as metallic borides, often considered as ultra high temperature ceramics (UHTC), are characterized by high melting point, high hardness, and good chemical inertness. These materials have many applications which require high temperature materials that can operate with no or limited oxidation. Ab initio, first principles methods are the most accurate modeling approaches available and represent a parameter free description of the material based on the quantum mechanical equations. Using these methods, many of the intrinsic properties of these material can be obtained. We performed ab initio calculations based on density functional theory for the UHTC materials ZrB2 and HfB2. Computational results are presented for structural information (lattice constants, bond lengths, etc), electronic structure (bonding motifs, densities of states, band structure, etc), thermal quantities (phonon spectra, phonon densities of states, specific heat), as well as information about point defects such as vacancy and antisite formation energies.

(ICACC-FS2-P083-2011) Thermo-kinetic Simulation of Low Temperature Sintering of Tableware Porcelain

I. M. Mroz*, U. Kahnert, J. G. Heinrich, Clausthal University of Technology, Germany

The optimization of sintering processes of porcelain by means of reduction of sintering temperature can lead to energy and time saving as well as lower CO_2 emission by approximately 25–30 %. In this study heating curves for low temperature sintering tableware using thermo-kinetic software are elaborated. The reduction of sintering temperature by 150°C is achieved by grinding of raw materials and changing of batch composition. The shrinkage of the modified materials is adjusted to the values of the manufacturer's requirements. The thermodynamics and the kinetics of the sintering reactions were described mathematically based on thermal diffusivity and

dilatometer measurements. Complex mechanism of sintering reactions is presented by means of multilevel models of thermo-kinetic software. The sintering behavior controlled by neck formation, volume diffusion and grain growth will be discussed. Based on models of analysis it was possible to predict the sintering behavior under desired conditions. The simulation enabled the generation and optimization of technical sintering curves. Furthermore the microstructure evolution of sintered materials has been studied by means of XRD, light microscopy and SEM. Density, water absorption and porosity were also determined. Finally promising laboratory results will be transmitted to the industrial kilns with controlled firing atmosphere.

(ICACC-S2-P084-2011) Effects of UV-radiation on the cleanability of titanium dioxide-coated glazed ceramic tiles

M. Emami*, Saveh University, Islamic Republic of Iran

Surface coatings based on nanotechnology have been used to improve the properties of glazed ceramics. One of the main functions of the coating is to make the surface easy-to-clean or self-cleaning. One of the available coating materials is titanium dioxide, TiO2, which is reported to improve the surface self-cleaning properties produced by UV-radiation. Commercial TiO2-based photocatalytic products can be grouped into five main categories: exterior construction materials, interior furnishing materials, road construction materials, purification matrices and household goods. A unique aspect of TiO2 is that it generates two separate photo-induced phenomena: a photocatalytic phenomenon and a superhydrophilic phenomenon. Sunlight and rainwater keep TiO2-based self-cleaning exterior products clean based on these two phenomena. In this paper, the effects of UV-radiation on the cleanability of three glazed tiles coated with ceramic sol–gel derived TiO2 were evaluated.The observed effects of UV-radiation were greatest on rough surfaces, implying that increasing roughness increases the surface area available for photo-induced phenomena in the TiO2-surface. Organic particle soil was removed more efficiently after UV-radiation than without UV treatment, whereas UV-radiation did not affect the removal of oil soil. Contact angles decreased significantly after UV-radiation.

(ICACC-S2-P085-2011) Effects of the surface coating on yellow phosphors with TiO2

J. Yoo*, Korea Institute of Ceramic Engineering & Technology, Republic of Korea; H. Lee, HanYang University, Republic of Korea

There have been various intensive efforts to improve the poor characteristics of the photoluminescence (PL) and the life span of phosphors, in particular, the orthosilicate phosphor that is used in white LEDs (Light Emitting Diode). Recently, it has been reported that the surface coating of phosphor with metal oxides yielded an improvement in PL and thermal stability. However, there is still no tangible evidence as to why the surface coating gives rise to a change in the optical properties of phosphors. Here, we report the effects of the TiO2 coating on the photoluminescence and thermal stability of the yellow phosphors. The TiO2 layer with 20 nm was uniformly coated over the phosphor surfaces. The photoluminescence (PL) properties of the TiO2-coated phosphors showed improved yellow-emission intensity about 10% compared to that of the pristine phosphors. The TiO2-coated phosphors showed more stable thermal quenching property than pristine phosphors. We concluded that the TiO2-coated surface of the phosphor is an effective way to improve the phosphor efficiency and enhance the thermal quenching stability.

(ICACC-S2-P086-2011) Melt Infiltration Processing of Titanium Carbonitride Cermets with a Ductile Nickel Aluminide Binder

S. T. Buchholz*, Z. N. Farhat, G. J. Kipouros, K. P. Plucknett, Dalhousie University, Canada

Titanium carbonitride (Ti(C, N)) cermets, formed from a solid solution of titanium carbide and nitride, exhibit an excellent combination of wear and corrosion resistance. In the present work three Ti(C,N) ratios ($TiC_{0.7}N_{0.3}$, $TiC_{0.5}N_{0.5}$, and $TiC_{0.3}N_{0.7}$) have been examined for the formation of cermets with a ductile nickel aluminide (Ni_3Al) binder. Samples have been prepared by dry pressing and melt infiltration, with Ni_3Al volume fractions varied between 20 and 50 vol. %. Good dimensional stability arises for the $TiC_{0.7}N_{0.3}$ materials, and to a lesser extent those prepared with $TiC_{0.5}N_{0.5}$. Conversely, when using $TiC_{0.3}N_{0.7}$ powder significant warping was observed, with partial dewetting of the binder phase on the lower surface of the samples. Fine grain sizes were retained for the infiltrated cermets, with mean values generally less than 2 μm. Initial testing determined the optimum sample preparation methods and the basic material properties, including hardness and fracture strength. In addition, preliminary assessment of fretting wear will also be presented.

(ICACC-S2-P087-2011) Laminated All Oxide Ceramic Composite Layers for Control of Radiation Heat Energy Transfer Direction and Energy at Elevated Temperatures

M. Yamazoe*, K. Matsumura, Y. Kagawa, The University of Tokyo, Japan

A black-colored Al2O3 layer was laminated with a transparent polycrystalline Al2O3 using aerosol deposition process. The thickness ratio between the black layer and transparent layer, number of layers and periodical geometry are chosen as materials parameters. Outermost surface of the composites were set to black Al2O3 layer to allow high absorption of heat energy. Optical properties of the constitute layers, black Al2O3 and transparent Al2O3 fabricated by aerosol deposition process, were measured to obtain baseline properties. Light-laminated composite interaction behaviors in the visible-infrared wavelength region was measured, especially, change of incident light intensity between two anti-symmetrical plane was measured using IR wavelength light; for example change of light intensity from in-plane to perpendicular to laminate structure etc. Temperature dependence of the intensity was also measured by tunable filtering optical microscope.

(ICACC-S2-P088-2011) Synthesisation and characterization of Nanocrystalline α-cordierite

F. Jahantigh*, R. Malekfar, University Tarbiat Modares, Islamic Republic of Iran

Nanocrystalline α-cordierite glass-ceramic are synthesized using a modified Pechini method. The structure and lattice mode of the products are investigated via XRD and Micro Raman back scattering spectroscopy. The Debye-Scherrer formula is used to confirm the grain sizes estimated by the SEM slides. Dielectric constant and DTA analyses are used to study this nanocrystallite property.

(ICACC-S2-P089-2011) Phase Stability and Thermal Conductivity of Composite Environmental Barrier Coatings on SiC/SiC Ceramic Matrix Composites

D. Zhu*, S. L. Benkel, NASA Glenn Research Center, USA

Advanced environmental barrier coatings are being developed to protect SiC/SiC ceramic matrix composites in harsh combustion environments. The current coating development emphasis has been placed on the significantly improved cyclic durability and combustion environment stability in high-heat-flux and high velocity gas turbine engine environments. Environmental barrier coating systems based on advanced HfO2 and ytterbium silicate, HfO2-Si nano-composite bond coat systems have been processed and their stability and thermal conductivity behavior have been evaluated in simulated turbine environments. The incorporation of Silicon Carbide Nanotubes (SiCNT) into high stability hafnia (HfO2) and/or HfO2-silicon composite bond coats, along with ZrO2, HfO2 and rare earth silicate composite top coat systems, showed promise as excellent environmental barriers to protect the SiC/SiC ceramic matrix composites.

(ICACC-S2-P090-2011) Slurry Based Environmental Barrier Coating (EBC) Infiltration on SiC/SiC Composite Preforms for Improved Oxidation Protection

S. Ramasamy*, G. Morscher, The University of Akron, USA; S. N. Tewari, Cleveland State University, USA; R. T. Bhatt, D. S. Fox, NASA Glenn Research Center, USA

SiC fiber reinforced SiC (SiC/SiC) composites are candidate materials for structural hot sections of next generation gas turbine engines due

to their superior thermal shock/oxidation resistances with enhanced durability. However, the environmental durability of these ceramics is adversely affected due to the presence of water vapor in high velocity combustion environment. Therefore, there is a need to develop environmental barrier coatings (EBCs) which can shield these silicon based ceramic components from harsh combustion environments and make them more durable. Slurry based mullite/rare-earth silicate EBCs were developed for SiC and SiC/SiC composite substrates, and their usefulness was evaluated by determining oxidation resistance in simulated combustion (90% H20–balance O2) environment by thermal cycling between 1300°C/1350°C and room temperature for up to 400 thermal cycles. Results showed that the multilayer EBCs furnished excellent protection with minimal oxidation at substrate/coating interface against the water vapor environment. To further improve the oxidation resistance, slurry based mullite/rare-earth silicate EBCs were infiltrated in the SiC/SiC preforms providing fool-proof oxidation resistance to SiC fibers.

(ICACC-S2-P091-2011) The Influence of Spraying Parameters on Indentation Fracture Toughness of Plasma-Sprayed Zirconia Coatings

S. Sadeghi-Fadaki*, MUT, Islamic Republic of Iran

Fracture toughness is one of the most important parameters which influence the development of plasma-sprayed zirconia coatings. In this study, Young's modulus (E) and fracture toughness (KIC) of zirconia coatings produced by air plasma spraying has been determined by the indentation method. The fracture toughness was evaluated at room temperature with a load of 49N using a Vickers's diamond indenter. X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used to characterize the coatings. The effects of spraying parameters; powder feed rate and spraying distance (SD), on fracture toughness of as-sprayed YSZ coatings were studied. By varying spray distance/ powder feed rate, significant changes were detected in the microstructure of the top coat. The obtained results revealed that with increasing powder feed rate and spray distance, the microhardness and Young's modulus of coatings increase to a maximum and then decrease. Also, the results showed that the fracture toughness of coatings ranged from 1.8 to 3.5 MPa√m by varying the powder feed rate and spray distance. All of the samples experienced half-penny cracking and were analyzed with correlations applicable to that crack system. Initial results presented here will serve as a baseline for comparison to irradiated samples in future work.

(ICACC-S2-P092-2011) Microstructure of Nanoporous ZrO2-4mol% Y2O3 Coatings Fabricated by Electron Beam-PVD

B. Jang*, Y. Sakka, National Institute for Materials Science, Japan; H. Matsubara, Japan Fine Ceramics Center, Japan; S. Kim, H. Kim, Korea Institute of Ceramic Engineering and Technology, Republic of Korea

Electron beam physical vapor deposition(EB-PVD) is a widely used technique for depositing thermal barrier coatings (TBCs) on metal substrates for high temperature applications, such as gas turbines, in order to improve the thermal efficiency. The controlled microstructure of coatings is one of the most important properties for obtaining superior TBCs. To optimize TBCs for integration into gas turbines, characterization of the relationship between microstructure and thermal properties of the coatings is necessary. This work describes the microstructure of ZrO2-4mol% Y2O3 (YSZ) coatings as a function of the substrate rotation speed. YSZ coatings were deposited by EB-PVD onto zirconia substrates. Coated specimens formed at different rotation speeds namely stationary, 1, 5 and 20 rpm. The average coating thickness was about 300 um. X-ray diffraction (XRD) and Raman spectroscopy were used to determine the crystal structures of the phases present and to determine if any preferred orientation developed in the coatings. The YSZ coatings consist of porous-columnar grains containing nano pores. Nano sized pores could be observed around feather-like grains as well as inside of columnar grains. The total porosity and numbers of nano pores of YSZ coatings increased with increasing substrate rotation speed during deposition.

(ICACC-S2-P093-2011) Indentation Stress-Strain Behavior and Thermal Stability of Layered Thermal Barrier Coatings

D. Lee, Kookmin University, Republic of Korea; Y. Jung, Changwon National University, Republic of Korea; U. Paik, Hanyang University, Republic of Korea; K. Lee*, Kookmin University, Republic of Korea

Thermal barrier coatings (TBCs) have been modified with a layered structure in both bond and top coats using different commercial feedstock powders using specialized coating system of TriplexProTM-200. Different shapes or size distributions of powders are used for TBC coatings. The mechanical behaviors of indentation stress-strain and load-displacement curve on TBC surfaces are evaluated using tungsten carbide sphere. The thermal exposure tests were performed at the surface temperature of 1100°C with the temperature difference of 150 °C between the surface and bottom of sample for a various dwell time. The thermal shock tests from over 1100oC to room temperature were conducted for various multiple-cycles. After 8000 EOH, the TBCs with the layered structure show a sound condition without an evidence for delamination at the interface. Both TBCs with the layered structure show thinner TGO thicknesses and less oxidation behavior in the bond coat in the thermal exposure, compared with the TBCs without layered structure, indicating that the layered TBC is more efficient in protecting the substrate from the thermal exposure and contact environments.

(ICACC-S2-P094-2011) Thermal Barrier Coatings Deposited Using the FARADAYIC EPD Process

J. W. Kell*, H. McCrabb, Faraday Technology, USA

Faraday Technology is developing a non-line of sight, pulse/pulse reverse electrophoretic deposition process (FARADAYIC EPD) for thermal barrier coatings for use in gas turbines. This process improves upon conventional EPD due to better control of the electric field, resulting in increased coating uniformity, decreased surface roughness, decreased hydrolysis, and decreased edge effects. A yttria-stabilized zirconia (8% YSZ) powder coating was deposited out of suspension onto NiCoCrAlY bondcoated, Ni-based superalloy substrates. Post deposition, the samples were then subjected to a combined binder burnout and sinter process and subjected to a battery of tests, including surface roughness measurements, microstructural examination, thermal conductivity measurements, and short and long term thermal cycling tests, to determine their feasibility for use in gas turbine engines. This research is intended to develop the EPD process to produce coatings with properties consistent with similar systems processed by EB-PVD and plasma spray and is expected to have decreased operating and capital costs.

(ICACC-S2-P158-2011) Mechanical Properties and Durability of Advanced Environmental Barrier Coatings in Calcium-Magnesium-Alumino-Silicate Environments

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This study focuses on the fracture toughness and stability of several candidate oxide and silicate environmental barrier coating (EBC) materials for protecting SiC/SiC ceramic matrix composites (CMCs) in harsh gas turbine engine environments. Vickers hardness testing was the method used to compare the EBCs, and for the stability tests, the samples were exposed to Calcium-Magnesium-Alumino-Silicate (CMAS or "sand") with a surface concentration of 39.4 mg/cm^2 CMAS for 150hrs-200hrs with 50 hr cycles at a temperature of 1500° C. Current results of the fracture toughness testing showed that the t' phase multi-component ZrO_2 had the highest toughness. The results from the CMAS reaction included analysis from SEM secondary electron and backscatter electron images, energy dispersive spectroscopy analysis as well as x-ray diffraction analysis. The results showed that the effects of the CMAS on the coatings consisted of reactions that caused melting, evaporation, and chemical changes in the silicates as well as penetration of the CMAS into the pores and cracks of the oxide or silicate materials. Advanced laser heat flux rig and high pressure burner rig tests were

also used to investigate coating degradation and help understand the stability and failure mechanisms in simulated turbine engine conditions.

(ICACC-S3-P095-2011) Sintering of Co_2MnO_4 spinels for protecting coating on stainless steel SOFC interconnectors

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SOFC lifetime is often limited by the poisoning of cathode with Cr-rich volatile species that evaporate from stainless steel interconnector. For this reason spinel ceramic coating is often deposited over the interconnector to reduce chromium evaporation. The production of spinel coating over the metallic interconnector is anyway far to represent a conclusive solution. Problems related to deposition procedures, sintering and mechanical reliability have to be solved yet. One of the major issue is the creation of a compact and impermeable coating at relatively low temperatures in order to preserve the metal substrate. In the present work, Co_2MnO_4 spinel was synthesized by gel-combustion and reverse micelle techniques and the influence of the obtained microstructure on sintering process was analyzed and compared with the behavior of commercial ceramic spinel. The analysis was carried out on both pressed pellets and screen-printed coatings on stainless steel substrate. Density evolution was correlated to the initial specific surface area, morphology and composition of the spinel powders. It was found that regardless the synthesis process the only obtained phase is Co_2MnO_4. Optical dilatometry analyses pointed out considerable changes in sintering temperature, this being even 100-200°C lower for materials with the highest specific surface area.

(ICACC-S3-P096-2011) Promising composite cathode materials on the base of La0.8Sr0.2MnO3 for apatite-like solid state electrolyte La10Ge6O27

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The apatite-like compounds such as silicates and germanates of rare-earth elements are interesting as potential solid oxide ion electrolytes for intermediate temperature SOFCs because of their high oxygen-ion conductivity at 873-1073 K. The present investigation focuses on the comparative study of interaction solid state electrolytes La10Ge6O27 (LGO) and ZrO2-stabilized Sc2O3 (SSZ) with composite cathode materials on the base of La0.8Sr0.2MnO3 (LSM): LSM-LGO (50:50), LSM-SSZ (50:50) and Ag-Pd alloy - LSM. Solid state electrolytes were prepared by ceramic method and sintered in gas-tight plates. Dual-layer electrodes were prepared by sequential brushing with composite cathode material and LSM and sintering at 1443 K, 1 hour. Chemical interaction in LSM-LGO system was investigated by layered scanning of cross section between two samples prepared from these materials and sintered at 1700 K during 4 hour under the pressure. It was found that dual-layer composite cathodes have a high electrochemical activity in contact with the LGO electrolyte and stably operate at 1073 K with the polarization resistance 0.25 Om/cm2 and the current density in the range of 250-350 mA/cm2 at overvoltage value about 100 mV.

(ICACC-S3-P097-2011) Assessment of the Electrochemical Properties of Samarium and Praseodymium doped BSCF Perovskites

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The oxygen nonstoichiometry and electrical conductivity of the mixed conducting p-type perovskite, Sm and Pr doped Ba¬0.5Sr0.5Co0.8Fe0.2O3-x (BSCF) have been determined simultaneously by a Coulometric titration cell. The measured data is used to elucidate the defect structure of the materials system. The overall trend of oxygen partial pressure dependence on the nonstoichiometry and electrical conductivity have been evaluated and interpreted on the basis of the defect equilibrium among oxygen vacancy and B-site cation valancy. Various equilibrium constants for the materials system were calculated and compared with the base Ba0.5Sr0.5Co0.8Fe0.2O3-x system.

(ICACC-S3-P098-2011) Investigation of the Benefits of Current Collection Methods for Microtubular SOFCs

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Solid oxide fuel cells (SOFCs) have received a great deal of attention recently, due in part to their high energy conversion efficiency and environmental compatibility. Miniaturization of the cell size and integration of multiple miniaturized cells can be considered as one of the most effective approaches in increasing the volumetric power density. Recently, various researchers reported excellent electrochemical performance and durability under thermal-cycling for microtubular SOFC designs. Most of the cells were supported by a porous anode tube, so the anode tubular support works as both of current collector and gas diffusion layer as well as support medium for the SOFC. Thus, the aim of this study is to investigate the benefit of the anode current collection method on the performance of the microtubular SOFC, by studying various current collection systems. In this presentation, we will report mainly on two different current collection methods for the anode support and compare it to a numerical simulation. It was very apparent that the contact resistance had a significant impact on the performance of the microtubular SOFCs. This study was supported by the Japan Society for the Promotion of Science (JSPS); Excellent Young Researcher Overseas Visit Program. We gratefully acknowledge Dr. Funahashi for supporting to prepare the cells.

(ICACC-S3-P099-2011) Synthesis of δ-bismuth oxide nanopowders via sol gel used in electrolyte of solid oxide fuel cell

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In this paper bismuth oxide nanopowders synthesized via sol gel method.the sintering temperature to complete phase transition are above 730°c .formation of cubic phase is confirmed by X-ray diffraction (XRD) study. Transmission electron microscope (TEM) investigations revealed that the average particle size is 50 nm for these powders.ionic conductivity measured by AC impedance spectroscopy.

(ICACC-S3-P100-2011) Effect of Co-doping on electrophysical properties of $LnBaCo_2O_{5+\delta}$ (Ln = Sm, Nd)

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Materials with general formula LnBaMe'Me"$O_{5+\delta}$ (Ln – rare earth element, Me', Me" – different 3-d metalls) possess high electronic conductivity and oxygen ion mobility at their lattice and may be applied as cathode in solid oxide fuel cells, membranes in gas separators. Influence of transitional elements ratio is also interest. Therefore electrophisical and mechanical-thermal properties of $LnBaCo_{2-x}Cu_xO_{5+\delta}$(Ln=Sm, Nd; x=0, 0.1…1) were investigated in present work. Dense samples were synthesized by the conventional ceramic method. Electrical conductivity was measured in the temperature range 623-1200 K and partial oxygen pressure range 10^{-6} – 0.21 by four-probe method. The thermal expansion was measured in air at temperatures 300 – 1200 K. Thermal expansion coefficient was calculated for low-temperature and high-temperature intervals. XRD-analysis achieved homogeneity of the samples. Orthorombic lattice of cobaltites transforms to tetragonal one by doping even a small amount of Cu. Conductivity of materials decrease with temperature increase. Cu-doping decreases total conductivity of cobaltites and changes conductivity type from metallic to semi-conductor one. TEC also decreases by Cu-doping from $21{,}2\times10^{-6}$ K^{-1} to 15×10^{-6} K^{-1} for Ln = Sm. Achieved results show that Cu-doping allows to vary properties of cobaltites to make them suitable for application in electrochemical devices.

(ICACC-S3-P101-2011) Investigation of BICUVOX Electrolytes for SOFC Applications

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This work will present methods of increasing the mechanical strength and redox stability of BICUVOX (copper substituted bismuth vanadate - Bi2CuxV1-xO5.5-z) electrolytes, and will present potential electrode strategies for solid-oxide fuel cell (SOFC) application. The widespread commercialization of SOFCs and solid-oxide electrolysis cells (SOECs) is primarily limited by materials degradation issues related to the required high-temperature operation (>800°C). Research is required to develop the next generation of solid-ionic electrolytes and electrodes for applications <700°C. The BICUVOX composition shows ionic conductivity similar to that of YSZ (yttrium-stabilized zirconia) at much lower temperatures (500-650°C). Unfortunately, the low mechanical strength, high coefficient of thermal expansion, and high redox instability has limited the demonstration of this electrolyte within SOFC applications. Through the use of submicron BICUVOX precursor powders, and the incorporation of nano-ceria within the microstructure, the mechanical strength was increased by greater than thirty percent, while enhancing the conductivity over published values. The redox stability was enhanced by incorporating <100 nm thick, dense doped ceria barrier layers onto the BICUVOX electrolyte at temperatures ≤600°C through sol-gel deposition methods.

(ICACC-S3-P102-2011) Influence of Ce or Y Doping on the Electronic Conductivity of Scandia-stabilized Zirconia

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The electronic conductivity of main components in the solid oxide fuel cells (SOFCs), the electrolyte and electrodes, determines its power generation performance. In specific relation to the electrolyte, a high electronic conductivity decreases the open circuit voltage due to short circuit currents. On the other hand, the active region for electrochemical reaction is expanded to the electrolyte surface via the contribution of the electronic hole and electron mobility. The Sc2O3-stabilized zirconia (ScSZ) is an attractive electrolyte for SOFCs, because of its higher ion conductivity compared to the conventional 8 mol% Y2O3-stabilized zirconia (YSZ). The high ion conductive cubic phase of ScSZ has been generally stabilized by co-doping with Ce or Y. In this study, the electronic conductivities for 10 mol% Sc2O3-stabilized zirconia co-doped with Ce or Y (10Sc1CeSZ or 10Sc1YSZ) were measured at 1073 – 1273 K in the oxygen partial pressure (Po2) range of log Po2 = -3 ~ -18 (MPa), and were compared to 11 mol% Sc2O3-stabilized zirconia (11ScSZ). The electronic hole conductivity at 1273 K was measured at the higher oxygen partial pressure region (log Po2 > -6 (MPa)), and was comparable among 10Sc1CeSZ, 10Sc1YSZ and 11ScSZ. On the other hand, the electron conduction observed at 1273 K at the lower oxygen partial pressure region (log Po2 < -12 (MPa)) was enhanced by Ce doping.

(ICACC-S3-P103-2011) Tape casting of (Sc2O3)0.10(CeO2)0.01(ZrO2)0.89 thin eletrolytes for the IT SOFCs

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Stabilized Zirconia, such as CeO2 and Sc2O3 doped ZrO2, is a common electrolyte material for solid oxide fuel cells (SOFCs) due to its high oxygen ion conductivity at the temperatures range of 700-800C. In this work, (Sc2O3)0.10(CeO2)0.01(ZrO2)0.89 (ScCeZrO2) powders (DKKK, Japan) were used to produce thin electrolytes for intermediate temperature SOFCs using tape casting technique. The ScCeZrO2 powders were mixed with an organic solvent, dispersant, binder and plasticizer in order to produce slurry with a proper viscosity. After the slurry was prepared, it was degassed in vacuum and tape casted into the 200μm thick tape. Then it was dried and punched into disks with 28mm in diameter. Four layers of green disks were laminated using 6MPa uniaxial pressure in order to build up the thickness of the electrolyte to about 140μm after sintering. The tapes were pressureless sintered at 1550C for 5 hours, and homogeneous and thin electrolytes were produced. The microstructures, ionic and electronic conductivities of the electrolytes were measured. The work is in progress on deposition of the anode and cathode porous layers.

(ICACC-S3-P104-2011) Solid state electrolytes on the base of CeO2 for intermediate temperature electrochemical devices

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Doped cerium dioxide materials have been attracting increasing interest as electrolytes in intermediate temperature solid oxide fuel cells, due to their higher ionic conductivity with respect to yttria stabilized zirconia and their lower cost in comparison with scandia stabilized zirconia and lanthanum gallate-based electrolytes. Moreover, their applications include composite electrodes and various electrochemical devices, such as sensors and catalytic membranes. The present work aims at the investigation of the influence of different dopants′ ionic radius and concentration on the electrical properties and stability in a reducing atmosphere of Ce1-xLnxO2-x/2 (x = 0-0.20; Ln = La, Nd, Sm, Eu, Gd, Dy, Ho, Er, Yb) solid solutions and multi-component Ce(1-x)Mx/2Mx/2O2-x/2 (x = 0-0.20; M = Sm, La, Gd and M' = Dy, Nd, Y) and Ce(1-x-y)SmxMyO2-x/2-y (M= Ca, Sr, Ba) systems. Moreover, the temperature dependence of the linear expansion of ceramics is examined in the range of 300-1173 K and the respective thermal expansion coefficients are calculated. To investigate electrolytic properties electrochemical cell N2, Ag|0.98Ce0.8(Sm0.75Ba0.05Sr0.2)0.2O1.875 +0.02TiO2|Ag, air was used. It was found that this electrolyte has a predominantly oxygen ionic conductivity up to a sufficiently low oxygen partial pressure (at 973 K - up to 3.5 × 10-25 atm).

(ICACC-S3-P105-2011) Electrophysical properties of Sr1-xPrxTi0.5Fe0.5O3-d materials with perovskite structure

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Membrane materials with mixed oxygen-ion and electronic conductivity are widely used for the high purity hydrogen production. Since these membranes are usually used in a reducing atmosphere the basic requirements for membrane materials are their chemical and structural stability in a broad range of oxygen partial pressures. This work presents the investigation of Sr1-xPrxTi0.5Fe0.5O3-d (x = 0.0, 0.05 - 0.5) with a perovskite structure in terms of use as membranes. Electrical measurements in the temperature range 600 - 1173 K and 0.21 - 10-17 atm were performed. The introduction of praseodymium leads to increase of total conductivity up to x = 0.1 (σ = 0.83 S/cm at 1173 K) due to the increase of electronic conductivity with the introduction of praseodymium with a variable degree of oxidation (3 +- 4 +). At higher content of additives conductivity slightly decreases because of the point defect interaction with the formation of associates. By means of linear thermal expansion measurements was found that with the introduction of praseodymium the phase transition in the strontium titanate-ferrite at temperatures near 873 K became "smoothing". Calculated values of TEC decrease with increase of praseodymium content in range from 16.5 to 10.5 K-1 .

(ICACC-S3-P106-2011) Investigation of Phosphene Tolerant Anodes for Solid Oxide Fuel Cells

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In order for Solid Oxide Fuel Cells to become a more marketable energy source, improvements need to be made to each of the cell's key components. One of the major problems with the SOFC is degradation of the anode upon exposure to trace amounts of impurities that exist within coal-derived syngas. Specifically, PH_3 has shown to have an immediate effect on cell performance to many

Ni-based anodes. The nickel and phosphorus react to form various nickel-phosphide phases that inhibit catalytic activity. Thus, this work will investigate mixed-conducting perovskite, double-perovskite, and fluorite structured oxides as alternate anodes and the effect of PH_3 on long-term performance. Testing will be conducted on electrolyte supported (8mol% YSZ) planar fuel cells with active areas ranging between 2-16 cm^2. This study will also examine the role that fuel delivery configuration has on cell performance and degradation. The cells will first be subjected to H_2 to establish baseline performance and then after several hours, PH_3 will be mixed into the anode stream. SEM and EDS in conjunction with the current-voltage and impedance spectroscopy will be used to draw conclusions about the cells behavior upon anode exposure to PH_3.

(ICACC-S3-P107-2011) The uncertainty in techniques for chemical composition determination of SOFC glass seal materials

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A design-of-experiments approach was followed to determine the uncertainty associated with the following analysis techniques when used to quantify the chemical composition of SOFC glass seals: (i) ICP-MS (inductively coupled plasma - mass spectroscopy), (ii) ICP-AES (inductively coupled plasma – acoustic emission spectroscopy) and (iii) NAA (neutron activation analysis). The results from the statistical analysis of data sets obtained with the above techniques for an alkali barium silicate glass and for a standard reference material (NIST SRM89) will be reported. In addition, local compositional information obtained by atom probe tomography will be compared with results determined by the above three chemical analysis techniques. The results of this study will be discussed in the context of efforts to determine the evolution of the chemical composition of glass seals subjected to SOFC-relevant environments for long periods of time. This work was sponsored by the US DOE - SECA Core Technology Program at Oak Ridge National Laboratory. Research at the Oak Ridge National Laboratory SHaRE User Facility is sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy.

(ICACC-S6-P108-2011) Investigation on Phase Transformation of YBCO-In2O3 Composite Superconductor Cooled Down Via Different Routes

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Abstract Samples of the composite superconducting system YBCO-In2O3 were prepared and investigated using XRD, SEM, EDX and Temperature-resistivity measurements. The samples were divided into two identical classes which were cooled down from sintering temperature 940 oC to room temperature by two different routes: 1- rapid quenching and 2- slow cooling (1- 2 oC/min.). XRD analysis showed that the addition of In2O3 caused a rapid phase transformation from tetragonal to orthorhombic in a very short time (45 seconds) upon quenching to room temperature. In all quenched doped samples, a phase difference between the sample surface (Orthorhombic) and its interior (Tetragonal) was observed while the slowly cooled samples didn't show such a phase difference. All slowly cooled samples showed a single orthorhombic phase. Doping the material YBCO with In2O3 led to the formation of a secondary phase that could be identified. This phase co-exists with the 123 parent phase without affecting its crystal structure and caused a gradual slight decrease in Tc-values with increasing In-content. The bulk densities of the samples and their resistivity to corrosion in water were found to increase with increasing In-content.

(ICACC-S6-P109-2011) Morphologies and electrochemical capacitor behaviors of Co(OH)2/polyaniline composite films

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We prepared the Co(OH)2 or Co(OH)2/polyaniline composite film by the electrolytic deposition and evaluated their specific capacitance (Cp) by the cyclic voltammetry (CV). We examined the effect of deposition conditions on morphologies of the Co(OH)2 particles in the film, where Co(NO3)2 aqueous solution without or with the water-soluble conducting polyaniline-derivative was used as the raw material. The scale-like alpha-Co(OH)2 particles were obtained at 303 K from the solution without polyaniline-derivative, while rather thicker beta-Co(OH)2 platelets were formed at 348 or 363 K. The alpha-Co(OH)2 film showed Cp of 790 F/g (at a scan rate of 2 mV/s, using 0.1 M KOH aqueous solution as an electrolyte). Here, the Co valency state was reported to change through insertion or extraction of proton. On the other hand, the beta-Co(OH)2 film showed much lower Cp of 41 F/g. Deposition from the solution with polyaniline-derivative gave the composite film of diminished sized alfa-Co(OH)2 particles with polyaniline. The Cp of the composite film was not enhanced to the value expected for the materials with increased the electrode-electrolyte interface area. CV with various scan rates indicated a possible suppression of proton diffusion for the composite film. These results suggest that the balance between proton diffusion and electron conduction be the key to enhancing Cp values.

(ICACC-S6-P110-2011) Fabrication of $LiCoO_2$ thin film using hydrothermal Process

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The development of electronic devices has emphasized on thinner, lighter and multiple function products. Therefore, the development of a high performance Li-ion thin film battery is essential for nano/micro electronics that require micro power source. In this study, main objective of this work was to fabricate a nano crystallized $LiCoO_2$ film as the cathode of the Li-ion thin film battery.The hydrothermal process was adopted for the thin film deposition of $LiCoO_2$. The solution were prepared from the lithium nitrate and coablt acetate in deionized water. $LiCoO_2$ thin film was precipitated on a substrate during hydrothermal process and followed by annealing at desired temperatures up to 4h in air. The crystallization of $LiCoO_2$ film was analyzed by DTA/TG and XRD. A well crystallized hexagonal $LiCoO_2$ film with a space group of R-3m was obtained. The surface morphology of as deposited $LiCoO_2$ film was examined by SEM. Finally, charge/discharge tests were conducted on an assembled Li battery using deposited $LiCoO_2$ film by hydrothermal process.

(ICACC-S6-P111-2011) Preparation of Pb-filled Chevrel-phase sulfides and their thermoelectric properties

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The metal-filled Chevrel-phase sulfides $M_xMo_6S_{8-y}$ (M: metal) have received attention as potential high-temperature thermoelectric materials. The Pb-filled Chevrel-phase sulfides are formed within a narrow compositional range. Therefore, it is difficult to prepare the single-phase samples. In this study, we prepared the single-phase of the Pb-filled Chevrel-phase sulfides and investigated their thermoelectric properties between 300 and 870 K. The Pb-filled Chevrel-phase sulfides $M_xMo_6S_{8-y}$ ($8 - y$: 7.0 to 8.2) powders were prepared by solid-state reacting PbS, Mo and MoS_2 at 1273 K for 8 h in vacuum. The crystal phase of the powders was studied by X-ray diffraction. The powders were then densified by pressure-assisted sintering at 1173–1223 K for 2 h at 30 MPa in vacuum to investigate their thermoelectric properties. We have successfully prepared the single-phase of the Pb-filled Chevrel-phase sulfides with $8 - y = 7.8$ ($PbMo_6S_{7.8}$). While the secondary Mo and PbS phases are formed in sulfur-poor powders, the secondary MoS_2 phase is formed in sulfur-rich powders. The sintered density of single-phase sample is about 85% of the theoretical value. The sample has a positive Seebeck coefficient. The See-

beck coefficient and electrical resistivity increase with temperature. The thermal conductivity is less than 3 W K^{-1} m^{-1}. The low figure of merit is due to the low sintered density.

(ICACC-S6-P112-2011) Optimization of Spark-Plasma-Sintering Conditions for Maximizing Figure of Merit of La-Doped SrTiO3

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La-doped SrTiO3 was prepared by a new method; combustion synthesis (CS) followed by a spark plasma sintering (SPS). The figures of merits of prepared samples were measured to study the effect of sintering temperature and holding time on the thermoelectric performance. Sr0.92La0.08TiO3 powders were prepared by CS from oxides, carbonates, metals, and sodium perchlorate. SPS was carried out in vacuum at different sintering temperatures ranged from 1,573 to 1,633K for different holding times of 1, 5, 15, and 30 min to decide the optimum sintering conditions. Our results show the sample sintered at 1,573K for 5 min reaches the maximum ZT value of 0.37 at 1,045 K. This is the largest ZT value reported thus far for SrTiO3-based bulk semiconductors as far as we know. The results also suggest that the combination of CS with post SPS can be used to commercially produce thermoelectric oxides for use in efficient electricity generation.

(ICACC-S6-P113-2011) Development of high temperature thermoelectric converters

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High temperature heat from solar insolation, geothermal or waste heat can be used to provide clean electricity, if the direct thermoelectric energy conversion from heat into electricity is fast and highly efficient. For the realisation of innovative, lightweight and environmentally harmless ceramic thermoelectric converters temperature stable p- and n- type thermoelectric oxides have to be developed and tested in Thermoelectric Oxide Modules (TOM). A promising approach to reduce the thermal conductivity, which is leading to very high theoretical values of ZT, is to increase the amount of grain boundaries by producing nano-scaled thermoelectric materials. Suitable candidates for the p- and n-legs are perovskite-type materials. Tailor-made compounds with various compositions are chosen following theoretical considerations and synthesised by chimie douce methods. Here the thermoelectric figure of merit is tuned by appropriate variations of the composition and crystallographic structure.

(ICACC-S7-P114-2011) How Safe are Nanomaterials for Human Beings?

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Engineered nanoparticles (ENs) present tremendous opportunities of industrial growth and development, and hold immense promise in a range of biomedical applications such as drug delivery, medical imaging and simultaneous monitoring of disease processes. However, several safety concerns of using nanoparticles have been dramatically raised. In order to investigate the cytotoxicity, most commonly studied nanomaterial (both commercial and lab made) such as zinc, titanium and iron oxides have been chosen to interact with different cells like human primary immune cell (macrophages-HMDM), immune cell lines (T- and B-cells) and human embryonic kidney cell line (Hek293). Preliminary results show that ZnO oxide naoparticles are highly toxic to all kinds of cells, which may mainly be caused by the releasing of Zn2+ ions, which can inhibit biochemical reaction necessary for cell vitality. Furthermore, in contrast to T- and B-cell lines, ZnO appears to induce some oxidative stress in HMDMs. On the other hand, non-toxic behavior was found in TiO2 and Fe3O4 nanoparticles, even though they are rapidly taken up into vesicular structures and remained in the cells.

(ICACC-S7-P115-2011) Visible Light Photocatalysis with Rare Earth Ions Doped TiO2 Nanocomposites

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Role of rare earth (RE) ions in the improvement of photocatalytic efficiency of TiO2 composites is investigated. RE ions doped TiO2 nanocomposites (NCs) [general composition R(x).TiO2(1-x) (R = Y, Yb, Gd; x = 0.1, 0.2)] were synthesized by co-precipitation/hydrolysis. Average particle size was estimated to be 12 – 19 nm. Similar compositions of polycrystalline (PC) materials, prepared through solid state reaction, produced particles of 34 – 57 nm size. Visible light photocatalytic activity of all samples was investigated in degradation of the Congo red (CR) dye. Both in terms of rate constant (kobs), and % degradation after 180 minutes (C'180), all NCs showed much enhanced activity as compared to pure TiO2 and PC samples. Best degradation resulted with Y3+ doped NC (x =0.2) for which C'180 of 95% and kobs = 2.6 x 10-2 min-1 were estimated. Other NCs also produced fairly good degradation. In comparison, PC materials showed much less degradation. For these samples also, the Y3+ doped composition showed better degradation than others, but the best results were obtained with x = 0.1. The observations clearly suggested that reduced particle size supports enhanced degradation of CR, and the latter is additionally improved due to the presence of rare earth ions. The added enhancement may be attributed to the efficient suppression of e-/h+ recombination through trapping of electrons by R3+ ions.

(ICACC-S7-P116-2011) Band Gap Engineering in Layered Oxides

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Layered Aurivillius phases are photochemically active for hydrogen production, water purification, and similar applications. We demonstrate that cation substitutions on the perovskite A-sites allows for the systematic manipulation of the band gap of these materials. Structural characterization of the three-layer phases $Bi_2LnTi_3O_{12}$ (Ln = La_2, LaPr, LaNd, Pr_2, PrNd, Nd_2) and $Bi_2ANb_2TiO_{12}$ (A= Ca, Sr, Ba) via combined Reitveld refinements of x-ray and neutron powder diffraction patterns will be discussed. The ionic radius of the A-site cations alters the coordination environment of the B-site cations and the octahedral tilts in the perovskite block in a systematic fashion. The resulting shifts in band gap can be as large as 0.3eV, which of course impacts the photocatalytic activity.

(ICACC-S7-P117-2011) The hydrothermal synthesis of pure BiFeO3 nanopowders and their applications as visible-light photocatalysts

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Perovskite-type $BiFeO_3$ (BFO) materials have attracted much interest due to their multiferroic properties at room temperature. In addition to the electronic applications, BFO powders show the photocatalytic properties under visible light illumination. Despite the fact that some work has been undertaken, various research avenues such as synthesis, characterization, and the effects of magnetic fields remain to be explored. In this study, pure BFO nanopowders without any secondary phases were synthesized at low temperatures via a hydrothermal process with aid of triethanolamine (TEA). BFO nanopowders exhibited a strong absorption in the visible light regime, which resulted in the efficient photocatalytic activity for decomposition of organic compounds. The crystal structural, morphology, and composition of the BFO nanopowders was confirmed by X-ray diffraction (XRD), a field emission scanning electron microscope (FE-SEM), a transmission electron microscope (TEM), and an electron probe X-ray micro analyzer (EPMA). The Absorption spectra of the BFO nanopowders and organic compounds were measured using a UV-Vis spectrophotometer.

(ICACC-S7-P118-2011) Formation of nanostructured carbonitride layers during implantation of NiTi

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The surface layer of an equiatomic TiNi alloy, which exhibits the shape memory effect in the martensitic state, is modified with high-dose implantation. TiNi samples are implanted by N+, Ni+-N+ and Mo+-W+ ions and studied by Rutherford backscattering. scanning electron microscopy, energy dispersive spectroscopy, X-ray dif¬fraction (glancing geometry), and by measuring the nanohardness and the elastic modulus. A Ni+ concentration peak is detected between two maxima in the depth profile of the N+ ion concentration. In the initial state, the elastic modulus of the samples is E = 56 GPa at a hardness of H = 2.13 ± 03 GPa (at a depth of 150 nm). After double implantation by Ni+-N+ and Mo+-W+ ions, the hardness of the TiNi samples is 2.78 ± 0.95 GPa at a depth of 150 nm and 495 ± 2.25 GPa at a depth of 50 nm; the elastic modulus is 59 GPa. A correlation between the elemental composition, microstructure, shape memory effect and mechanical properties of the near-surface layer in TiNi is found.

(ICACC-S7-P119-2011) Deposition and characterization of Zr-based multi component nanocomposite coatings for tribological applications

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In this study, Zr-based nanocomposite coatings were deposited at room temperature by reactive DC magnetron sputtering process from a single alloying target with more than 4 elements. The chemical composition, microstructure and mechanical properties of the coatings were investigated. After a sputtering in Ar atmosphere, the composition of the deposited coating was almost same with the composition with the target. Also the deposition by reactive sputtering in Ar + N2 atmosphere, the coatings had the same composition with that of the target if the composition was calculated without nitrogen. With the reactive sputtering, the microstructures of the coatings were consisted of nano-sized hard phase (nitrides) and nano-sized soft phase (metal). Their size was less than 10 nm. The fraction of the soft phase was controlled by inserting amount of metal elements that would not react with nitrogen gas during sputtering process. The hardness of the coating was linearly decreased from 32 GPa to 17 GPa with the increase amount of the soft phase. This Zr-based multi component nanocomposite coatings exhibited much improved wear properties and corrosion properties as compared with conventional nitride hard coatings of multi-component transition metals.

(ICACC-S7-P120-2011) The properties of nanocomposite Al-X-Y-N (X= Ti, Cr, Zr), (Y= Cu, Si, Ni, B) coating synthesized by magnetron sputtering process with single alloying targets

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In this study, various Al-based single alloying targets such as AlTi, AlCr, AlZr were prepared by powder metallurgy of mechanical alloying and spark plasma sintering. Also, Si, Cu, Ni added targets were prepared to improve wear, thermal and oxidation properties. The investigation on the alloying targets showed that their microstructure was nano-sized about 20-30 nm and all the elements were homogeneously distributed. Al-based nano-composite coatings were deposited by unbalanced magnetron sputtering method with various nano-composite alloying targets. The composition of the coating was almost same with that of the target. Their microstructures and mechanical properties were investigated by XRD, SEM, TEM, nano-indenter, tribometer, est. The easiness of the nanocomposite structure was reviewed with alloying properties between alloying elements. Also, the effect of the 3rd element on the wear and endurance properties of the Al based nanocomposite coatings were reviewed in this study.

(ICACC-S7-P121-2011) Design and Construction of Complex Nanostructed Al2O3 Coating for Productive Applications

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In the present investigation, alumina nanopowder was obtained by spray pyrolysis using an inexpensive precursor of aluminum nitrate synthesized from raw bauxite. The powders produced were comprehensively characterised employing X-ray diffraction (XRD), particle size distribution (PSD), Fourier transform infrared spectroscopy (FTIR), Brunauer- Emmett-Teller surface area and pore size analysis, energy-dispersive spectroscopy (EDS), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) studies. The nanopowder of γ-Al2O3 with an average crystallite size of 5 nm and an average particle size of 28 nm with a specific surface area (SSA) of 336 $m^2 g^{-1}$ was produced. The obtained result reveals that the obtained nano powders were having spherical morphology with free flowing structure. Design and construction of complex nano structured Al2O3 coating on stain steel specimen was performed by a dip-coating technique. The thickness of nano- Al2O3 engineered silica film coating on steel specimen was controlled and varied by using layer-by-layer coating method. The effect of nano-coating on anti-corrosive properties of stain steel in acid media was performed using conventional weight loss method.

(ICACC-S7-P122-2011) TiO2 Nanoparticle Array Patterning by Freeze Casting

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Patterning of nanoparticle arrays represents exciting opportunities in solar cell, electronic, biomedical, chemical, and catalytic applications. In this work, a freeze casting process is pursued for TiO2 nanoparticle-based array patterning. Different templates are produced by focused ion beam lithography followed by mold making using polydimethylsiloxane (PDMS) and silicone. TiO2 nanoparticle suspensions are produced by a multi-step colloidal process. Finally, different TiO2 nanoparticle based arrays are made by freeze casting. The templated molds allow reproduction of different feature arrays using the TiO2 nanoparticle suspensions. This opens numerous opportunities for direct-device fabrication due to the pressureless and large surface area templating nature of the liquid-based process.

(ICACC-S7-P123-2011) Preparation of Silica Nanotubes using CNT-Silatrane Hybrid Material as Precursor

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The CNT-SiO2 hybrid material was successfully prepared using silatrane, as inexpensive and moisture stable precursor. Use of benzyl alcohol as a surfactant enables SiO2 to interact with the hydrophobic surface of pristine CNTs without the need of covalent functionalisation. The quality of the SiO2 coating is strongly affected by various reaction conditions, including the order of mixing, the presence of benzyl alcohol, and the reaction temperature. Furthermore, the effect of heat treatment on the crystallization of amorphous SiO2 to cristobalite is discussed in detail. By just adding a small amount of BA, very small and uniform cristobalite nanocrystals with very high specific surface areas (127–421 m2/g) were produced. In addition, pure silica nanotubes were successfully prepared for the first time using a carbon nanotube template for the deposition of an amorphous silica coating, and subsequently to support it during the phase transformation to cristobalite. The EDS analysis confirmed the presence of Si on the surface of CNTs and revealed the advantage of using BA which has enabled the synthesis of CNT-hybrids with maximum interfacial area and excellent control of morphology. Both FT-IR and WAXD results confirmed that the microstructure of the nanotubes was composed predominately of cristobalite, a high-temperature polymorph of crystalline silica.

(ICACC-S7-P124-2011) Investigation into the Nucleation and Growth of Boron Nitride Nanotubes Utilizing Metal Oxide Catalysts

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Boron nitride nanotube synthesis has been reported by a variety of processing methods, including but not limited to chemical vapor deposition, wet chemistry, arc discharge, and ball milling. While each processing method has reported some success, the mechanism of nucleation and growth is still not fully understood. One thing that is clear, however, that processing yield is improved by the availability of a metal catalyst to assist in nucleation. A wide variety of catalysts have been utilized in previous attempts at synthesis. Popular catalysts include magnesium oxide, nickel boride, and various iron and zinc compounds. In this study, an assortment of metal oxide catalysts will be used in the synthesis of boron nitride nanotubes at high temperatures in an attempt to better understand the underlying mechanism of nucleation and growth.

(ICACC-S7-P125-2011) Synthesis of Nitrogen-doped Carbon Nanotubes Cups Using Two Stage Furnace

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Nitrogen doped carbon nanotubes (CNTs) were synthesised using thermal chemical vapour deposition method with two stage furnace. Cyclohexanol was used as precursor with aniline as nitrogen source and ferrocene as catalyst. The morphology and size were controlled by varying the carries gas, argon with 5% hydrogen (Ar/5% H2) and nitrogen gas and the flow rate of the carrier gas. The multi-walled CNTs produced were investigated by high resolution transmission electro microscopy (HR-TEM), thermogravimetric analyser and Raman spectroscopy. The 100ml/min of Ar/5% H2 prove to be the better flow rate as high-purity tubes were produced. The nanotubes cup with a diameter of 10-60 nm was produced. The characterisation and elemental analysis designate the successful doping of CNTs with nitrogen.

(ICACC-S7-P126-2011) Visible Light Sensitized CdS@TiO2 Nanorod Arrays Grown on FTO and Their Application as Photocatalyst

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We present here the synthesis of highly ordered rutile-phase TiO2 nanorods on conducting substrates (FTO) by a hydrothermal method. Crystallinity and growth mechanism of TiO2 nanorods were analyzed by SEM, HRTEM and XRD studies. Decoration of CdS QDs on TiO2 via chemical bath deposition was used to make the material sensitive to visible light whereas different coverages were realized to study the influence of the semiconductor QDs on photon-electron interaction of the composite system. UV-Vis, photoluminescence and photoconductivity measurements revealed the enhanced visible light absorption and the electron transfer from CdS QDs to the TiO2 nanorods. The photocatalytic activity showed a direct dependence of current density on the amount of CdS decoration. The system performance was additionally enhanced from 1 mA/cm2 to 2 mA/cm2 by the deposition of a thin anatase layer on the rutile nanorods. Single QD decorated TiO2 rods were contacted by focused ion beam (FIB) assisted platinum writing and electrically characterized in analogy to the multiwire devices.

(ICACC-S7-P127-2011) Enhancement of the near-band edge emission from ZnO nanowires by SnO2 coating

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The ZnO nanowires synthesized by using vapor-liquid-solid (VLS) mechanism were 30 – 60 nm in diameter and up to 0.2 in length. The ZnO-core/SnO2-shell nanowires were also successfully prepared by coating the ZnO nanowires with SnO2 by atomic layer deposition (ALD). Both the ransmission electron microscopy (TEM) and X–ray diffraction (XRD) analysis results reveal that the cores and shells of the as-prepared core-shell nanowires are single crystal wurtzite type ZnO and amorphous SnO2, respectively. The near-band edge (NBE) photoluminescence (PL) emission of the ZnO nanowires is found to be significantly enhanced in intensity by coating them with SnO2. The low-temperature PL analyses suggest that the NBE emission enhancement is attributed to the confinement of the photo-generated carriers inside the ZnO cores due to the larger bandgap of the neighboring SnO2 shells, the suppression of visible emission and nonradiative recombination due to the formation of a depletion region in the ZnO cores, and the suppression of carrier capture by surface states due to the passivation of the ZnO cores by the SnO2 shells.

(ICACC-S7-P128-2011) The Comparison in the Efficiency of Nitrogen-doped and Undoped Carbon Nanotubes in the Anchoring of Silver Nanoparticles

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Nitrogen-doped carbon nanotubes (N-CNTs) provide unique structure, controlled electrical properties and strong interactions with deposited nanoparticles due to the presence of nitrogen. The aim of this presentation is to present the preliminary results obtained after investigating the efficiency of N-CNTs and undoped-CNTs in the anchoring of silver (Ag) nanoparticles. N-CNTs synthesized in a tubular quartz reactor that was inserted in a horizontal furnace. Microwave-assisted polyrol synthesis and wet impregnation method were used to successfully load silver nanoparticles on both N-CNTs and undoped CNTs. The samples have been characterized by Transmission electron microscopy (TEM), Scanning electron microscopy (SEM), Energy dispersive X-ray spectroscopy (EDS), thermal gravimetric analysis (TGA), Inductively coupled plasma optical emission spectrometry (ICP-OES), X-Ray Diffraction (XRD), BET, and Raman Spectroscopy. N-CNTs provide a good support for Ag nanoparticles despite a lower surface area and less surface defects when compared to undoped CNTs. The metal particles were uniformly dispersed on the surface of the N-CNTs. The results suggested that the N-CNTs have strong interactions with the metal nanoparticles which may prevent agglomeration / sintering of the metal nanoparticles during use in water purification and catalytic reactions.

(ICACC-S7-P129-2011) Micro-CVD on Multifunctional Substrates

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Metal-oxide semiconductors like SnO2, WO2 or VO2 are widely used as active materials for gas sensors. Especially nanostructured surfaces like nanowires combine an enhanced sensitivity with reduced power consumption in gas sensors. For synthesis of anisotropic nanostructures, vapor phase techniques such as the chemical vapor phase deposition (CVD) yield single crystalline nanowires via the metal catalyzed vapor-liquid-solid (VLS) growth mechanism. The major drawback of these classical CVD synthesis of anisotropic nanostructures, is the poor control of positioning nanowires for later integration in multifunctional sensor arrays, whereas the widely used post-synthesis integration with FIB or similar methods is very costly and time consuming. We here present a new method of growing nanowires directly on electrodes of multifunctional sensor substrates and micro-hotplates in a special micro-CVD reactor. Different substrate materials (Si, Al2O3) and geometries are evaluated for the optimal growth of metal-oxide nanowires and heterostructures and the gas sensing properties of these directly grown sensing materials towards CO, and other test gases will be demonstrated.

(ICACC-S7-P130-2011) Nanomaterials Based Devices by Ink-Jet Printing

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The ink-jet printing has found increasing applications as a free-form fabrication technique for building diverse 2D or 3D micro-structures

on various substrates. We present the fabrication of printed gas sensors based on metal oxide (SnO2, Fe2O3, V2O5) nano-inks and the investigation of their gas sensing behaviour in dependence of their morphologies. Furthermore ink-jet printing was used for site selective chemical patterning of substrates with metallic nanoparticles, which could be used as catalysts for chemical vapour deposition based growth of metal oxide nanowires. The site selective growth was achieved either by chemical anchoring of the catalyst particles by printing a monolayer of bi-functional molecular linkers or by direct printing of metal based nano-inks. Additionally we present a new method to produce patterned conductive circuits by low cost precursors on polymer substrates. The water based inks of silver salts were printed on polycarbonate and polyimide substrates and subsequently converted to silver by soft argon plasma reduction.

(ICACC-S7-P131-2011) The crystallization behavior of b–cristobalite gel synthesized by sol-gel route

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The beta-cristobalite gel was synthesized by sol-gel route, starting from aluminum nitrate, tetra-ethyl-orthosilicate (TEOS) and calcium nitrate dissolved in absolute ethanol (EtOH) with water. TEOS/Water/EtOH ratios keeping at 1:4:1 to 1:16:1. The gel composition was designed as where . After drying, the gel samples were sintered at different temperatures (1000-1450°C). Differential thermal analysis (DTA), X-ray diffraction (XRD) and IR analysis were done to study the crystallization and phase transformation behavior on the sintered powder samples. Results indicate that the water/TEOS ratio has great importance on the crystallization of the samples as b-cristobalite without some secondary crystallization such as quartz and a-cristobalite. The water/TEOS ratio being 4 and sintering temperature applied at 1100°C leads to b-cristobalite crystallization. The fully crystallization could be obtained at 1150°C. At the temperature increased up to 1400°C, then the a-cristobalite crystallization appeared and the crystallization increases with the higher temperatures. Sintering at 1300°C is critical where X-ray analysis shows the powder being fully b-cristobalite but IR analysis indicates that the sample contained some alpha-cristobalite-like structures.

(ICACC-S7-P132-2011) Synthesis of nano-size CaB_6 powders using various boron sources

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CaB_6 (calcium hexaboride) powder has been investigated to be one of the filler material for bipolar plate in PEM fuel cells. CaB_6 is utilized as wear resistant material, abrasive, high electronic conductivity and surface protection material. These properties creates a gradually ascending interest as a part of advanced technology. In this study, various types of boron sources are utilized in carbothermal based reactions for synthesis of nano-size CaB_6 powder. The formation studies were performed in a tube furnace in flowing Argon gas. The optimal conditions, such as temperature, holding time, milling time for producing single phase, nano-size CaB_6 powders were determined as a function of boron source. The XRD patterns showed that single phase powders of CaB_6 can be synthesized at 1500°C for 4 hrs. in flowing Argon gas. TEM and BET results confirmed that the powders had nano-size particles with uniform size distribution.

(ICACC-S7-P133-2011) Synthesis and characterization of nanocrystalline TiO2 powders by a novel combustion synthesis method

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Nanocrystalline TiO2 powders have been synthesized by a novel, quick and simple combustion synthesis method using glycine as fuel and titanium nitryle as oxidant. The starting materials were directly mixed and a slurry precursor with high homogeneity was formed due to the hygroscopicity of the reactants. The precursor could be ignited at room temperature, resulting in dry, loose and voluminous TiO2 powders. The reaction process of the precursor was investigated by using cheap titanium compounds and reaction was studied TG-DTA techniques. The as synthesized TiO2 powders, characterized by XRD, SEM, and BET. Results showed that final product is pure and has high specific surface area and possess small primary crystallite size (25 nm). On the other hand some processing parameters were studied and effect of them was investigated on the structure and properties of nano TiO2 products.

(ICACC-S7-P134-2011) Physical-Chemical, Mechanical, Thermal, and Radiation Resistance of Hard and Super-Hard Nano-Structured Coatings

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The report deals with investigation results on structure and properties of hard Zr-Si-N, Zr-Ti-N, and super-hard Zr-Ti-Si-N coatings of 1.8 to 3.2μm thickness. Coated samples were γ-irradiated during several months in a reactor and cobalt gun. Hardness of Zr-Si-N coatings was 28 to 32GPa, that of Zr-Ti-N reached 35 ±2.6GPa, and hardness of Zr-Ti-Si-N was 40 to 48GPa. Thermal annealing of coated samples to 550oC increased their hardness to 53GPa, and subsequent γ-quantum-irradiation under 108 to 109Grey essentially decreased their hardness. Nano-grain sizes increased as a result of annealing and subsequent γ-quantum-irradiation. Inter-layers of amorphous phase (α-Si3N4) surrounding nano-grains (Zr, N)-nc, ….(Zr, Ti)N-nc increased by several per cent, which seemed to be related to enhanced processes of relaxation-accelerated diffusion. γ-quantum-irradiation of samples with super-hard coatings till high-temperature annealing resulted in a shift of hardness maximum to 150oC (as a result of subsequent annealing in vacuum) closer to the beginning of temperature interval. The work was funded within the framework of project "Nano-Systems, Nano-Composite Coatings, and Nano-Materials" of National Academy of Science of Ukraine. Key words: Hardness, γ-quantum-irradiation, nanocomposite, annealing,structure

(ICACC-S7-P135-2011) Multilayered Micro and - Nanocomposite Coatings Ti-N-Al/Ti-N/Al2O3/substrate, Their Structure and Properties

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The works presents first results on formation and investigation of structure and properties of nanocomposite combined coatings. Modeling the deposition processes (deposition conditions, current density-discharge, plasma composition and density, voltage) we formed the three-layer nanocomposite coatings of Ti-N-Al/Ti-N/Al2O3/.The coating composition, structure and properties were studied using physical and nuclear-physical methods. We applied the Rutherford proton and helium ion back scattering (RBS), Scanning Electron Microscopy with microanalysis (SEM with EDS and WDS),X-Ray diffraction (XRD) including a sliding beam to 0.5o,as well as nanohardness tests(hardness),Measurements of wear resistance, corrosion resistance in NaCl, HCl and H2SO4 solution. Also we measured such characteristics as H(hardness),elastic modulusE:H3/E2 etc .It was demonstrated that the formed many-

layered(three-layer) nanocomposite coating had hardness 32 to 36GPA,328+- 18 to 364+ -14 GPa elastic modulus. Its wear resistance (cylinder-surface friction) increased by a factor of 17 to 25 in comparison to the substrate(stainless steel). The layers thickness was 56-120 mkm. The work was funded by the Project NAS Ukraine and ISTC K-1198.

(ICACC-S7-P136-2011) Preparation and Characterization of LiMn2O4 Ion-sieve with High Li+ Adsorption Rate by Ultrasonic Spray Pyrolysis

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This study presents the preparation of LiMn2O4 spinel type ion-sieves, characterization of their Li+ extraction/insertion rates and discussion about the effect of the particle structure and morphology on the lithium adsorption rate. Nanostructured LiMn2O4 spinel powders were synthesized by ultrasonic spray pyrolysis and solid state reaction. The mean particle size and surface area of the powders were relatively the same; however their particle structure and morphology were different. LiMn2O4 powder prepared by pyrolysis has agglomerate structure and spherical shape with very uniform morphology while the other has needle like structure with sharp edges and rough surface. The Li+ uptake capacity of the sieve (delithiated lithium manganese powder) which has agglomerate structure was 34,9 mg/g in which the maximum adsorption capacity of the sieve was 38,67 mg/g in theoretically. Beside this, the sieve uptake about % 94 of the maximum amount within 3 hours while the other sieve required 24 hours for the relatively equal uptake amount (32,8 mg/g).

(ICACC-S8-P137-2011) Observation of Crack Propagation Behavior of Si_3N_4 ceramics by Scanning Probe Microscopy

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Observation of fracture behavior of ceramics provides useful information to improve their mechanical properties. Scanning probe microscope (SPM) has atomic or nanoscale resolution and SPM is able to provide three-dimensional and quantitative information. In this study, crack propagation behavior of Si_3N_4 ceramics was observed by using SPM. We observed the fracture surface and the crack induced by Vickers indentation of several kinds of ceramics by using SPM in nanoscale. Inthe direct observation of crack propagation, one-sided Chevron notch was machined to the sample so that the crack can stably propagate during observation by SPM. The sample was loaded by three-point bending apparatus. As a result, it was observed that a crack in the Si_3N_4 ceramics stably propagated. The crack in the Si_3N_4 ceramics did not always propagate continuously from the tip of the crack. It was also observed that some of the micro cracks discontinuously formed and they connected.

(ICACC-S8-P138-2011) Synthesis and characterization of lithium aluminate red phosphor

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The compounds in the ternary Li-Al-O system are known to exist three phases of LiAlO2, LiAl5O8 and Li5AlO4. LiAlO2, and LiAl5O8 compounds have been selected as a host material, and the relationships between the crystalline phase, crystallinity and the dopant-derived luminescent properties have been studied systematically.The luminescent materials were synthesized by the sol-gel method. The chemical composition and the amount of dopant in the materials were carefully controlled at molecular or atomic scale level. As primary results, the precursor gel having Li/Al=1/1 was found to be successfully converted into α-LiAlO2 at 800 °C. Subsequently α/γ-LiAlO2 phase transformation complicated at 1000 °C. Further heat treatment at and above 1200 °C resulted in yielding another phase of LiAl5O8. The sample exhibited the maximum PL emission peak around 680 nm (λex.=270 nm) and the highest peak intensity was achieved for the precursor gel-derived LiAl5O8:Fe3+ by heat treatment at 1600 °C. However, another host material of α-LiAlO2 exhibited completely different luminescent properties, and the red emission intensity was apparently enhanced by the doping of Mn4+ instead of Fe3+. Further study on absorption spectra, excitation spectra and CIE color coordinate of lithium aluminate (Li/Al=1/5, 1/1) will be shown and discussed from a viewpoint to develop novel red phosphor materials composed of the ternary Li-Al-O system.

(ICACC-S8-P139-2011) Machinability Evaluation in the Ultrasonic Drilling (USD) Process of Aluminum Oxide-Based Ceramics

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The ultrasonic drilling (USD) has been used in the manufacture of the hard, fragile, and materials difficult to cut, nonconductive ceramic materials. In this study, the mathematical models of material removal rate (MRR) and surface roughness (SR) used for the machinability evaluation in the USD process of aluminum oxide-based ceramic material have been carried out. The experimental plan adopts the face centered central composite design (CCD). The mathematical models using the response surface methodology (RSM) are developed so as to investigate the influences of three machining parameters, including the power rating, grit size and slurry concentration on the performance characteristics of MRR and SR. It has been proved that the proposed mathematical models in this study would fit and predict values of the performance characteristics, which would be close to the readings recorded in experiment with a 95% confidence level. The significant parameters that critically affect the performance characteristics are examined.

(ICACC-S8-P140-2011) Patterning Thick Film by Sand Blasting for High Resolution in Display Devices

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The issues of plasma display panel (PDP) are high efficiency, picture quality, low cost and high resolution, of which the high resolution is the most interesting topic due to the competitive pressure from the liquid crystal display. Various methods of manufacturing barrier ribs are sand blasting, chemical etching, screen-printing, molding and photosensitive methods. The sand blasting of those methods is mostly used for barrier ribs in PDP. However, it is difficult to make a micro pattern and high aspect ratio with a normal green barrier rib by the sand blasting. We investigated the erosion of the thick films prepared with two different pastes: normal and photosensitive for high resolution. The various properties of the resulting thick films were determined by thermal gravimetric analysis, atomic force microscopy, nano-indentation, and peel testing. The photosensitive thick film had better adhesion with a dry film resist and showed lower porosity, surface roughness, stiffness and elastic modulus than a normal thick film, which were attributed to the remaining polymer. In the process, the developed photosensitive thick film and the dry resist film were able to withstand the impact of the separated particles or clusters. These results support the use of sand blasting to fabricate the high resolution of barrier ribs with two layers of photosensitive paste.

(ICACC-S8-P141-2011) Er2O3- BaTiO3-Ceramics Microstructure Fractal Analysis

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BaTiO3-ceramics as one of the most important electronics materials, used in a wide range of applications, can be modified with various additives. The goal of the present investigation was to study the influence of Er2O3 on microstructure properties of BaTiO3-ceramics. The solid solubility of Er3+ ions in the BaTiO3 perovskite structure has been studied by different methods of microstructural analysis including SEM-JEOL 5300 and energy dispersive spectrometer (EDS)

system. For characterization we used as well as the methods of quantitative metalography. BaTiO3-ceramics doped with 0.01 up to 1, wt% of Er2O3 were prepared by conventional solid state procedure and sintered from 1320°C to 1370°C for four hours. For better understanding of BaTiO3-ceramics microstructure and more complete simulations and modeling of the structures, what's very important for prognosis the final characteristics of these electronic materials, we applied the fractal method as well.

(ICACC-S8-P142-2011) Thermal and Electrical Conductivity of AlN Ceramics with Low Temperature Sintering

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The Aluminum nitride (AlN) is the most promising material for ceramic substrate due to its outstanding thermal conductivity, electrical resistivity and mechanical stability. Because of its strong covalent bonding and its low self-diffusion coefficient, AlN has been typically densified at high temperature (>1800 °C). However, the high sintering temperature not only increases the production cost of AlN ceramics but also causes significant grain growth, which results in a reduction of mechanical strength. In this regard, the research in AlN ceramics is mainly focused on attaining full densification at low sintering temperature by using various sintering additives. A further investigation on the optimization of sintering conditions and appropriate sintering additives are necessary for low temperature sintering of the AlN ceramics. In this study, effects of multiple additives on the low temperature sintering of AlN were examined. Low temperature sintering mechanism was investigated by TGA, dilatometery and SEM. In addition, thermal conductivity was characterized by laser flash method. Electrical resistivity was also characterized by AC impedance spectroscopy at high temperature.

(ICACC-S8-P143-2011) Synthesis and Characterization of Si-Y-O-N phosphors

T. Ishii*, Nagoya Institute of Technology, Japan; Y. Zhou, K. Hirao, National Institute of Advanced Industrical Science and Technology, Japan; S. Honda, Y. Iwamoto, Nagoya Institute of Technology, Japan

The Eu-doped yttrium-silicon-oxide-nitride (Eu-SiYON) phosphor materials were synthesized from Si-based polymeric precursors chemically modified with monomer precursors. As our primary study, the composition of starting material was controlled to be Si : Y = 10 : 1, in mole ratio. EuCl3 was added to the precursor solution in weight percentages of 1.0 %. The solution of mixed precursors was stirred for 24 h at room temperature. Then, the organic solvent was removed under vacuum. The residue of the inorganic-organic hybrid materials were converted into inorganic materials by heat treated at 1000 °C for 1 h in flowing N2 gas, subsequently at 1800 °C for 2 h in a pressurized N2 atmosphere of 0.9 MPa. The inorganic materials were studied by X-ray diffraction (XRD), photoluminescence spectroscopy (PL) and scanning electron microscope (SEM). The XRD analysis revealed that the sample was composed of silicon nitride (Si3N4) and Y5(SiO4)3N (apatite-type structure), and amorphous phase due to slightly-high background. The sample shows yellowish-white emission and the PL spectrum has broad emission from 400 nm to 700 nm, maximum at 500 nm with 365 nm excitation wavelength. At the presentation, relationships between chemical composition of the starting polymeric precursors, the major crystalline phase of final Eu-SiYON, morphology and luminescent properties will be discussed from a viewpoint to develop novel oxynitride phosphors.

(ICACC-S8-P144-2011) Microporous polymer-derived organoamino group-functionalized amorphous silica membranes for carbon dioxide separation

K. Sekimoto*, S. Honda, Y. Iwamoto, Nagoya Institute of Tech., Japan

Microporous amorphous silica-based membranes containing organoamino groups have been designed and synthesized. This is expected to be essential to enhance the CO2 permselectivity of the amorphous silica-based membranes by the CO2 facilitated transport mechanism, preferential adsorption of CO2 on the walls of the micropores and subsequent blocking of permeation of other gases. As our primary study, the organoamino groups containing amorphous silica-based inorganic-organic hybrid materials were synthesized through polymer precursor route. Commercial perhydropoysilazane (PHPS) in xylene solution was modified with aminosilane-coupling agents under mild condition, below 373 K in Ar. The molar ratio of polymer-derived Si/NH2 was controlled to be 0.138. 1H NMR and FT-IR spectroscopic analyses revealed that aminosilane-coupling agent could react with PHPS to form N-Si(OR)nR'[R=CH3, R'=(CH2) m-NH2, n<2]. The thermal stability evaluated by the TG analysis of the polymer-derived inorganic-organic hybrid materials was found to be approximately 473 K. Further study of membrane formation on a tubular Al2O3 ceramic support and evaluation of the gas permeations through the membrane are in progress. The results will be discussed from a viewpoint to develop novel membranes for CO2 separation through polymer precursor route.

(ICACC-S8-P145-2011) Synthetic study of ceramic-based insulating thin film on a metal substrate

Y. Takeuchi*, S. Honda, Nagoya Institute of Technology, Japan; H. Usami, Meijyo University, Japan; Y. Iwamoto, Nagoya Institute of Technology, Japan

Ceramic-based composite thin film was fabricated on an aluminum substrate by following two steps, (1) formation of porous ceramic thin film by spray coating, and (2) subsequent silica filler loading using polymer precursors. As our primary study, several kinds of ceramic particles such as SiC and BN were used as a film source, and a porous thin layer with a thickness of approximately 1 μm was successfully fabricated on an aluminum substrate. Amorphous silica filler could be successfully loaded within the porous thin layer by in-situ formation below 423 K of the amorphous silica through ammonia-catalyzed oxidation of perhydropolysilazane (PHPS). Relationships between the ratio of the ceramic particles/silica in the composite film, film thickness, thermal diffusivity and dielectric breakdown properties are in progress, and the results will be discussed from a view point to develop novel insulating substrates.

(ICACC-S10-P146-2011) Graphite Foams – Addressing Technology Challenges

A. L. Gyekenyesi*, M. Singh, C. Smith, Ohio Aerospace Institute, USA; P. Stansberry, GrafTech International Holdings, Inc., USA; K. Alam, Ohio University, USA; D. Vrable, TMMT, Inc., USA

Graphite foams are excellent candidate materials for thermal management applications due to their extraordinarily high ligament conductivity and large surface area. These open pore foams have reported ligament conductivities greater than 1700 W/m-K and bulk values up to 245 W/m-K. The Ohio Aerospace Institute, GrafTech International Holdings, Inc., Ohio University, and TMMT, Inc. are cooperatively attending to multiple technological issues that need to be addressed prior to full-scale, commercial implementation of the material system. The categories of research include the development of new/modified manufacturing procedures for optimizing the morphology of the graphitic carbon foam while increasing the quality and quantity; the study of various coatings for increased durability and functionality; the investigation of joining technologies to allow for optimal system integration regarding strength and thermal conductivity; as well as an extensive modeling campaign addressing mechanical, thermal and fluid flow simulations/predictions from the material to system levels (multi-scale modeling). Exceptional progress has been made since the start of the project (2 years) and a summary of the results are reported.

(ICACC-S12-P147-2011) Diffraction study of self-recovery in decomposed Al2TiO5 during annealing in vacuum

I. Low*, Curtin University of Technology, Australia; E. Wu, Institute of Metal Research, China

The ability of decomposed Al2TiO5 to undergo self-recovery or reformation in vacuum at elevated temperature has been characterised by neutron diffraction. It is shown that the process of phase decom-

position in metastable Al2TiO5 is reversible and that reformation occurs readily when decomposed Al2TiO5 is re-heated above 1300°C. Subsequent decomposition of reformed Al2TiO5 during cooling below 1200°C is governed by the temperature-dependent atomic diffusion rates. The influence of grain-size on this phenomenon will also be discussed.

(ICACC-S12-P148-2011) Oxidation Resistance of ZrB_2-SiC: WC-NbC and WC-TaC Additions

E. W. Neuman*, W. Faherenholtz, G. Hilmas, Missouri University of Science and Technology, USA

Previous research at Missouri S&T has demonstrated that tungsten carbide additions to zirconium diboride and zirconium diboride – silicon carbide based ceramics results in improved oxidation resistance by promoting densification of the zirconia scale. Studies by other research groups have also shown that niobium and tantalum based additions also be used to improve oxidation resistance of zirconium diboride based ceramics. ZrB_2–30 vol% SiC ceramics were prepared by pressureless sintering. Nominally pure and compositions each with additions of either 4 mol% WC, NbC, and TaC were prepared as a baseline. Compositions with additions of 4 mol% WC and between 2 and 8 mol% NbC or TaC were prepared. Oxidation behavior was evaluated using thermal gravimetric analysis up to 1500°C and isothermal furnace oxidation at 1500 and 1600°C. Oxide scale thickness and morphology were investigated using scanning electron microscopy. Oxide scale composition was evaluated using X-ray diffraction and energy dispersive spectroscopy. The influence of additions of WC-NbC and WC-TaC on the sintering and oxidation behavior of ZrB_2-SiC ceramics will be discussed.

(ICACC-S12-P149-2011) Diffusion Bonding between Ti_3SiC_2 and NiTi Shape Memory Alloy

S. Basu*, F. Ozaydin, M. Radovic, I. Karaman, Texas A&M University, USA

A pressureless diffusion bonding process is demonstrated to form a stable bond between Ti_3SiC_2 and NiTi shape memory alloy, forming a thin Si-rich intermetallic layer. The microstructure and phase composition of the interfacial layer has been characterized by electron microscopy and microprobe elemental analysis. The elastic modulus and hardness of different phases present in the interfacial layer were determined using nanoindentation. Vickers microindentation data showed considerably higher hardness at the interface compared to both Ti_3SiC_2 and NiTi. However, the absence of any significant cracking near the indents also confirms a high fracture toughness of the interfacial bonding phase. The practical importance of pressureless bonding of Ti_3SiC_2, as one of the MAX phases, to the NiTi shape memory alloys for their application in extreme conditions is also discussed.

(ICACC-S12-P150-2011) Effects of atmosphere on the pressureless sintering behavior of ZrB_2 ceramics

A. Els*, H. Brown-Shaklee, G. Hilmas, W. Fahrenholtz, Missouri University of Science & Technology, USA

The effects of atmosphere on the pressureless sintering behavior, microstructure development, and thermal properties of ZrB_2 ceramics were studied. ZrB_2 powders were sintered in a carbon free, refractory metal furnace under controlled atmospheres including helium, hydrogen, nitrogen, mild vacuum (~ 5 Pa) and high vacuum (~ 5 x 10-3 Pa). The sintering temperatures were varied from 1900°C to 2400°C with hold times ranging from 1 to 4 hours. Sintering in hydrogen resulted in higher weight loss than sintering in helium. Thermodynamic equilibrium calculations indicated that formation of $ZrO_{(g)}$ and $H_2O_{(g)}$ were favorable in the presence of excess $H_{2(g)}$ at temperatures above 1800°C. These vapor species increased in concentration above 2000°C and were removed by the flowing $H_{2(g)}$, which resulted in the observed mass loss increase. No increase in density was observed between the mild vacuum and the high vacuum. Other effects of atmospheric conditions will be discussed such as those on thermal conductivity and microstructure development.

(ICACC-S12-P151-2011) Pressureless Sintering And Hot-Pressing Of Ti_2AlN Powders Obtained By SHS Process

L. Chlubny*, J. Lis, M. M. Bucko, AGH-University of Science and Technology, Poland

In the Ti-Al-N system ternary materials called MAX-phases can be found. These materials are characterised by heterodesmic layer structure. This specific structure consisting of covalent and metallic chemical bonds influence its pseudoplastic behaviour is locating them on the boundary between metals and ceramics, which may lead to many potential applications, for example as a part of a ceramic armour. Ti_2AlN is one of this nanolaminate materials. To obtain sinterable powders of Ti_2AlN of relatively large quantities, Self-propagating High-temperature Synthesis (SHS) was applied. Utilization of heat produced in exothermal reaction in adiabatic conditions to sustain process until all substrates are transformed into product is one of the key advantages of the method that result in low energy consumption, simple apparatus and low cost combined with high efficiency. Various substrates such as elementary powders, and titanium and aluminium compounds were used as a precursors to produce fine powders of ternary material. Phase compositions of obtained powder were examined by XRD method. After phase analysis, selected powders were densified by pressureless sintering and hot pressing process in various conditions. Some properties and phase composition of obtained products were examined.

(ICACC-S12-P152-2011) On the diffusivity and reactivity in Ti_2AlC - Ti system at 800-1400°C temperature range

E. Ormond*, S. Basu, K. Drideger, I. Karaman, M. Radovic, Texas A&M University, USA

The reaction mechanisms and diffusion paths between titanium (Ti) and titanium-aluminum-carbide (Ti_2AlC) at temperatures ranging from 800°C to 1400°C were investigated. Ti and Ti_2AlC powders were mixed in different ratios, cold pressed and pressureless sintered under vacuum. The phase composition and morphology, observed by X-ray diffraction (XRD) and scanning electron microscopy (SEM), was found to be a strong function of Ti/Ti_2AlC ratio, sintering temperature and time. The phases detected by XRD and energy dispersive spectroscopy (EDS) were Ti_2AlC, Ti_3AlC, TiC_{1-x}, Ti_3Al, and Ti-Al solid solution. The results suggest that Al from Ti_2AlC takes part in an evaporation-condensation process, and reacts with Ti, forming Ti-Al solid solution and Ti_3Al. Additional diffusion of C from Ti_2AlC leads to the formation of Ti_3AlC and TiC_{1-x}. The ways to prevent reaction of the Ti with Ti_2AlC by suppressing evaporation and diffusion of Al were also discussed in this paper.

(ICACC-S12-P153-2011) Effect of Heating Rate on the Densification of ZrB2

M. Thompson*, W. G. Fahrenholtz, G. Hilmas, Missouri University of Science and Technology, USA

Zirconium diboride (ZrB2) ceramics were densified by hot pressing and spark plasma sintering with heating rates varying from as low as 2°C/min up to 300°C/min. Slower heating rates produced larger grain sizes due to the longer times spent at temperatures between 1500°C and 1900°C, which is the temperature range in which ZrB2 grains coarsen. In this temperature range, non-densifying sintering mechanisms reduced surface area by rounding and coarsening grains, which decreased the driving force for densification at higher temperatures. Heating rates above 50°C/min resulted in rapid densification, but this led to the formation of entrapped porosity. As a result, rapid heating led to some ceramics reaching a limiting density that was below 100%. After densification, changes to the microstructure were examined to evaluate the effect of heating rate on thermal and mechanical properties. To separate the effects of heating rate from processing method, mechanical and thermal properties were measured for materials that were prepared by conventional hot pressing or spark plasma sintering, but with the other processing conditions (i.e., powder processing, densification heating rate, etc.) that were nominally the same.

In addition, spark plasma sintering was used to investigate heating rates >100°C/min in order to determine if trends in mechanical and thermal properties that were observed for hot pressing held for higher heating rates.

(ICACC-S12-P154-2011) Solid solution effects on thermal and mechanical properties of metal-diborides toughened with SiC

B. J. Lai*, J. Watts, G. Hilmas, W. G. Fahrenholtz, Missouri University of Science and Technology, USA

Metal-diboride ceramics were sintered to near theoretical density by hot pressing with different transition metal species; i.e. hafnium (HfB_2), niobium (NbB_2), titanium (TiB_2), and zirconium (ZrB_2), as well as fine SiC particulates. Hot pressed specimens were fabricated utilizing 32 MPa and a final densification temperature of 2100° C. Previous work has employed SiC additions to improve strength and/or oxidation resistance. This study focused on determining the effect of diboride solid solutions on thermal and mechanical properties of the ceramics. Specifically, thermal diffusivity, conductivity, heat capacity, elastic modulus, strength, and hardness were measured. The role of solid solutions on oxidation resistance as it compares to single metal-diboride ceramics was also investigated. Strength values ranged from 480-660 MPa for SiC containing specimens. Hardness values exceeded 20 GPa for all compositions. The presence of solid solutions was confirmed by powder X-ray diffraction analysis. Electrical conductivity measurements were also performed to compare and contrast the role of several transition metal species in solid solution on thermal and electrical conductivity.

Thursday, January 27, 2011

S1: Mechanical Behavior and Performance of Ceramics & Composites

Processing-Microstructure-Properties Correlations I

Room: Coquina Salon A

Session Chairs: Yu Zhou, Harbin Institute of Technology; Guo-Jun Zhang, Shanghai Institute of Ceramics

8:00 AM

(ICACC-S1-053-2011) Processing, Microstructure and Properties of C/C-SiC Composites Containing Ti3SiC2 (Invited)

X. Yin*, L. Zhang, L. Cheng, National Key Laboratory of Thermostructure Composite Materials, China

Carbon fiber reinforced carbon/SiC binary matrix composites (C/C-SiC) fabricated by liquid silicon infiltration (LSI) are attracting more and more attentions owing to their excellent oxidation resistance and thermal shock resistance, light weight and good thermal stability and wear resistance. Dense C/C-SiC composites have low mechanical properties and high content of residual silicon, which limit their wide applications at elevated temperatures. Owing to the inherently nano-laminated crystal structure, Ti3SiC2 ceramics show both fascinating mechanical and tribological properties. The delamination, deformation, buckling, and kinking of Ti3SiC2 can pin, deflect, and bridge the matrix microcracks, which may improve the mechanical properties of the composites. The fabrication of Ti3SiC2-based composites by liquid silicon infiltration is novel and promising, which may promote their applications. In the present contribution, recent progress on the processing, microstructure, mechanical properties and friction behaviors of C/C-SiC composites containing Ti3SiC2 fabricated by liquid silicon infiltration will be summarized and discussed.

8:30 AM

(ICACC-S1-054-2011) Innovative multi-stage spark plasma sintering to obtain strong and tough ultrafine grained ceramics

B. Basu*, Indian Institute of Technology, Kanpur, India; M. Reddy, A. Mukhopadhyay, N. Kumar, D. Jain, IIT Kanpur, India

In the context of using spark plasma sintering(SPS)to develop nanostructured ceramics,a major concern in the materials community is that rapid heating and less holding in single stage SPS process causes inhomogeneous radial/axial temperature distribution.In this presentation, we will report that how multi-stage SPS schedule can be successfully adopted to consolidate ultrafine grained ceramics with uniform and better mechanical properties than single-stage SPS schedule.From fundamental aspect,it is important to assess the microstructure development during final stage of sintering.With a set of exploratory experiments on oxide ceramics(Al2O3,ZrO2),our results will demonstrate as how grain growth is significantly inhibited during multi stage SPS route.The results are explained in terms of competition between grain boundary diffusion and grain boundary migration.In the next part of the presentation, the experimental results obtained with ZrO2 and TiB2-TiSi2 composite will be presented.The development of finer microstructural scale,with the presence of tabular TiB2 grains(1-1.5μm in size)and TiSi2 grains(200-300 nm in size)allowed much higher hardness(~27-31GPa)to be achieved on sintering via MSS.Also, more uniform microstructural development in the case of MSS led to an improvement in fracture strength(~500 MPa)

8:50 AM

(ICACC-S1-055-2011) Densification and Characterization of Boron Carbide Nanopowders through Field Assisted Sintering (FAST)

L. R. Vargas-Gonzalez*, U.S. Army Research Laboratory, USA; C. D. Haines, D. Martin, U.S. Army ARDEC, USA; C. Hung, N. R. Vanier, PPG Industries, Inc., USA

Dense, nano-crystalline ceramics are of high interest to the research community, as these specimens exhibit interesting mechanical, thermal, and electrical properties. Recently, low-cost synthesized boron carbide nanopowders have become available for evaluation. Densification of these nanopowders through solid-state sintering trials have been met with some success, however, cracking and densification issues exist with the high surface area nanopowder possibly due to its higher oxide content. Efforts are currently underway to characterize the sintering behavior of boron carbide nanopowders through employment of field assisted sintering (FAST) techniques, which theoretically could provide dense specimens with nano-crystalline microstructural features due to lower densification temperatures and quicker sintering cycles. The effect of ramp rate, soaking temperatures, sintering times, ram pressures, and oxide removal techniques on the densification, growth, and evolution of the microstructure will be examined to determine the sintering mechanisms and structure/property relationships.

9:10 AM

(ICACC-S1-056-2011) Pressureless sintering of titanium diboride using metallic additives

H. Heidari*, Université Laval, Canada; H. D. Alamdari, Université Laval, Canada; D. Dubé, Université Laval, Canada; R. Schulz, Institut de Recherche d'Hydro-Québec, Canada

Titanium diboride has extraordinary properties including very high melting point, low density, excellent strength, and good thermal and electrical conductivity, but low toughness and poor sinterability. Using metallic additives can act as sintering aid to enhance sinterability and toughness and prevent rupture failure of TiB2-based parts. In this work, TiB2-based ceramic parts were consolidated using metallic additives followed by pressureless sintering. Different proportions of iron and titanium (≤ 10wt%) were added to lower the sintering temperature. Sintering was conducted at 1400–1700oC under controlled atmosphere. The effect of chemical composition, processing parameters and sintering temperature on density, mechanical properties and microstructure was studied. It was found that processing parameters have a remarkable effect on the porosity size and distribution in the microstructure as well as grain boundary composition and mechanical properties.

9:50 AM

(ICACC-S1-057-2011) Thermal Stability and Effect of Texture on Ultrahigh Damping of Nanocrystalline Mg-Matrix Composites Reinforced with MAX Phases

S. Amini, University of California Santa Barbara, USA; M. W. Barsoum, B. Anasori*, Drexel University, USA

We developed a unique, simple and cost effective technique to fabricate Ti2AlC-reinforced Mg-matrix composites – wherein the Mg-grain size is in the ~35±15 nm range – by pressureless melt infiltration. Not only do these nano-grains form spontaneously, but more importantly, they are so thermally stable that taking the composite to 50 °C over the melting point of Mg three times, does not result in their coarsening. Because of their nano-size, their melting point is depressed, in some cases by 40C. The composites exhibit exceptional damping capabilities because of the presence of the MAX phase. The presence of the Mg, allows the Ti2AlC to form larger incipient kink bands than in bulk dense Ti2AlC. It also imparts the composite with exceptional Vickers hardness (2 GPa), compressive (700+-10 MPa), and tensile (380+-20 MPa) strengths. The technological implications of having a readily machinable, relatively inexpensive, strong, stiff (effective moduli ≈ 100 GPa) and damping solid will be discussed.

10:10 AM

(ICACC-S1-058-2011) Development of Glass Ceramic Proppants for Hydrofracturing in Oil and Natural Gas Bearing Shales

D. Hartwich*, P. J. McClure, R. P. Koseski, B. E. Scheetz, J. R. Hellmann, The Pennsylvania State University, USA

The goal in hydrofracturing and stimulation of gas and oil wells is maintaining high permeability paths for resource recovery over the life of the well. A slurry of surfactants, corrosives, and ceramic aggregates (proppants) under pressure induce and maintain fractures emanating from the well bore. Current state of the art proppants, derived from sintered aluminosilicates are becoming increasingly expensive resulting in the need for an alternative proppant material. This presentation summarizes our work on the development of high strength, high performance proppants from alternative raw materials derived from industrial/domestic waste streams. Proppants manufactured from basalt-based glass-ceramics have been developed. This non-traditional proppant material is being tailored to rival commercially available sintered bauxite-based materials with regard to strength, hardness, specific gravity, and behavior in American Petroleum Institute testing (API-60 and 61). Our studies for achieving enhanced fracture resistance by controlled devitrification in rhyolite-, andesite-, and basalt-based proppants will be discussed. The ability to manufacture high performance proppants from these inexpensive indigenous raw materials, closer to the site of application, offers significant potential for reducing the cost of hydrofracturing operations.

10:30 AM

(ICACC-S1-059-2011) Silicon carbide based sandwich structures: processing and properties

A. Ortona*, S. Pusterla, SUPSI-ICIMSI, Switzerland; S. Gianella, Erbicol, Switzerland; C. D'Angelo, SUPSI-ICIMSI, Switzerland

Reticulated SiC foams have been successfully employed in several high temperature applications such as porous burners or heat exchangers. These foams can withstand oxidative conditions for long time with low material degradation. Foams used for high temperature applications have porosities in the range 80-90%, and pore densities in the range 5-50 pores per inch. They typically exhibit good convective and radiative heat transport due to their large internal surface area. Cf/SiCm Ceramic Matrix Composite (CMC), thanks to their toughness, can be applied as structural materials in high temperature applications. SiC based sandwich structures made of reticulated SiC foams and C fibres (with C interphase) porous preforms have been assembled and further densified via Polymer Infiltration and Pyrolysis. Samples, were thermally and mechanically characterised and result shown

10:50 AM

(ICACC-S1-060-2011) Sintering behaviour of lithium-titanate pebbles Modifications of pore morphology and pore size distribution

D. Mandal*, M. R. K Shenoi, Bhabha Atomic Research Centre, India; D. Sen, S. Mazumder, D. Sathiyamoorthy, Bhabha Atomic Research Centre, Trombay, India; D. V. Khakkar, Indian Institute of Technology, Bombay, India

Lithium-titanate has attractive properties, viz. high lithium-density; high melting point and tritium release behavior. Lithium-titanate is the primary contender for use as test blanket module (TBM) materials for tritium breeding in fusion reactor. For the development of solid tritium breeding materials it is important to study the process parameters to improve the desired material properties. These properties depend significantly on microscopic and mesoscopic structures of these pebbles, like grain size, porosity, pore size distribution etc.Further, the thermal conductivity of this ceramic material varies significantly with grain size, porosity pore morphology, pore size distribution, cracks etc. The above variables may be tuned by various process parameters e.g. sintering temperature, rate of heating, duration of sintering etc.Scattering measurements using neutrons and x-rays along with the electron microscopy and porosimetric techniques can throw light on the evolution of microscopic and mesoscopic structures of such ceramic materials. The experimental results on the effects of various thermodynamic parameters on the micro and mesoscopic structures of lithium titanate pebbles during sintering, will be discussed.

11:10 AM

(ICACC-S1-061-2011) Effect of heat treatment on Thermal properties of Pitch-based and PAN-based Carbon-Carbon Composites

S. S. Iqbal*, Southern Illinois Univ, Carbondale, USA

Thermal properties of two directional (2D) pitch-based carbon fiber with charred resin and three directional (3D) PAN-based carbon fiber with CVI carbon matrix C/C composite were investigated for non-heat treated (NHT) and heat treated (HTT) materials through the thickness (z-direction). Heat treatment was performed at 1800, 2100 and 2400 °C for 1-hr in inert argon atmosphere. Thermal diffusivity, heat capacity and density were measured to calculate thermal conductivity. Thermal diffusivity and conductivity was the highest for 3D C/C heat treated at maximum temperature with non-heat treated one exhibiting the lowest one. Similarly, 2D C/C heat treated at maximum temperature exhibited the highest thermal diffusivity and thermal conductivity. Polarized light microscopy (PLM) images of HTT C/C show a progressive improvement in microstructure when compared to NHT C/C. However, HTT 2D and 3D C/C composites exhibited extensive shrinkage of charred resin and CVI carbon matrix, respectively, from fibers resulting in intra and inter-bundles cracking when compared to NHT one. Raman spectroscopy and XRD results of NHT and HTT C/C indicated increased ordering of structure. A progressive improvement in thermal properties was observed with increased heat treatment temperatures.

11:30 AM

(ICACC-S1-062-2011) Processing, sintering behavior and mechanical properties of phlogopite based glass-ceramic/PSZ zirconia composites

Z. Hamnabard*, Nuclear Science & Technology Research Institute (NSTIR),, Islamic Republic of Iran; B. Eftekhari yekta, Nuclear Science & Technology Research Institute (NSTIR),, Islamic Republic of Iran

In this study, a mica based glass-ceramic composition was reinforced with 10,15,20 and 25 wt% partially stabilized zirconia. The glass-ceramic matrix composites were prepared by direct sintering of glass and zirconia powder mixtures. Sintering behavior, 4-point bending strength, Vickers micro-hardness, fracture toughness and machinability of composite samples were investigated. The sintered samples

were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). The results showed that partially stabilized zirconia dissolve in glass matrix and cause to formation of zircon crystals, which precipitated in the glass matrix. Also, By increasing of zirconia powder, mechanical properties of the composite samples initially reduced and then increased, Whilst fracture toughness of the composites were increased. Microstructural analysis of the samples showed agglomeration of zirconia powder in the glass matrix. In addition, Machinability was destructed due to decreasing of phlogopite phase.

11:50 AM

(ICACC-S1-063-2011) Strengthening and toughening of Al2O3–13wt.%TiO2 coatings fabricated by plasma spraying and laser remelting on titanium alloy

C. Li*, Shanghai University of Engineering Science, China; Y. Wang, Harbin Institute of Technology, China; Z. Yu, Shanghai University of Engineering Science, China; W. Tian, Y. Yang, Harbin Institute of Technology, China

Plasma sprayed microstructured and nanostructured Al2O3–13wt.%TiO2 coatings were prepared on Ti–6Al–4V titanium alloy substrates. The nanostructured feedstock was reconstituted agglomerates derived from nanoparticles by wet ball milling, spray drying, sintering and plasma treatment. The as-sprayed coatings were remelted by a CO2 laser. The effects of laser remelting on the microstructure, phase constituents and properties of the ceramic coatings were investigated. The results indicate that the laser remelted coatings exhibited more compact and homogenous structure as well as strong metallurgical bonding to the substrates. The microhardness of the as-sprayed Metco 130 and nanostructured Al2O3-13wt%TiO2 coatings was in the range of 700 to 1000 HV0.3, while the microhardness of the corresponding remelted coatings was enhanced to 1000 to 1350 HV0.3 and 1100 to 1800 HV0.3, respectively. In addition, the laser-remelted nanostructured Al2O3–13wt.%TiO2 coatings possessed higher crack growth resistance than the corresponding conventional coatings. The higher strength and toughness of the laser-remelted nanostructured coatings was mainly related to their unique structures.

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

Advanced Coating Processing and Nanostructured Coating Systems

Room: Coquina Salon G
Session Chairs: Rainer Gadow, IFKB University of Stuttgart; Yutaka Kagawa, The University of Tokyo

8:00 AM

(ICACC-S2-051-2011) Advanced Ceramic Coatings: from "Passive" to "Engineered" Layers and from Micrometer-Sized to Nanometer-Sized Structural Scale (Invited)

G. Montavon*, University of Technology of Belfort-Montbéliard, France

Thermal spray routes and thin films processes have proven to be suitable for manufacturing a large variety of ceramic coatings on vastly different substrate compositions and geometries. They are nowadays implemented to fulfill requirements for a large diversity of functionalities for dedicated applications. Nevertheless, most of the developments were considering until recently functional coatings as "passive" layers: materials selection and coating structural optimization resulted most of the time from a trial-and-error approach and materials selection and coatings requirement were often an "end-of-pipe" process. More demanding requirements for enhancing system performances require "passive" coatings to evolve toward "engineered" ones to take full advantage of unique coating characteristics resulting from these surface processes and to guarantee their conformity to specifications. To reach this goal, a strong scientific baseline is required more than ever to hardness the new opportunities offered by new emerging processes allowing manufacturing nanometer-sized coatings with improved performances. This presentation aims at covering those two topics (i.e., "passive" to "engineered" coatings and micrometer to nanometer structured layers) by developing various examples of coating developments and resulting properties.

8:30 AM

(ICACC-S2-052-2011) Innovative plasma spray technology for advanced coatings (Invited)

T. Yoshida*, University of Tokyo, Japan

The global trend in the field of materials R&D is shifting from "bulk" to "coating" technologies. Needless to say, the primary factor in materials R&D is "viability", without which, efforts are only the material research for the sake of research. Also for the process development, viability must be considered unexceptionally. In this regard, it is a natural consequence that plasma spraying is attracting attention. The term "plasma spraying" is however somewhat ambiguous. According to the state of the sprayed feedstock, this technique is classified into three categories: plasma spray CVD, plasma spray PVD, and plasma powder spraying. Each process has its own deposition characteristics. When considering technological transfer to industry, the capacity that each process accommodates has to be taken into account. Recent plasma destruction treatment of CFCs at a rate as fast as 100 kg/h has suggested that a 100-kW-class plasma spray system can treat powder, liquid, or vapor feedstock at 1, 10, and 100 kg/h, respectively. Therefore, firstly in this lecture, I will point out the important issues involved in the advancement of plasma spraying technology. It is followed by the future potential of novel plasma spraying by presenting our recent projects aiming at a development of novel deposition processes for advanced coatings by plasma spray CVD and plasma spray PVD.

9:00 AM

(ICACC-S2-053-2011) Microstructural evolution of AlN coatings in room temperature vacuum cold spraying

C. Park*, K. Baik, Chungnam National University, Republic of Korea

In this study, aluminum nitride (AlN) coatings on a glass substrate using a room temperature vacuum cold spraying have been evaluated in terms of their film structure and mechanical properties. Submicron AlN particles were accelerated by gas flow in the nozzle up to velocity of several hundred m/s. During interaction with substrate, these particles formed a thick (1~50μm), uniform, hard and dense AlN coating. XRD and TEM analyses revealed that the AlN coating retained an initial crystal structure of wurtzite and severe particle impact formed nanocrystalline AlN grains of 20-100nm. Optimization of processing parameters including particle size, gas flow rate and nozzle-to-substrate distance produce a much dense AlN coating which had a modulus of ~150 GPa and a hardness of ~10 GPa.

9:20 AM

(ICACC-S2-054-2011) Graded Ceramic Coatings with Nanostructured Surface Layer

T. Chraska*, K. Neufuss, Inst. of Plasma Physics ASCR, Czech Republic

A novel way to fabricate ceramics coatings with highly abrasion-resistant nanostructured surface is presented. Initially, amorphous coating is produced by plasma spraying a near-eutectic mixture of the alumina-zirconia-silica system. The as-sprayed amorphous coating surface is heat treated by a laser to temperatures above 1000 C and below the melting point to induce solid state crystallization in the surface layer. The resulting coating is thus graded with nanocomposite structure at the free surface and amorphous layer at the substrate. Separate DSC experiments show an exothermic peak between 940 and 990 C. Values of the Avrami coefficients together with results of the microstructural observations indicate that tetragonal zirconia nanocrystallization proceeds by a diffusion-controlled mechanism.

Significant increase of microhardness and abrasion resistance values in the surface heat-treated samples can be attributed to the fine nanocomposite structure, in which round nacrystallites are tightly packed in remains of the amorphous matrix.

10:00 AM

(ICACC-S2-055-2011) Advanced thermal spraying for oxide ceramic coatings as enabling technologies in product engineering (Invited)

R. Gadow*, A. Killinger, IFKB University of Stuttgart, Germany

Processing of sub-micron and nano scale powders by advanced thermal spray techniques offers new potentials for high performance oxide ceramic coatings. Air Plasma Spraying (APS), High Velocity Oxyfuel (HVOF) and High Velocity Suspension Flame Spraying (HVSFS) have been developed for thermal spraying of fine powder agglomerates and suspensions containing micron, submicron and especially nano particles with hypersonic speed. For this purpose i. e. the suspension is introduced directly into the combustion chamber of a modified HVOF torch thereby featuring a safe work place conditions while handling nano powders. Dense and well adherent coatings with a refined microstructure are obtained. Especially from nanostructured coatings superior physical properties are expected for various industrial applications. Direct spraying of suspensions offers high flexibility in combining and processing different materials. It is a cost saving process and opens entirely new application fields. The paper gives an overview of the thermal spray methods and will present actual results in coating and product development achieved by spraying nano oxide ceramic materials like Al2O3, TiO2, MgO, 3YSZ and Cr2O3 and binary phases like Al203 x TiO2, TiO2x TiC and others.

10:30 AM

(ICACC-S2-056-2011) High velocity suspension flame spraying (HVSFS) deposition of innovative bioactive glass coatings (Invited)

V. Cannillo*, G. Bolelli, University of Modena and Reggio Emilia, Italy; R. Gadow, A. Killinger, Universität Stuttgart, Germany; L. Lusvarghi, A. Sola, University of Modena and Reggio Emilia, Italy; N. Stiegler, Universität Stuttgart, Germany

The present research activity was addressed to produce and characterize bioactive glass coatings by the innovative High-Velocity Suspension Flame Spraying (HVSFS) technique. Bioglasses are extensively used in medical devices, due to their ability to bond to human. However the application is limited by their relatively poor mechanical properties. To overcome this drawback, bioglasses can be deposited as bioactive coatings onto a tougher substrate, which, in turn, confers the wanted mechanical reliability to the device. Thermal spraying is an ideal approach to fabricate bioactive coatings. In particular High-Velocity Suspension Flame Spraying can be particularly suitable, since ultrafine glass powders can be directly processed. In this work, two bioactive glasses were tested, i.e. the well-established Bioglass® 45S5 discovered by Hench and the and an innovative composition named BioK, derived from the former substituting the sodium oxide with potassium oxide. Various samples were produced under different spraying conditions. The microstructure of the glass coatings was characterised by SEM, XRD and Raman spectroscopy; their adhesion strength was measured by tensile adhesion testing; their bioactivity was evaluated by soaking in simulated body fluid (SBF) for different times.

11:00 AM

(ICACC-S2-057-2011) High velocity suspension flame sprayed (HVSFS) hydroxyapatite coatings for biomedical applications (Invited)

N. Stiegler*, R. Gadow, A. Killinger, IFKB University of Stuttgart, Germany

Thermal spraying of suspensions containing particles of submicron or nano size offers new possibilities in functional coating development and creates up new application fields. Spraying nano Hydroxyapatite (HAp) suspensions by means of hypersonic flame spraying, results in coatings with a refined microstructure and a layer thickness typically ranging from 20–50 μm can be achieved. HVSFS is a novel thermal spray process developed at IMTCCC, for direct processing of submicron and nanosized particles dispersed in a liquid feedstock. Thermally sprayed HAp coatings are widely used for various biomedical applications due to the fact that HAp is a bioactive, osteoconductive material capable of forming a direct and firm biological fixation with surrounding bone tissue. Bioceramic coatings based on nanoscale HAp suspension were sprayed on Ti plates by HVSFS and compared to APS as well as HVOF ones. Different combustion chamber designs were developed to optimize the HVSFS coating process. The deposited coatings were mechanically characterized including surface roughness, micro hardness and coating porosity. Phase content and crystallinity of the coatings were evaluated using X-ray diffraction. The bond strength of the layer composites was analyzed by the pull-off method. The coating composite specimen and initial feedstock were further analysed by SEM, rheology and zeta potential analysis.

11:30 AM

(ICACC-S2-058-2011) Ceramics coating by plasma spraying : control online, new developments and challenges for structured coatings (Invited)

A. Denoirjean*, P. Fauchais, SPCTS / CNRS, France

The plasma spraying process is well adapted to produce ceramic coatings. With the new devolpment of the injection of liquide inside the plasma allows to produce nanostrutured coating. Moreover the achitecture can be monitored with deifferent material or porosity level. The obtained properties seem to be interesiting in the field of energy applications (thermal barrier, Fuel cell). The key of success is mainly the diagnostic and control on line of the parameters during the process.

S3: 8th International Symposium on Solid Oxide Fuel Cells (SOFC): Materials, Science and Technology

Electrolysis

Room: Coquina Salon E
Session Chairs: Teruhisa Horita, AIST; Alexander Michaelis, Fraunhofer Institute

8:00 AM

(ICACC-S3-050-2011) Water Electrolysis at High Temperature (Invited)

M. Zahid, J. Schefold, A. Brisse, Q. Fu*, European Institute for Energy Research, Germany

Water electrolysis at high temperature for hydrogen and oxygen production using protonic or ionic conducting electrolytes constitutes an advanced concept aiming at increased electrical-to-chemical energy conversion efficiency. At high temperature higher efficiencies are achievable owing to favorable thermodynamic conditions and also because of improved kinetics for the electrode reactions. The thermodynamic reason for higher efficiencies is a decrease of the molar Gibbs energy of the reaction with increasing temperature while the molar enthalpy remains essentially unchanged. Reversible operation of SOFCs as H2O electrolyzer cells (SOECs) is well known from pioneering works in the 1980ies on tubular cells. In the recent years renewed interest has arisen for the SOEC, driven by the availability of cells with improved performance. Different durability tests of solid oxide electrolyzer cells and stacks over thousands of hours were performed at the European Institute for Energy Research. The cells and stacks showed very low degradation rates (around 2%) at an absolute humidity up to 90% and a current density up to 1A/square cm. In this presentation, the actual state of research on SOECs will be briefly summarized, the players in the filed mentioned, and potential hurdles for the future development identified.

8:30 AM

(ICACC-S3-051-2011) High Temperature CO2 Electrolysis using ODF Catalysts

H. Guo, G. Iqbal, B. Kang*, West Virginia University, USA; A. Manivannan, National Energy Technology Laboratory (NETL), USA

CO2 decomposition into carbon or conversion into methane or syngas can play an important role to reduce the greenhouse effect. In this research, oxygen-deficient ferrite (ODF) is integrated with the high temperature fuel cell technology as electrode materials for CO2 decomposition and energy conversion. The test setup consists of a NexTech ProbostatTM apparatus integrated with EIS/Potentiostat and Gas Chromatography (GC). CO2 or a combination of CO2/CO (with or without H2O/H2), is fed to the cathode side in solid oxide fuel cell setting as an oxidant. Initial tests demonstrated its capability of reducing CO2 electrochemically into CO with mechanisms similar to H2O electrolysis. In addition, it is found that the electro-catalytic decomposition of CO2 would prolong the ODF activity life and efficiency as compared to catalytic reaction. Through the in-situ EIS and exhaust gas analyses, and post-test study such as SEM, XRD, XPS of the ODF, the capability and efficiency of CO2 decomposition are evaluated. The electro-catalytic decomposition of CO2 related to ODF activity life and efficiency will be discussed.

8:50 AM

(ICACC-S3-052-2011) Improving Long term stability of solid oxide electrolysis cells

S. Elangovan*, J. Hartvigsen, D. Larsen, F. Zhao, I. Bay, Ceramatec, Inc., USA

High conversion efficiency of solid oxide electrolysis cells (SOEC) to electrolyze steam into hydrogen, and co-electrolyze steam-carbon dioxide mixture into syngas provides the means to store electricity from renewable sources in chemical form. Performance stability of SOEC is critical in achieving a commercially viable system. While the materials that are used for solid oxide fuel cells (SOFC) are applicable to high temperature solid oxide electrolysis cells (SOEC), there are degradation mechanism that are unique to SOEC mode of operation. The delamination of air electrode is found to be the primary source of performance degradation along with chromium poisoning of air electrode, metal interconnect corrosion and phase instability of current distribution layer. In collaboration with Idaho National Laboratory under the DOE Nuclear Hydrogen Initiative and support from the Office of Naval Research support, systematic evaluation of various materials was undertaken to address the stability issues. Significant reduction in degradation rate has been achieved by the use of new electrode materials set and protective coatings on interconnects. The stability improvement however came at the expense of initial stack performance. The use of higher conductivity current distribution layer restored the high performance while maintaining the stability gain. An overview of materials evaluation work will be presented.

9:10 AM

(ICACC-S3-054-2011) Observations on the Anode-Electrolyte Interface Stability in Solid Oxide Electrolysis Cells (SOEC)

M. Keane*, A. Verma, P. Singh, University of Connecticut, USA

Delamination of the anode from the electrolyte in solid oxide electrolysis cells (SOEC) is a major contributor to long-term electrical performance degradation. In this study, we have investigated the mechanism of anode delamination from the electrolyte. The half cells consisting of 8 mol% YSZ electrolyte and LSM electrodes were fabricated by screen printing method and tested in air at atmospheric pressure and 840 °C for 100 hours under voltage ranging from 0 to 2 volts. Changes in microstructure and phase evolution at the electrode-electrolyte interfaces as a function of testing parameters have been studied using SEM-EDS, FIB, TEM and XRD. Results will be presented and possible mechanisms responsible for such delamination will be discussed.

Surface/Interfacial Reactions

Room: Coquina Salon E

Session Chairs: Alexander Michaelis, Fraunhofer Institute; Teruhisa Horita, AIST

10:00 AM

(ICACC-S3-055-2011) Imaging of Oxygen Ionization and Diffusion in Flatten Tube Stacks

T. Horita*, T. Shimonosono, H. Kishimoto, K. Yamaji, M. E. Brito, AIST, Japan; H. Yokokawa, Tokyo City University, Japan

We have examined isotope labeling/SIMS technique for imaging oxygen ionization and diffusion at the SOFC cathode/interlayer/electrolyte interfaces. In this study, we applied these methods to observe the oxygen diffusion in practical flatten tube type stacks (Kyocera type). Isotope oxygen (18O) labeling was successful for imaging the active sites for oxygen ionization and incorporation into solids. CeO2-based interlayer was active sites for oxygen ionization. Also, the diffusion of 18O through the YSZ electrolyte was analyzed under fuel cell reaction. There is some difference of the amounts of oxide ion diffusion through the YSZ electrolyte, which suggests the difference of ionic flow in the YSZ.

10:20 AM

(ICACC-S3-056-2011) The influence of impurities in air on SOFC cathode degradation

I. M. Torres da Silva*, J. Hjelm, M. Mogensen, Risø DTU, Denmark

Degradation of composite LSM-YSZ cathodes for solid oxide fuel cells was investigated in different atmospheres. The aim was to determine the extent of degradation (irreversible) or deactivation (reversible) caused by impurities in the gas phase. The performance of LSM-YSZ/YSZ/LSM-YSZ symmetrical cells was monitored at 750°C in different qualities of air by Electrochemical Impedance Spectroscopy. The atmospheres applied were stagnant air, compressed air, artificial air (21% O2 in N2), and purified air. Deactivation was observed in all cases. A clear trend was observed; the more impurities present in air, the greater the deactivation. The polarization resistance increased by 36% in 260 hours in compressed air, while it increased by only 20% when purified air was used. Possibly, impurities adsorb at the triple phase boundary, blocking the active sites for oxygen adsorption and dissociation. Likely impurities include: residues of dust (stagnant air), oil from compressor pumps (compressed air), H2O, CO2 and traces of many other compounds. The performance of the symmetrical cells was partially regained when the temperature was increased to 850°C for a short period of time, possibly indicating that some impurities desorbed from the triple phase boundaries. It was concluded that impurities in the gas phase caused a significant part of the degradation observed on symmetrical cells, and therefore possibly on single SOFCs.

10:40 AM

(ICACC-S3-057-2011) Cathode Microstructure and Composition Effect on Interaction with Interconnect in Solid Oxide Fuel Cells

K. Lu*, T. Jin, Virginia Polytechnic Institute and State University, USA

In solid oxide fuel cell operation, cathode microstructure and composition are important factors to consider for its interaction with interconnect and long-term cell performance. In this work, (La,Sr)MnO3 (LSM) cathode is fabricated on the surface of yttria stabilized zirconia (YSZ) electrolyte by screen printing and then bonded with AISI 441 stainless steel interconnect. At 800°C, the samples are thermally treated in wet air atmosphere. The cathode microstructures are controlled at the same porosity but different pore sizes by using different particle sizes or the same pore size but different porosity by changing the cathode processing parameters. The cathode composition is varied by changing the x value in

(La,Sr)xMnO3 from 0.95 to 1.05. The vapor phase diffusion of chromium species is the main focus in studying the cathode degradation. The LSM/AISI 441 interaction and the reaction of vapor phase chromium species on the LSM surface are characterized by SEM and EDS element analysis.

11:00 AM

(ICACC-S3-058-2011) In-situ Investigation of Structural and Electrochemical Degradation of SOFC Anode Exposed to PH3

H. Guo, G. Iqbal, B. Kang*, West Virginia University, USA

Nickel yttria-stabilized zirconia (Ni-YSZ) is a common choice for SOFCs anode material due to its excellent performance in hydrogen and simulated syngas. However, trace amount of impurities which are commonly present in coal-derived syngas (e.g. PH3) interact with anode material and degrade its electrochemical performance and material properties. In this paper, the poisoning effects of phosphine (PH3) are investigated on the anode electrochemical performance and structural properties. An optical system integrated with ProboStatTM is utilized for in-situ monitoring of anode surface deformation, IR temperature and electrochemical performance under PH3. The degradation effects of PH3 on the SOFCs anode are also analyzed by post experiment characterization using SEM, EDX, and XRD. The experimental results indicate that the Ni-cermet-based SOFC anode is more susceptible to degradation due to PH3 in moist hydrogen than in dry hydrogen condition. It is proposed that the deleterious effect of PH3 on SOFC Ni-YSZ anode performance is due to the formation of Nickel Phosphate.

11:20 AM

(ICACC-S3-059-2011) Oxygen transport properties of La0.6Sr0.4Co0.2Fe0.8O3-δ

Y. Li*, West Virginia University, USA; K. Gerdes, National Energy Technology Laboratory, USA; X. Liu, West Virginia University, USA

Electrical conductivity relaxation (ECR) technique is a widely used method for investigating oxygen transport properties of mixed ionic and electronic conductors. However, there are still some problems with this method. First, oxygen surface exchange coefficient (k) and bulk diffusion coefficient (D) can not be fixed by testing samples with same thickness. The values of D and k, which fit the original data with small error, can vary over a large range. Second, oxygen bulk diffusion coefficient is assumed to be a constant for ECR technique but it is well accepted that D is depend on the oxygen partial pressure. To solve these issues, different thickness La0.6Sr0.4Co0.2Fe0.8O3-δ pellets were tested with small oxygen partial pressure step change ($\Delta \log PO_2 < 0.1$). More reliable kinetic parameters were obtained, and the effects of oxygen partial pressure on oxygen transport kinetic parameters are discussed.

11:40 AM

(ICACC-S3-060-2011) A Comparative Assessment of Chromia and Alumina Forming Alloys for SOFC Balance of Plant Applications

S. Bhowmick*, G. Le, A. Verma, P. Singh, University of Connecticut, USA

This paper reviews the status of both chromia and alumina forming alloys for applications in SOFC balance of plant. The microstructure, chemistry and phase formation of the oxide scales, and the morphology of the metal-oxide interface were studied using XRD, SEM, FIB and EDS. In this presentation, a comparative assessment of Cr evaporation from the alloys will also be reported, along with the nature of the oxide scale. Chromium evaporation and transportation from selected alloys (AISI 310S, Aluchrom, 602CA, aluminized 310S) were investigated in humidified air environment conditions. Pre-oxidation and surface scaling were also studied in the range of 850 °C to 1000 °C for 2, 5 and 20 h to form protective oxide scales. Experimental results will be presented and scaling mechanisms will be discussed.

S5: Next Generation Bioceramics

In Vitro and In Vivo Characterization of Bioceramics

Room: Ponce de Leon
Session Chair: Jay Hanan, Oklahoma State University

8:00 AM

(ICACC-S5-013-2011) Tough, strong and stable zirconia based ceramics for orthopaedic and dental applications : past issues, current state and future trends (Invited)

J. Chevalier*, L. Gremillard, INSA-lyon, France

Alumina and zirconia ceramics have been historically ceramics of choice in the process of orthopaedic implants or dental restorations. Zirconia was developed in the 90's to overcome the problems of brittleness of alumina, but problems related to its stability under hydrothermal conditions, in vivo, have stopped its use in orthoapedics after critical events in 2001-2002. Zirconia is however in the development phase in the dental field. After describing briefly the specifications for such products and past issues related to the problem of zirconia hydrothermal degradation, we will focus on current strategies to process tough and stable zirconia based composites (mainly alumina-zirconia composites). We will discuss on solutions showing the best balance between crack propagation and aging resistance. Current commercial products under clinical use will be reviewed and assessed. Future development combining virtual design and new process technologies will be presented.

8:30 AM

(ICACC-S5-014-2011) Biomimetic Mineralization of Bone Tissue Engineering Scaffolds (Invited)

P. X. Ma*, University of Michigan, USA

Bone fractures and damage result in more than 1.3 million surgical procedures each year in the United States alone. The shortage of replacement bone tissue remains a major clinical challenge. Tissue engineering is a promising approach to bone repair and replacement. In the tissue engineering approach, scaffolds play a pivotal role to provide three-dimensional templates and synthetic extracellular-matrix environments for regenerative cells. We take a biomimetic approach to design nanofibrous polymer scaffolds emulating the structural features of collage, which is the primary organic component of bone. We also develop technologies to generate bone-like apatite coating on the polymer scaffolds to further mimic the extracellular matrix of bone. A novel technique has been developed recently in our laboratory to rapidly mineralize nanofibrous scaffolds with tunable chemical composition and surface topography, enhancing osteoblastic cell proliferation, differentiation and bone regeneration. The results demonstrate the significance of the novel biomimetic polymer/ceramic composite scaffolds for bone tissue regeneration.

9:00 AM

(ICACC-S5-015-2011) Selective Laser Sintered Ca-P/PHBV Nanocomposite Scaffolds with Sustained Release of rhBMP-2 for Bone Tissue Engineering

B. Duan, M. Wang*, The University of Hong Kong, Hong Kong

Ca-P/PHBV nanocomposite scaffolds for bone tissue engineering were fabricated via selective laser sintering. The surface modification of Ca-P/PHBV scaffolds was conducted firstly by physical entrapment of gelatin. Heparin was then immobilized on gelatin-modified scaffolds through covalent conjugation. Human umbilical cord derived mesenchymal stem cells (hUC-MSCs) were seeded onto the scaffolds. Compared to non-modified scaffolds, heparin-immobilized scaffolds exhibited higher cell proliferation at the early stage of cell culture. hUC-MSCs became confluent after 21 day culture on scaffolds and covered the whole scaffold surface, strongly adhering to

the scaffolds. Recombinant human bone morphogenetic protein (rhBMP)-2 was loaded onto scaffolds with or without surface modification and its release behavior was studied. An initial burst release of rhBMP-2 was observed for both types of scaffolds. The immobilization of heparin on the surface of Ca-P/PHBV scaffolds not only provided a means to protect the rhBMP-2 but also improved the sustained release. Surface modified scaffolds loaded with rhBMP-2 promoted significantly higher ALP activity of hUC-MSCs than the scaffolds with simple adsorption of rhBMP-2. The strategy of combining advanced scaffold fabrication technology, nanocomposite and growth factor delivery is promising for bone tissue regeneration.

9:20 AM

(ICACC-S5-016-2011) Methods of Evaluating Bioactive Orthopedic Implants (Invited)

T. D. McGee*, Iowa State University, USA

Orthopedic implants must be evaluated. In vitro methods are first for ethical reasons. Evaluation in simulated body fluids for solubility microstructure and function often use optical microscopy, SEM, and XRD. Specific cell cultures give greater insight to cellular compatibility and the presence of biochemical signals. Traditionally biocompatibility tests in vivo compare bulk specimens to existing biomaterials; where the inflammatory response and cellular responses within a fibrous capsule around the implant were evaluated by a pathologist. Experiments using bioglasses or CP had intimate contact with new bone but did not induce bone formation and were considered bioconductive and not bioinductive. This conclusion has been challenged because new bone has been found in the pores of CP implants in soft tissue. More sophisticated experiments using powdered samples verified CP can induce bone formation in muscle. The structure of new bone formed in muscle or on tissue engineering scaffolds is not organized like adjacent bone. Fluorescent bone labels and microradiographs help determine the physiological response induced by a bioactive implant. The ultimate test for orthopedic implants is to show biocompatiblilty in bone organization and structure as well as in composition.

10:10 AM

(ICACC-S5-017-2011) Substituted Apatites: New Perspectives by Computer Modelling and Ab Initio NMR Calculations (Invited)

C. Bonhomme*, F. Babonneau, C. Gervais, universite P et M Curie, France; D. Laurencin, ICG, France; M. E. Smith, J. V. Hanna, University of Warwick, United Kingdom; A. Osaka, S. Hayakawa, Laboratory of Biomaterials, Japan

In this presentation, the latest developments in solid state NMR techniques and ab initio calculations will be presented and applied to the full description of substituted apatites and calcium phosphates. Both anionic and cationic substitutions will be taken into account (carbonates, Sr2+, Na+ ...). A general approach combining spectroscopy and computer modelling will be proposed: it appears to be valid for all types of substitution.

10:40 AM

(ICACC-S5-018-2011) Comparison of Bone Growth on Scaffolds Made From Silicate, Borosilicate, and Borate Glasses (Invited)

D. E. Day*, Missouri University of Science and Technology, USA; L. Bonewald, University of Missouri - Kansas City, USA; S. B. Jung, Missouri University of Science and Technology, USA; L. Bi, University of Missouri - Kansas City, USA

Bone growth was investigated for scaffolds made from a bioactive borate glass, a borosilicate glass, and two silicate based bioactive glasses (45S5 and 13-93) implanted in a calvarial defect in a laboratory rat. Scaffolds made from randomly oriented bioactive glass fibers and loose particulates were placed in calvaria defects (4mm diameter) of rats for 12 weeks to compare the proliferation of bone in the respective bioactive glass scaffolds. Micro-CT analysis of the scaffolds after 12 weeks showed that on average, n=4, the borate glass scaffold had the highest bone coverage on top and bottom of the scaffolds at 82±13% and 51±12%, respectively. Histomorphometry analysis of the calvaria implanted scaffolds showed that the borate glass scaffold had statistically more bone ($p<0.05$) than the borosilicate or silicate based bioactive glass scaffolds. An assessment of the bone tissue that infiltrated the bioactive borate scaffold showed no adverse biological reactions, no necrotic tissue, and no increased presence of macrophages or other immune cells.

11:10 AM

(ICACC-S5-019-2011) "In-vivo" Ageing of Dental Zirconia Ceramics: 12-months Results (Invited)

T. Kosmac*, Jozef Stefan Institute, Slovenia; P. Jevnikar, Medical Faculty, University of Ljubljana, Slovenia; A. Kocjan, Jozef Stefan Institute, Slovenia

An in-vivo experiment was designed to monitor the propagation of the t-m transformation of two bio-medical grade 3Y-TZP ceramics which were directly exposed to the aggressive environment of the oral cavity. Two high-purity "bio-medical-grade" powders (TZ-3YB-E and TZ-3YSB-E, Tosoh, Japan) were used to produce disc-shaped specimens with mean grain sizes of 0.51 um and 0.59 um, respectively. Four patients were provided with removable lower full-dentures, each with two fine-grained and two coarse-grained discs implanted in the lingual flange. After six months the discs were removed and subjected to XRD and FEG-SEM surface analyses. Both sintered materials initially consisted of nearly 100% t-zirconia. After twetve months, no change in the phase composition was observed on the surface of the control groups (specimens stored in ambient air). In contrast, about 10% of the m-phase was detected on the surface of the specimens that were exposed to the oral environment. A similar amount of transformed m-zirconia was detected on the surface of the sintered specimens that were subjected to accelerated ageing for 5 hours at 134 C in artificial saliva indicating that thermal cycling in the oral cavity fosters the diffusion-controlled transformation on the surface of the zirconia ceramics. The "naked" surfaces are vulnerable and represent a potential threat of premature failure for all-ceramic dental restorations.

11:40 AM

(ICACC-S5-020-2011) Tissue In-Growth in Resorbable Porous Tissue Scaffolds

J. J. Liu, A. Wallen*, K. Patel, R. Dahl, Bio2 Technologies, USA; C. Kearney, M. Spector, VA Boston Healthcare System, USA

In this study, highly porous scaffolds fabricated using a proprietary Cross-Linked Microstructure (CLM) process in a resorbable glass composition were subjected to a small animal in-vivo study to determine and evaluate the feasibility for use as weight bearing tissue engineering scaffold. The CLM scaffolds were manufactured by processing resorbable glass fibers to create a cross linked microstructure of an interconnected open pore network. The CLM structure in a resorbable composition with open and interconnected porosity exhibits the potential to provide adequate mechanical properties and bioactivity at the same time. Preliminary in-vivo results suggest that a new bone has formed around and in the pores of the CLM implants. There is also clear evidence of bone formation directly on the surface of the CLM implants, with continuity of the mineral phase between the bone and implant demonstrating direct bonding to the scaffold.

S7: 5th International Symposium on Nanostructured Materials and Nanotechnology: Development and Applications

Industrial Development and Application of Nanomaterials

Room: Coquina Salon C
Session Chairs: Sanjay Mathur, University of Cologne; Hao Shen, University of Cologne

8:00 AM

(ICACC-S7-039-2011) Fabrication and characterization of Ni/Cu/YSZ cermet for high temperature electrolysis cathode prepared by mechanical alloying

H. Hong*, J. Kim, S. Lee, Institute for Advanced Engineering, Republic of Korea

Ni/YSZ (Y2O3-stabilized ZrO2) cermets has been generally used as an electrode for solid oxide fuel cell and high temperature electrolysis (HTE). The effect of ball-milling times on electrical conductivity and microstructure of Ni/Cu/YSZ cermets for high temperature electrolysis was investigated. It was successfully prepared by high-energy ball-milling of Ni, Cu and YSZ powders, pressing into disc and subsequent sintering process at 900 °C under reducing atmosphere. The Ni/Cu/YSZ cermets material thus fabricated was characterized using various analytical tools such as XRD, SEM, TEM, and laser diffraction and scattering method. Electrical conductivity of sintered Ni/Cu/YSZ cermets discs thus fabricated was measured by using 4-point probe technique for comparison with that of conventional Ni/YSZ cermets. As the milling time is increased, the particle size decreases with Ni/Cu/YSZ ball-milled powder, on the other hand, well-connected particles are thought to be the reason for the enhanced electrical conductivity

8:20 AM

(ICACC-S7-040-2011) Influence of amorphous nano additive on sintering behavior and electrical properties of BaTiO3 ceramics

S. Sohn*, H. Kim, M. Hong, S. Kwon, K. Hur, Samsung electro-mechanics co., ltd., Republic of Korea

Barium titanate(BT) is known as the most common dielectric material for multilayer ceramic capacitor due to its high dielctric constant. Both for increasing the electrical reliability and for decreasing the sintering temperature, BT ceramics are generally sintered with the various additives such as MgO, rare-earth oxide and SiO2. However, these additives play role of lowering the dielectric constant as well as the sintering temperature. In addition, it is not easy to obtain the homogeneous mixture of BT and these additives in slurry state, in case of using the nano scale powders. In this work, we synthesized the nano scale amorphous complex oxide containing several additives by vaporization treatment, in order to overcome the dispersion problem and lower the sintering temperature of BT at one time. The synthesized particles were proven to be uniform in composition, 30~50nm in size, and amorphous in phase from TEM observation. The BT specimen with the addition of this nano complex oxide was sintered at lower temperature, showing the high dielectric properties.

8:40 AM

(ICACC-S7-041-2011) Development of an Aqueous Synthesis Route for Nano-crystalline PLZT

M. R. Winter*, C. B. DiAntonio, T. Monson, A. W. Roesler, D. L. Huber, T. P. Chavez, T. E. Stevens, Sandia National Laboratories, USA

Nano-crystalline dielectrics may possess improved electrical properties over larger grained materials; however powder synthesis is often complex. Processing typically requires difficult and complicated techniques and raw materials, with small powder yields. A simple, pH-based aqueous synthesis route has been developed utilizing relatively benign precursor materials, with excellent initial yields. The precipitate is easily converted to phase pure material at low temperatures, but requires control over the synthesis steps. The synthesis route is discussed, from precursor precipitation and dispersal to drying and calcining. Finally, preliminary results of device fabrication are presented to demonstrate the potential benefits of nano-crystalline PLZT for dielectric applications. Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

9:00 AM

(ICACC-S7-042-2011) Combustion Chemical Vapor Deposition of Ceramic Cathode Electrodes

E. Koep, IREC, Catalonia Institute for Energy Research, Spain; J. R. Morante*, University of Barcelona, Spain

Since high temperature annealing of ceramic components is often incompatible with most microelectronic components, new method is needed for the development of high performance electrodes for integrated μSOFC elements. Thus, novel film fabrication methods have opened the possibility to lower temperature fabrication of SOFC materials. Dense thin films of electrolyte materials and electrode materials have been developed with much lower sintering temperatures. Even some porous electrodes have been developed with the potential for low-temperature fabrication. These advances notwithstanding, low-temperature co-sintering of all SOFC components may also be necessary for wafer-level implementation. Combustion CVD is a flame-based process in which the required environment for transformation of precursors is provided by the flame conditions. During the CCVD process, film precursors are dissolved in an organic solvent and fed through a nozzle into the flame. Sintering and chemical transformation occur in-flight so that the particles arriving at the substrate surface are already of the correct phase. Because of this, no annealing is necessary. In this contribution, we present the synthesis and characterization of thick film LSC and LSM cathodes fabricated using by combustion CVD. These cathodes have also been evaluated via impedance spectroscopy.

9:20 AM

(ICACC-S7-043-2011) Characterization of Thermal Properties of Cordierite Ceramics Prepared by Using Spherical Shaped and Hollow Particles

C. -. Ozgur*, Dumlupinar University, Turkey

Spherical shaped and hollow or dense cordierite precursors have been prepared by ultrasonic spray pyrolysis technique by controlling the reactor temperature gradient. The heating rate of the droplets within the reactor directly affects the particle density where hollow particles (density is smaller than 1) have been obtained in a case of high rate heating. The particles sizes of the hollow and dense precursors were 1.345 and 1.121 μm, respectively. The wall thickness of the hollow precursor is about 50 nm. Two types of cordierite ceramics have been prepared by using hollow or dense cordierite precursors at a sintering temperature of 1250oC for 4 hours. Mechanical properties, thermal expansion, thermal conductivity and microstructures of the prepared ceramics have been researched. The thermal properties of the cordierite ceramic prepared by using hollow particles have better than the other cordierite ceramic. Beside this, there is no significant difference between the mechanical properties of the cordierite materials. According to the results, the cordierite ceramics prepared with hollow type precursor are good candidates for industrial applications where the thermal properties of classical cordierite ceramics are not enough.

10:00 AM

(ICACC-S7-044-2011) Technological Development for a Next-generation Highly-reliable Gas Sensor (Invited)

F. Hernandez-Ramirez, IREC, Catalonia Institute for Energy Research, Spain; J. R. Morante*, University of Barcelona, Spain

Environmental surveillance; safety and control relative to chemical materials used for energy production and its rational use; pollutant emission from the industry, from combustion system or from the automobile; gas safety; gas leak accidents; working place environment; air quality; volatile organic control and a very long list of applications involving gas molecules have been recognized as a highly critical social issue. All these cases require effective and immediate measures to deal with these chemical materials. Currently, however, there are no highly sensitive or reliable detectors that can detect these gas molecules in real time in the field. Also, in order to effectively manage species that are known to be potentially toxic, it is necessary to develop highly sensitive detectors to calculate the total volume as well as to detect some representative components that are found to be toxic, in order to comprehensively manage them. This contribution reports on the advancement in new metal oxides nano materials with the aims for developing new sensors with high reliability and with very low power consumption technology that can be powered by a battery (i.e., cordless) or harvesting systems.

10:30 AM

(ICACC-S7-045-2011) Carbide-metal composites, gradients and coatings through solution processing (Invited)

G. Westin*, Uppsala University, Sweden; K. Jansson, Department of Materials and Environmental Chemistry, Sweden

WC-Co composites consisting of 1-10 micron sized WC grains and a cobalt matrix provide a very beneficial combination of hardness, toughness for a wide range of applications ranging from circuit board drilling via metal shaping to rock excavation. Further, coatings and gradients can be added to the tool bit surfaces to optimize the combination hardness, toughness and chemical resistance of cutting and other tools in demanding applications, as well as be used for adjusting the bulk properties of a tool bit to be suitable for adding a hard ceramic coating. Solution based synthesis routes provide low cost, flexible and efficient processes to complex nano-materials of different forms, but have not been much explored for the hard composite coatings and gradients. Here we describe solution routes to homogeneous WC-Co composite compacts built of large WC grains and low Co content, desired for mining, and oil- and tunnel-drilling applications. These structures are unattainable with conventional powder metallurgical techniques and have superior properties. New solution decomposition routes to WC and VC, as well as nano-composites of them with Ni and Co were developed for preparation of coatings and gradients. In combination with WC and (Ta,Nb)C powders, up to 300 micron thick grain size and Co content coatings and gradients were built in WC-Co cemented carbides

11:00 AM

(ICACC-S7-046-2011) Production of silica nanoparticle with the controlled size and shape from the microemulsion solution (Invited)

T. Hwang*, Korea Institute of Industrial Technology, Republic of Korea

Sol-gel synthesized silica nanoparticle is one of the most frequently studied materials for various kinds of applications such as high performance liquid chromatography, drug delivery, inorganic-organic hybrid nano composites, optical coatings and more. In the production of silica nanoparticle, the size and shape control is the important technical issues. In that respect, the microemulsion synthesis is considered as a useful method. In our laboratory in KITECH, Hollow spherical silica particles were synthesized by using the acidic water-in-oil (W/O) microemulsion solution which was composed of cyclohexane, surfactant mixture, and acidic aqueous phase. The hydrolysis and polycondensation of tetraethoxysilane was induced in the aqueous micelles where an acidic catalyst HCl was contained. Importantly, after a few hr of synthetic reaction hollow spherical silica particles were obtained and the TEM observation showed that the most of the particles were hollow spheres where the void space was completely sealed with the silica shell. Since many of the synthetic reactions of functional organic material are occurring in the acidic condition, the synthetic method of hollow silica nanoparticles in this study could well be used to make the inorganic-organic hybrid particles.

11:30 AM

(ICACC-S7-047-2011) Nanomaterials: Research, Development and Technology Roadmaps - 2020 (Invited)

M. H. Van de Voorde*, Technische Universiteit Delft, Netherlands

An overview of nano-ceramic and composite development in the world will be given. Fundamental research will be the backbone for future industrial success including new theories. Design of third generation nano-ceramics, macro/mico-nano computer modelling, potential nanoceramic materials and composites will be highlighted.

S8: 5th International Symposium on Advanced Processing and Manufacturing Technologies for Structural and Multifunctional Materials and Systems (APMT) in honor of Professor Katsutoshi Komeya

Design-Oriented Manufacturing III

Room: Coquina Salon B

Session Chairs: Vojislav Mitic, University of Nis; Guo-Jun Zhang, Shanghai Institute of Ceramics

8:30 AM

(ICACC-S8-050-2011) Reactive Hot Pressing and Microstructure Tailoring of Group IVB Metal Diboride Ceramic Composites (Invited)

G. Zhang*, Shanghai Institute of Ceramics, China

Titanium diboride (TiB2), zirconium diboride (ZrB2), and hafnium diboride (HfB2) demonstrate similar features in crystalline structures, processing, and properties. Usually diboride ceramics and their composites are prepared by sintering compacts of the mixed powders of diborides and other components. As an alternative route, diboride composites can be manufactured by reactive processing. The advantages of this approach include controllable microstructure and a high chemical compatibility of the in situ formed individual phases. We used reactive route to produce diboride ceramic composites of TiB2, ZrB2 and HfB2 in the recent years. Boron-bearing precursors such as B, BN, and B4C were used as the starting materials. The composites were produced by reactive hot pressing (RHP) or pressureless reactive sintering. Very recently, platelet-reinforced diboride-based ultra-high temperature ceramics (UHTCs) and further textured UHTCs were prepared by RHP. The mechanism of the microstructural developments and densification process during the reactive synthesis and the material properties will be discussed.

9:00 AM

(ICACC-S8-051-2011) Mechanical Properties of Chemical Bonded Phosphate Ceramics with Fly Ash as Filler

H. A. Colorado*, C. Hiel, T. Hahn, J. Yang, UCLA, USA

This paper is concerned with the use of fly ash filler in chemically bonded phosphate ceramics (CBPC) composites, with the goals of reducing production costs and developing an environmentally benign structural material. Traditional ceramics are usually associated with high temperature processing which increases the global warming. Fortunately, CBPC manufacturing can be performed at room temperature and the material itself is biocompatible. The CBPC was pro-

duced by mixing a phosphoric acid formulation and a controlled wollastonite powder (both from Composites Support and Solutions) with fly ash. Bending and compression strength, microstructure and different manufacturing process parameters were evaluated. Microstructure was identified by using optical and scanning electron microscopes, x-ray micro tomography, and X-ray diffraction. The microstructure characterization shows that CBPC is a composite itself with several crystalline (wollastonite and brushite) and amorphous phases.

9:20 AM

(ICACC-S8-052-2011) Effect of TiO_2 addition on thermal and mechanical properties of Y-Si-Al-O-N glasses

T. Wakihara*, J. Tatami, K. Komeya, T. Meguro, Yokohama National University, Japan; A. Kidari, S. Hampshire, M. J. Pomeroy, University of Limerick, Ireland

Y-Si-Al-O-N glasses are intergranular phases in silicon nitride based ceramics in which the composition and volume fraction of such oxynitride glass phases determine the properties of the sintering shrinkage behavior. A number of investigations on oxynitride glass formation and properties have shown that nitrogen increases glass transition and softening temperatures, viscosity, elastic modulus and hardness. In the present study, effect of TiO_2 addition on thermal and mechanical properties of Y-Si-Al-O-N glasses was investigated since the most typical Si_3N_4 ceramics for bearing applications are fabricated using a Si_3N_4-Y_2O_3-Al_2O_3-TiO_2-AlN system. It was clarified that addition of TiO_2 is effective to prepare Y-Si-Al-O-N glasses with lower glass transition temperature and with higher hardness.

10:00 AM

(ICACC-S8-053-2011) BaTiO3-Ceramics Doped by Rare Earth Additives Intergranular Microelectronics Properties Structural Fractal Analysis (Invited)

V. Mitic*, L. Kocic, V. Paunovic, University of Nis, Serbia; A. Terzic, Institute for Technology of Nuclear and Other Raw Mineral Materials, Serbia; V. Pavlovic, Serbian Academy of Sciences and Arts, Serbia; P. Petkovic, University of Nis, Serbia

Ferroelectric BaTiO3 as one of the most important ceramics materials in electronic, used on wide range of applications, can be modified via deformation of solid solutions with various dopant ions. In this paper, the influence of Er2O3, Yb2O3 and Ho2O3 on microstructure, microelectronic and dielectric properties of BaTiO3-ceramics has been investigated. The solid solubility of rare earth ions in the BaTiO3 perovskite structure has been studied by different methods of structural analysis including SEM-JEOL 5300 and energy dispersive spectrometer (EDS) system. BaTiO3-ceramics doped with 0.01 up to 0.5 wt% of rare earth additives were prepared by conventional solid state procedure and sintered up to 1380°C for two hours. We also applied the fractal method in microstructure analysis of sintered ceramics, especially as influence on intergranular capacitor and dielectric peoperties of BaTiO3-ceramics. This fractal nature effect has been used for better understanding integrated microelectronics characteristics and circuits.

10:20 AM

(ICACC-S8-054-2011) Ceramics Micro Processing of Photonic Crystals and Amorphous

S. Kirihara*, T. Niki, N. Ohta, S. Tasaki, Osaka University, Japan

Photonic crystals with periodic arrangements in dielectric constants can exhibit forbidden gaps at specific frequency ranges comparable to the lattice spacing through Bragg diffraction. In this investigation, alumina photonic crystals and amorphous with ordered and disordered arrangements of inverse spheres were fabricated by using micro stereolithography for terahertz wave controls. Terahertz wave spectroscopic methods are expected to detect and analyze bacteria in foods, micro cracks in electric devices or cancer cells in human skin. Micro air spheres were designed to realize periodical arrangements of with face or body centered cubic structures in dielectric bulks. Center points and diameters of spherical cavities were fluctuated following to random number functions to realize amorphous arrangements with fractal dimensions. Subsequently, photo sensitive resins including nanometer sized alumina particles were spread on a substrate, and cross sectional UV images were exposed on the surface. Solid precursors formed by the layer stacking could be dewaxed and sintered successfully to obtain dense alumina components. Terahertz wave properties measured by spectroscopic analysis were compared with calculated results obtained by finite difference time domain method. Electromagnetic wave Bragg diffractions and Anderson localizations in dielectric crystal and amorphous were investigated, respectively.

10:40 AM

(ICACC-S8-055-2011) Development of Numerical Method for Evaluating Microstructural Fracture in Smart Materials

H. Serizawa*, S. Tomiyama, T. Hajima, H. Murakawa, Osaka University, Japan

Advanced multifunctional materials have been developed by controlling their microstructure, and both elastic-plastic mechanical deformation and debonding & slipping at grain boundary have to be taken into account in order to estimate their fracture behavior. Although the finite element method has been widely employed to estimate the fracture behavior, only elastic-plastic deformations were mainly discussed in the most of previous studies. As one of the methods to demonstrate the interfacial behavior in the finite element analysis, the interface element has been developed and the crack propagation behavior based on the classic fracture mechanics could be demonstrated where only the elastic deformation was considered. So, in this research, in order to examine the applicability of interface element for the elastic-plastic behavior, the crack propagation behavior in the plate with a center crack was simulated by using the interface element. As a result of serial computations, it was found that by changing the yield stress the fracture behavior could be divided into three modes, which were "Plastic Deformation Dominant Mode", "Transient Mode" and "Crack Growth Dominant Mode". Also, by using a virtual polycrystal model, the influence of microstructure on the elastic-plastic deformation of grain and the debonding & slipping of grain boundary was discussed by using the interface element.

11:00 AM

(ICACC-S8-056-2011) Mechanical Property Improvements of Ceramic Dental Crowns Modelled by Using Laser Scanning Stereolithography and Powder Sintering Processes

S. Tasaki*, S. Kirihara, T. Soumura, Osaka University, Japan

Fabrication processes and component materials of ceramic dental crown with low risks for metallic allergies and aesthetic sensuousness for natural human teeth are investigated and developed actively in worldwide medical industries. In this investigation, the dental crown models of acrylic resins including ceramic particles were fabricated by using laser scanning stereolithography. Moreover, complete ceramic objects as biomedical components were created successfully through powder sintering processes. Graphic data obtained by computer tomography scanning were converted into file sets of cross sectional images through slicing operations. Subsequently, photo sensitive acrylic resins including alumina at 60 vol. % were spread on a substrate with 60 μm in layer thickness. An ultraviolet laser beam of 100 μm in spot size was scanned on the slurry surface to create cross sectional images. After these automatic micro stacking processes, the dental crown models were fabricated. These precursors were dewaxed at 700 °C and sintered at 1400 to 1600 °C in air atmosphere, and uniformly dense and defect free microstructures were obtained successfully. Through bending tests for plate specimens, these ceramic bodies obtained by the optimized heat treatment could exhibit enough intensities required for the single crown in present dental technologies.

11:20 AM

(ICACC-S8-057-2011) Influence of process parameters on microstructure and mechanical properties of friction stir welded aluminum-magnesium alloy

K. S. Sandhu*, Baba Farid College of Engineering and Technology, India; S. S. Chatha, H. Singh, Yadavindra College of Engineering, India

Friction Stir Welding (FSW) is an advanced manufacturing technology which is being extensively used in the joining of the structural aluminum alloys. In the present work, the influence of tool geometry, welding speed and transverse speed on the microstructure and mechanical properties of the aluminum-magnesium alloy were examined. The FSW was carried out at rotational speeds from 1200 to 1600 rpm and transverse speed of 40 to 132 mm/min with shoulder diameters of 18 to 22 mm to fabricate the joints. The mechanical properties such as tensile strength and hardness were determined. The study revealed that hardness is greater in friction stir processing (FSP) zone than base material. X-ray diffraction (XRD) scans have been used to confirm the phase transformation. The average crystallite size was determined using Scherrer relation. Optical microscopy and scanning electron microscopy (SEM) were employed to study the microstructure of welded aluminum alloy and base metal. It revealed that the grain size was refined with the stirring action.

S10: Thermal Management Materials and Technologies

Advanced Materials and Design for Thermal Management

Room: Coquina Salon F
Session Chairs: Andrew Gyekenyesi, Ohio Aerospace Institute; Mrityunjay Singh, Ohio Aerospace Institute

8:40 AM

(ICACC-S10-009-2011) Microstructural and Mechanical Characterization of Brazed Titanium-to-Graphite Foam Joints for Thermal Management Applications

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

High-conductivity graphite foams with open microcellular structure and densities in the range 126.1–870.4 kg.m-3 were vacuum brazed to titanium using a Ti-active braze, Cusil-ABA (63Ag-35.25Cu-1.75Ti). The joints were characterized for integrity, braze infiltration, chemical interaction, composition, mechanical strength, and microhardness. Low-density foams exhibited greater braze penetration than high-density foams. The carbon/braze interfaces were well-bonded and enriched in Ti suggesting titanium carbide formation at the interface. Room-temperature tension tests revealed that the fracture strength depended upon the foam type and increased with increasing foam density. Critical cracks initiated and propagated within the foam usually in the vicinity of the joint. Knoop microhardness distributions along the joined interfaces exhibited a consistent and reproducible pattern. One-dimensional, steady-state thermal analyses were conducted to predict the overall thermal resistance of the plate/joint/foam system based on foam and metal conductivities, depth of braze penetration and metal-to-foam thickness ratio.

9:00 AM

(ICACC-S10-010-2011) Tensile and Compressive Properties of Graphite Foam for Thermal Management

C. Smith*, A. Gyekenyesi, J. Bail, M. Singh, Ohio Aerospace Institute, USA

Graphite foams offer many advantages in terms of thermal management (e.g., high specific conductivity, large surface area, potential for elevated temperature applications, etc.), and there are many relevant arenas where the foams can prove to be an enabling technology. Although graphite foams are destined for thermal applications, the mechanical behavior needs to be well understood prior to system integration. In this work, mechanical test procedures were developed to obtain compressive and tensile properties. In addition, a full-field, noncontact optical strain system was utilized to assess localized strains in effort to better understand deformation and damage progression at both the local and global levels. Multiple densities of the graphite foam were tested and the results will be presented.

9:20 AM

(ICACC-S10-011-2011) Engineered Versus Natural Thermal Transfer and Thermal Management Media – Using Science to Improve Upon Nature

T. Szymanski*, J. Reid, D. Sherman, Saint-Gobain NorPro, USA

Recent years have seen the development of several industrial processes that require a ceramic media either to transfer or manage thermal energy. Silica sand is a typical choice because it is relatively common, easy to obtain and inexpensive. Despite these attributes it is often not the best option for either thermal transfer or thermal management. By comparison, engineered ceramic media can be designed to optimize specific properties such as attrition, density, particle size, sphericity and operating temperature range which can greatly improve process performance. This paper will present some typical uses for ceramic heat transfer and thermal management media. It will also compare and contrast the physical, chemical and thermal management properties of engineered various ceramic media with sand.

10:00 AM

(ICACC-S10-012-2011) Impact of Oxidation on thermal properties of heat treated 2D pitch-based and 3D PAN-based carbon-carbon composites

S. S. Iqbal*, Southern Illinois Univ, Carbondale, USA

Thermal properties of oxidized samples of two directional (2D) pitch-based carbon fiber with charred resin and three directional (3D) PAN-based carbon fiber with CVI carbon matrix C/C composite were investigated for non-heat treated (NHT) and heat treated (HTT) materials through the thickness (z-direction). Heat treatment was performed at 1800, 2100 and 2400 °C for 1-hr in inert argon atmosphere. Oxidation of NHT and HTT C/C materials was performed in oxygen plasma etcher for 120 hours. Thermal diffusivity, heat capacity and density were measured to calculate thermal conductivity. Thermal diffusivity and conductivity of 2D and 3D C/C decreased appreciably after oxidation with C/C heat treated at maximum temperature exhibiting superior thermal properties, before and after oxidation. However, overall thermal diffusivity and conductivity of 3D PAN-based C/C was superior to 2D pitch-based C/C before as well as after oxidation, which could be attributed to the presence of fibers in z-direction when compared to 2D pitch-based C/C composites. SEM images of fractured surface of 2D C/C showed the absence of z-direction fibers. Crystallographic parameters determined by XRD exhibited steady decrease in interplanar spacing (d002) and increase in lattice parameters (La, Lc) with increasing heat treatment temperature.

10:20 AM

(ICACC-S10-013-2011) Hybrid ceramic-metal tubes for steam pipes

C. Spatz*, Fraunhofer ISC, Germany; C. S. Modén, University Bayreuth, Germany; W. Krenkel, Fraunhofer ISC, Germany

In order to meet the energy demand in the future, power plants with steam temperatures up to 700°C are planned. Current austenitic steel tubes are limited in their life time due to tertiary creep. In order to use steel tubes for an extended period of time, this paper describes a technology approach to reinforce these metal tubes with outer CMC reinforcements. Two main issues in the joining steel tubes with ceramics are the design and fabrication of such hybrid constructions. Firstly, the manufacturing temperature of CMCs is much higher than the maximum allowable temperature of austenitic steel. Hence, a novel manufacturing process and a material concept is developed with re-

gard to the different material phases of the hybrid materials. Secondly, due to the mismatch of the CTE, the CMC tube must have a larger inner diameter than the outer diameter of the unloaded metal tube to prevent high tensile stress levels in the ceramic tube when the temperature is increased to 700 °C. It is important to make sure the gap is small enough giving enough support preventing creep deformation of the metal tube, thus design parameters are examined using FE modeling. The FE model utilizes temperature dependent material properties of the ceramic-metal hybrid tube, and examines the influence of gap distance on the studied material concept. Material systems and the FE results are discussed with respect to the process temperature and other specifications.

10:40 AM

(ICACC-S10-014-2011) Oxide Materials with Exceptionally Low Thermal Conductivity: Natural Superlattices and Structural Complexity

D. R. Clarke*, T. D. Sparks, Harvard University, USA

The usual engineering approach to reducing thermal conductivity is to incorporate a high concentration of porosity. While highly effective it is usually at the cost of structural integrity. Also, the approach is limited at high temperatures by radiative heat transfer. The alternative is to search for materials having intrinsically low thermal conductivities. Until recently, the materials with the lowest thermal conductivity were fused silica, non-stoichiometric uranium oxide, partially stabilized zirconias and gadolinium zirconate. In the last decade, and in the last three years in particular, oxides having exceptionally low thermal conductivity (~ 1 W/mK up to 1000oC) have been identified by systematic investigation of the characteristics of various crystal structures. Concurrently, artificial superlattice structures have been synthesized with exceptionally low thermal conductivity at low temperatures. I will describe two approaches to identifying oxides with very low thermal conductivity. The first is based on the concept of "natural superlattices", crystal structures consisting of two or more nanometer spaced blocks, which can also be stable up to high temperatures. The second is based on highly disordered or defective oxides with multiple sub-lattices. The low thermal conductivity of these compounds is not dependent on achieving a nanometer grain size.

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

Oxidation Behavior

Room: Coquina Salon H

Session Chairs: William Fahrenholtz, Missouri University of Science and Technology; Guo-Jun Zhang, Shanghai Institute of Ceramics

8:00 AM

(ICACC-S12-018-2011) Modeling Oxidation Kinetics of UHTCs (Invited)

T. Parthasarathy*, Air Force Rsearch Laboratory, USA; R. A. Rapp, The Ohio State University, USA; M. Opeka, Naval Surface Warfare Center, USA; M. K. Cinibulk, Air Force Research Laboratory, USA

Materials needs of hypersonic aircraft have resulted in significant research and advances in materials resistant to aggressive environment at very high temperatures, while a search for optimal compositions of Ultra High Temperature Ceramics (UHTC) continues. Use of these materials in an aggressive environment which is difficult to reproduce under laboratory conditions requires an understanding of the various factors that affect the kinetics of recession and oxidation product development. Towards this need, and to help predict possible compositions that might enhance the oxidation resistance further, we have developed a mechanistic model that interprets the various unique aspects of the oxidation kinetics of zirconium and hafnium diborides. We have extended our prior work on monolithic diborides of Zr and Hf, to materials that contain SiC. We show that the model is able to capture key elements of the dependencies including internal depletion of SiC underneath the external oxide scale. An overview of challenges that have been met and those that remain are presented.

8:30 AM

(ICACC-S12-019-2011) Oxidation studies of ZrB_2 and ZrB_2-SiC composites using HTXRD

P. Sarin*, P. E. Driemeyer, R. P. Haggerty, D. Kim, J. L. Bell, Z. D. Apostolov, W. M. Kriven, University of Illinois at Urbana-Champaign, USA

HTXRD (high temperature X-ray diffraction) methods provide useful information, complementary to the conventional TGA/DSC methods, when used to study the oxidation of diboride ceramics. The presence of concurrent phases, amorphous or crystalline, or simultaneous reactions, is not limiting and the oxidation of ZrB_2 phase can be followed independently. In this study oxidation of ZrB_2, and the effect of SiC in controlling the oxidation of ZrB_2 in ZrB_2-SiC composites was studied using HTXRD. Crystalline phase changes during oxidation of the diboride samples were followed quantitatively, both non-isothermally, as a function of temperature, up to ~1650 °C, as well as isothermally, as a function of time, at ~1300 °C. During the non-isothermal studies of pure ZrB_2 sample, the formation and transformation of intermediate crystalline phases of ZrO_2 were observed. Isothermal HTXRD studies confirmed that increasing the SiC content, from 30 to 50 vol% in the ZrB_2-SiC composites, markedly retarded the oxidation of ZrB_2. Moreover, the change in SiC content during isothermal oxidation of ZrB_2-SiC composites, was similar in the examined temperature range, regardless of sample microstructure and composition. A novel approach to quantify the extent of oxidation of ZrB_2 and ZrB_2-SiC composites, in-situ, by estimating the thickness of the oxidation layer, based on fractional conversion of ZrB_2 to ZrO_2, is also proposed.

8:50 AM

(ICACC-S12-020-2011) Phase Stability and Initial Oxidation at 500 °C of Ti_2AlC Thin Films (Invited)

J. Frodelius, P. Eklund*, L. Hultman, Linkoping University, Sweden

Ti_2AlC thin films deposited onto Al_2O_3 by magnetron sputtering have been annealed in vacuum and ambient air. The microstructure of the films consists of mainly basal-plane-oriented grains with a contribution of nonbasal-plane-oriented grains with an out-of-plane orientation of [103] and [106] as shown by x-ray diffraction, scanning electron microscopy, and helium ion microscopy. The surface of the basal-plane-oriented grains contains terraces with a height of a discrete number of unit cells. Terraces from different grains are combined to form valleys. In situ x-ray diffraction shows that initial decomposition temperature in vacuum occurs as low as 700 °C and decomposition is completed at 900 °C, lower than reported for bulk material. When oxidized in ambient air at 500 °C for 5 min oxide clusters of amorphous Al_2O_3 form at the valleys. The oxides are formed by out-diffusion of Al along the basal planes and migration across the surface where it gets trapped in valleys before it reacts with oxygen. X-ray photoelectron spectroscopy of a Ti_2AlC film oxidized at 500 °C for 15 min shows the presence of both Al- and Ti-oxides due to growth of the amorphous Al_2O_3 and parallel oxidation of the remaining $Ti_2Al_{1-x}C$ into TiO_2 and CO_2.

9:20 AM

(ICACC-S12-021-2011) UHTC Sol Gel Coatings to Improve the High-Temperature Oxidation Resistance of Carbon Preforms

S. Venugopal*, B. Vaidhynathan, J. Binner, Loughborough university, United Kingdom; A. Heaton, P. Brown, Defense science and research laboratories, United Kingdom

Ultra high temperature ceramic (UHTC) coatings applied to carbon fibres have been prepared by a sol-gel route, complementing work being carried out on the impregnation of C-C specimens with UHTC

powders. Sols of SiO2-C, HfO2 –C, and HfO2-B2O3 have been produced and coated onto carbon fibres. These sols have since been subjected to suitable high temperature treatments for the formation of SiC, HfC, and Hf-borocarbides etc, respectively. The density, thickness and nominal composition of the coatings produced have been analysed using X-ray micro-CT, SEM and EDX. Oxidation resistance tests have been conducted in air at high temperature. The mass change was recorded and the specimens re-analysed using the characterisation techniques outlined above. The preliminary results obtained will be presented and discussed along with the observations on the adhesion, continuity and uniformity of these coatings.

Mechanical Properties

Room: Coquina Salon H
Session Chairs: Sylvia Johnson, NASA Ames Research Center; T. Parthasarathy, UES, Inc.

10:00 AM

(ICACC-S12-022-2011) High Temperature Tensile Test Rig for High Resolution in-situ Synchrotron X-ray micro-tomography of Woven Ceramic Matrix Composites

H. Bale*, University of California, Berkeley, USA; J. Nasiatka, A. MacDowell, Lawrence Berkeley National Laboratory, USA; B. Cox, Teledyne Scientific Co. LLC, USA; R. Ritchie, University of California, Berkeley, USA

Woven ceramic matrix composites(CMC) with multi directional fiber architectures offer breakthroughs in the development of structural components for ultra-high temperature environments. Aerospace structures such as turbine engines, rockets, hypersonic flow paths, and thermal protection systems frequently experience temperatures easily exceeding 1500°C combined with severe mechanical loads. The structural intricacy of the woven CMC's, the complexity of the associated mechanical and thermal loads leads to complex damage initiation and propagation mechanisms. Damage occurs at numerous length scales and involves multiple cracking, fiber-matrix debonding and delamination. A tensile test rig for conducting in-situ tension tests in a high temperature environment exceeding 1500°C has been developed. The thermal rig operates in-situ in a synchrotron X-ray micro-tomography setup. In-situ tensile loading at higher temperatures enables the observation of damage initiation, propagation and other associated failure mechanisms in the woven CMC's at a spatial high resolution. Preliminary results from in-situ tests of the woven CMC's under the high temperature environment are presented. The advanced imaging technique will provide deeper insights into damage characterization and life time prediction of these complex class of advanced structural materials.

10:20 AM

(ICACC-S12-023-2011) Evaluation of mechanical properties of ultra-high temperature ceramics (UHTCs)

E. Zapata Solvas*, D. D. Jayaseelan, Imperial College London, United Kingdom; E. Sanchez Gonzalez, Universidad de Extremadura, Spain; H. Lin, Oak Ridge National Laboratory, USA; P. Brown, DSTL, United Kingdom; W. E. Lee, Imperial College London, United Kingdom

Ultra high temperature ceramics (UHTCs) include borides, carbides, and nitrides with melting temperatures above ~ °2700 C. UHTCs have been investigated for high temperature applications including thermal protection systems for hypersonic aerospace vehicles, high temperature electrodes, and molten metal crucibles. Recently, ZrB2 and HfB2 based ceramics have been studied because of their unique combination of low density, high melting temperature and thermal shock resistance as well as excellent mechanical and chemical stability at high temperatures. However, hypersonic vehicles require materials operating at temperatures above 2000 °C in oxidising environments and hence, improving UHTCs oxidation resistance together with high temperature mechanical properties is a major issue. Fully dense 20 vol.% SiC-reinforced with ZrB2 (ZS20) and HfB2 (HS20) with and without 2 wt.% La2O3 (ZS20La, HS20La) were fabricated by spark plasma sintering (SPS). A detailed test matrix was designed and carried out to characterize the effect of UHTC reinforcement on the microstructure, oxidation resistance, and mechanical performances (such as hardness and fracture strength) at room and elevated temperatures. Also, post-mortem microstructural analyses were carried out to understand the strengthening mechanisms of UHTC at different test conditions. These results and findings will be presented and discussed in the paper.

10:40 AM

(ICACC-S12-024-2011) Temperature and strain-rate dependent plasticity of ZrB2 composites from hardness measurements

J. Wang*, F. Giuliani, L. J. Vandeperre, Imperial College London, United Kingdom

The hardness of ZrB2 decreases from ~24 GPa at room temperature to ~13 GPa at 400 °C. As the hardness is a measure for the resistance to dislocation motion, it is conceivable the dislocation movement is an active deformation mechanism at the very high temperatures, where the use of ZrB2 is being considered. In this work, nano-indentation experiments were carried out at temperatures up to 400 °C to determine the strain-rate and temperature dependence of the hardness of ZrB2 and its composites. Cross-sections through indents where prepared by focused ion beam milling to allow TEM observations of the deformation and active slip systems. The experimental information is used to construct a constitutive law to allow extrapolation of the expected flow stresses at very high temperatures.

11:00 AM

(ICACC-S12-025-2011) Effect of Carbon Additions on the Thermal and Mechanical Properties of Hot Pressed ZrB2

G. Harrington*, G. Hilmas, W. Fahrenholtz, Missouri S&T, USA

Due to its prevalence in the processing of commercial ZrB2 powders, carbon is a major impurity that affects the densification behavior, and the resulting thermal and mechanical properties, of ZrB2. Samples consisting of as-received ZrB2 powder with up to 1 wt% carbon additions were studied. The powders were not milled with the intention of avoiding unnecessary or unaccountable contamination from typical milling media (i.e., WC or SiC). Carbon additions were in the form of amorphous carbon through the use of phenolic resin. The ZrB2 powders were coated with carbon by mixing phenolic, dissolved in acetone, and then charring the mixture at 600°C in an inert atmosphere. Hot pressing was performed at 2000°C, 2100°C, and 2200°C under 32MPa of pressure until ram travel stopped for 10 minutes to achieve near theoretical density. The effects of carbon content on the density and microstructure were investigated. In addition, thermal diffusivity and heat capacity were measured using the laser flash method and used to calculate the thermal conductivity of the ceramics. Four point bend strength, hardness, and elastic modulus were also evaluated and compared to other ZrB2 ceramics.

11:20 AM

(ICACC-S12-026-2011) Damping, High Temperature Neutron Diffraction and Rietveld Analysis of Select MAX Phases

N. J. Lane*, Drexel University, USA; S. C. Vogel, Los Alamos National Laboratory, USA; M. Radovic, Texas A & M University, USA; M. W. Barsoum, Drexel University, USA

Recent resonant ultrasound spectroscopy (RUS) results have shown that ultrasonic attenuation (damping) is greatly enhanced in some MAX phases as they are heated. The reasons for this effect are not fully understood. Herein, high temperature neutron diffraction is used to investigate the crystal structures of Ti_3SiC_2, Ti_3GeC_2, $Ti_3Si_xGe_{1-x}C2$, Ti_2GeC, Cr_2GeC, and Ti_2SC in the 100-1100 °C, temperature range. Rietveld refinement shows that in all MAX phases the A-group atoms vibrate anisotropically, with the highest amplitude, and within the basal planes. In some cases, the bond lengths derived from the Rietveld refinement demonstrate unphysical behavior

which is why we conclude that the thermal motion of these structures must follow a model that cannot be described by the harmonic anisotropic thermal motion determined through space- and time-averaged atomic positions with powder diffraction. Other models that may be invoked to explain the high-temperature mechanical damping and anharmonic thermal motion will be discussed.

11:40 AM

(ICACC-S12-027-2011) High-Temperature Testing and Characterisation of UHTC Composites

A. Paul*, J. Binner, B. Vaidhyanathan, Loughborough University, United Kingdom; A. Heaton, P. Brown, Dstl, United Kingdom

Current generation C-C and C-SiC materials are limited to service temperatures below 1800°C and materials are sought that can withstand higher temperatures. One potential materials solution for higher temperatures is carbon fibre-based composites with matrices composed of one or more ultra high temperature ceramics (UHTCs); the latter potentially protecting the carbon fibres at high temperatures whilst the former provides increased toughness and thermal shock resistance to the system as a whole. Carbon fibre-UHTC powder composites have been prepared via a slurry impregnation and pyrolysis route. Five different UHTC compositions have been used for impregnation, viz. ZrB_2, ZrB_2-20 vol% SiC, ZrB_2-20 vol% SiC-10 vol% LaB_6, HfB_2 and HfC. Their high-temperature oxidation resistance has been studied using a purpose built oxyacetylene test facility at temperatures above 2500°C for up to 6 min and also using a defocused laser ablation facility, with comparisons made between the two tests. Preliminary results have shown that hafnium based UHTC composites appear to offer the greatest resistance to ultra high temperature oxidation. The effect of UHTC powder particle size, carbon fibre orientation and the composite porosity on the oxidation behaviour have also been studied and will be presented.

S13: Advanced Ceramics and Composites for Nuclear Fusion Applications

Irradiation Effects on Advanced Ceramics and Composites I

Room: Oceanview
Session Chair: Lance Snead, Oak Ridge National Laboratory

8:00 AM

(ICACC-S13-038-2011) Irradiation Effects in Nanocrystalline SiC (Invited)

W. J. Weber*, University of Tennessee, USA; F. Gao, W. Jiang, Pacific Northwest National Laboratory, USA; Y. Zhang, Oak Ridge National Laboratory, USA

We have investigated the role of nanoscale grain structures on irradiation effects in 3C-SiC. Molecular dynamics simulations, with 10 to 20 keV Si recoils, were used to study cascade damage in nanocrystalline 3C-SiC with average grain diameters of 5 to 21 nm. The simulations indicate that local stresses near the grain boundaries strongly affect damage evolution. For grain sizes less than 12 nm, energy deposition and displacement events occur preferentially along the amorphous grain boundaries. For larger grains, the majority of defects are produced within grain interiors. The most common defects created are antisite defects, following by vacancies and interstitials, which is in contrast to single crystal SiC, where the dominate defects are Frenkel pairs. Experimentally, the response of nanocrystalline 3C-SiC films, with grain sizes of 2.0 to 3.8 nm, to 1 MeV Si ion irradiation has been studied and compared to single crystal response under identical conditions. For irradiations at room temperature and 400 K, the average grain size is observed to decrease with increasing dose as the films undergo irradiation-induced amorphization. For a grain size of 3.8 nm at room temperature, the dose for complete amorphization is slightly less than that for single crystal SiC. At 400 K, the dose for complete amorphization is much lower than that for single crystal SiC, and the rate of amorphization increases with decreasing grain size.

8:30 AM

(ICACC-S13-039-2011) Size effects in the radiation response of silicon carbide

N. Swaminathan, D. Morgan, I. Szlufarska*, University of Wisconsin - Madison, USA

There is a significant interest in knowing whether radiation resistance of nanocrystalline (nc) SiC is better than that of its coarse-grained counterpart. Two mechanisms can lead to differences in radiation responses of nc and coarse-grained materials. Firstly, the large grain boundary (GB) fractions in nc materials may alter the defect production rates and secondly, increased GB fraction can also lead to more efficient annihilation of the irradiation defects. We have performed molecular dynamics (MD) simulations of radiation cascades in nc SiC with varying grain sizes. We found that grain size does not have a significant effect on the initial (few picoseconds after cascade initiation) defect production rates. This result suggests that size effects on radiation damage may be due to long-term evolution of the point defects, as they interact with each other and with GBs. To investigate this long-term behavior of defects we extended a rate theory model to binary alloys and we used this model to predict size effects on radiation-induced amorphization. Defect production rates are derived from MD simulations while the kinetic parameters for diffusion and defect reaction rates are taken from ab initio calculations. Our model reveals a complex dependence of dose to amorphization on grain size and temperature. Results show that grain size can both enhance and reduce the dose to amorphize SiC depending on the temperature regime.

8:50 AM

(ICACC-S13-040-2011) Irradiation Response of Nanocrystalline Cubic Ceria and Zirconia

Y. Zhang*, Oak Ridge National Laboratory, USA; P. D. Edmondson, University of Tennessee, USA; S. Moll, W. Jiang, T. Varga, M. E. Bowden, Pacific Northwest National Laboratory, USA; F. Namavar, University of Nebraska Medical Center, USA; W. J. Weber, Oak Ridge National Laboratory, USA

Cubic ceria and zirconia are well known ionic conductors that are also isostructural with urania, plutonia, and thoria nuclear fuels. Understanding role of nanograined structures on radiation effects have significant implication in advanced nuclear energy systems, including nuclear fuels, immobilization and/or transmutation of radioactive actinides. Grain growth, oxygen stoichiometry and phase stability of nanostructurally-stabilized cubic zirconia and ceria are investigated under energetic Au ion bombardment at 160, 300 and 400 K to doses up to 35 displacements per atom. The grain size increases from ~8 nm with irradiation dose to a saturation value that is temperature dependent. Slower grain growth is observed in zirconia under 400 K irradiations, as compared to 160 K irradiations, indicating that thermal grain growth is not activated and irradiation-induced grain growth is the dominating mechanism. Faster grain growth in ceria is observed with increasing temperature, indicating a thermally-enhanced dynamics. While cubic structure is retained to high fluencies at all temperatures for both zirconia and ceria, oxygen reduction in the irradiated films is detected. The loss of oxygen suggests a significant increase of oxygen vacancies in nanocrystalline zirconia and ceria under ion irradiation. The oxygen deficiency may be essential in stabilizing cubic phase to larger grain sizes.

9:10 AM

(ICACC-S13-041-2011) Irradiation effects on SiC/SiC composites

A. Michaux*, C. Sauder, M. Auclair, B. Bourdiliau, CEA, France

SiC/SiC composites materials are considered as possible structural material for Gas Fast Reactor (GFR) fuel containment. Among the different studies on this material, it is necessary to get information

about mechanical behavior and especially irradiation creep at high temperature under fast neutron and high fluence operating conditions. Two irradiations have been developed and conducted in the French reactor OSIRIS up to 5 dpa. The first one called CROCUS (Characterization Rig in OSIRIS for cooking of usual specimen) allowed (i) to test the junction of SiC/SiC composites at high temperature (900°C) under fast neutron and (ii) to study different kind of composites. The second one called CEDRIC (Creep Experimental Device for Research Innovative Ceramics) has been designed to measure the in-pile deformation of a SiC/SiC minicomposite at a temperature of nearly 900°C. A reference sample without stress was irradiated in the same device. Dimensional measurements, tensile tests and SEM observations have been conducted in hot cells on samples after CROCUS and CEDRIC irradiations. These irradiations and post-irradiation examinations will be described.

9:30 AM

(ICACC-S13-042-2011) Irradiation creep of SiC during self-ion irradiation

S. Kondo*, T. Koyanagi, T. Hinoki, Kyoto University, Japan

Excellent irradiation stabilities of SiC at wide temperature range and fluence have been reported so far, where the saturatable swelling itself is not considered to limit the operating temperature of the nuclear energy systems. However, the significant internal share stress through the differential swelling will be introduced in the thick structures, such as the flow-channel-insert wall, by the tans-thickness temperature gradient. In this work, the irradiation creep in SiC which is indispensable to mitigate the internal stress was studied by ion-irradiation. High purity CVD SiC samples mechanically thinned to 50, 75, and 100 μm were firmly fixed on the uniformly-curved irradiation base and they were irradiated to 0.01-3 dpa at 280-1200°C. The initial applied stresses at the irradiated surface were 150, 225, and 300 MPa, respectively, depending on the sample thickness. Creep strains were estimated from the sample curvatures based on comparisons with the curvatures of strips irradiated under non-stressed conditions. Creep rates were strongly dependent on both the applied stress and irradiation temperature, where the general trends of larger creep rates of 10^{-6}-10^{-5} [dpa-MPa]$^{-1}$ proportionally depending on the logarithm of fluence were observed at <~1 dpa and steady creep rates of 10^{-8}-10^{-7} [dpa-MPa]$^{-1}$ were observed at >1 dpa. The highest creep compliance was observed at 800°C.

Fuel Ceramics II and Irradiation Effects II

Room: Oceanview
Session Chair: Gerald Pintsuk, Forschungszentrum Juelich

10:10 AM

(ICACC-S13-043-2011) Mechanical Properties of SiC in high temperature reactor fuel particles

H. Zhang, E. Lopez-Honorato, P. Xiao*, University of Manchester, United Kingdom

For high temperature reactors (HTR), SiC coatings, together with pyrolytic carbon coatings, have been applied to nuclear fuel particles to contain the nuclear reaction fission products during the HTR operation. The mechanical property of the SiC coating is a key factor for the safe operation of a HTR. In this study, three SiC coatings with different composition (stoichiometric, extra Si and extra C SiC) were deposited by the condition of fluidised bed CVD. Hardness and Young's modulus of the SiC coating have been measured with use of nano-indentation. The fracture toughness of SiC was measured with the Vickers indentation method. Then phase content, grain boundaries and microstructure of the SiC were examined to understand the factors causing differences in mechanical properties. Finally, mechanisms on strengthening the SiC are discussed.

10:30 AM

(ICACC-S13-044-2011) Crush Testing of SiC Hemispheres in TRISO-Coated Fuel Particles

B. Hansford, I. Reimanis*, R. Kirchhofer, B. Gorman, Colorado School of Mines, USA; D. Butt, Boise State University, USA

Significant effort has been directed at understanding the mechanical behavior of TRISO-coated fuel particles in relation to the performance and reliability of the fuel during operation. These spherical particles comprise a layered geometry of graphite, SiC, and graphite surrounding a fissile fuel kernel about 500 μm in diameter, leading to a rather complex thermo-mechanical situation which is known to evolve under irradiation. In the present work, a hemisphere of the SiC layer is extracted from each TRISO-coated particle and subsequently fractured with an instrumented crush test. The test is modeled with the finite element method to establish the influence of various geometrical parameters (for example shell sphericity and wall thickness variation) on the subsequent stress state in the SiC. TEM, EBSD and micro-Raman spectroscopy are used in conjunction with the crush tests to correlate microstructure and crack behavior. Microcracks were found to exist in the SiC at regions near large grains, and these are likely a source of fracture. A second type of controlled fracture test was performed by introducing flaws into the SiC shells with a Vickers indenter prior to crush testing. These results are discussed in the context of the utility of the hemisphere crush tests to determine microstructure-mechanical property correlations in TRISO-coated fuel particles.

10:50 AM

(ICACC-S13-045-2011) Determination of Hoop Strength for Fuel Cladding of Ceramic Composite

K. Toyoshima*, T. Hinoki, Kyoto University, Japan; F. Kano, S. Higuchi, Toshiba Corporation, Japan

High burn-up fuel is required to improve the efficiency in terms of nuclear economy and reduce spent fuel generation. As fuel is pushed to higher power density and burn-up, the traditional zirconium alloy cladding becomes increasingly embrittled, corroded, and deformed. Silicon carbide may be a replacement for zircaloy because its strength and radiation and chemical resistance may permit fuel to achieve higher burnup. Post irradiation experiment by existing test method has some issues as to notch processing or large equipment. In our research new testing methods have been developed to determine the hoop strength for fuel cladding of SiC. In this method hoop stress is applied to a tubular specimen using a polyurethane insert which expands toward radial direction by pressurization toward axial direction. The strain was measured by the strain gauges attached on the outer surface of the specimen. Crosshead displacement rate was 0.5mm/min for compression. Some metal specimens were tested to check the validity of this test method. Mean yield hoop strength of stainless steel or zircaloy was relatively the same as reported value in handbook, and small value of standard deviation (lower than 10%) proves the reliability of this testing method. In the case of SiC, hoop strength were 200MPa to 400MPa, which depend on the fiber direction. The factors which affect the strength will be discussed.

11:10 AM

(ICACC-S13-046-2011) A comparison of helium effect on swelling between CVD and LPS SiC

T. Koyanagi*, S. Kondo, T. Hinoki, Kyoto University, Japan

Helium effects on radiation swelling is one of the key issues for SiC/SiC composites as a fusion blanket component because of the high He production rate in SiC exceding ~1 at% He accumulation in their lifetime at a significant case. As to liquid phase sintered (LPS) monolithic SiC, the radiation swelling without He production has reported to be larger than that of high purity CVD SiC due primary to being of sintering additives. The knowledge of He effects on the swelling in LPS SiC has been extremely limited comparing to CVD

SiC which showed slight higher swelling rates under He production. The purpose of this study is to clarify the He effect on radiation swelling of LPS SiC by means of dual-ion irradiation. Both the CVD and LPS monolithic SiC were irradiated with Si2+ for single-irradiation case and additional He+ was simultaneously irradiated for the dual-irradiation case. Swelling was determined by step-height at irradiated/unirradiated boundary at the specimen surface using atomic force microscope. Microstructural defects in SiC were also studied by TEM. In case of 100 appmHe/dpa irradiation, both the CVD and LPS SiC showed higher swelling comparing to non-He case at 3 dpa, 600 oC. It is noted that the He effect was insignificant at 800 and 1000 oC. The magnitude of additional swelling introduced by He injection for LPS SiC were similar to that of CVD SiC.

11:30 AM

(ICACC-S13-047-2011) Radiation effect on advanced SiC/SiC composites in high temperature, high fluence conditions

Y. Katoh*, L. L. Snead, Oak Ridge National Laboratory, USA; T. Nozawa, Japan Atomic Energy Agency, Japan; K. Ozawa, Oak Ridge National Laboratory, USA; T. Hinoki, Kyoto University, Japan

SiC has been studied for fuel applications in gas cooled reactors for several decades, and for the past two decades as the base material for SiC fiber-reinforced SiC-matrix (SiC/SiC) composites, a potential high-temperature, low-activation structural material for fusion and fission power applications. Over the past decade significant progress has been made towards this goal with the development of what is now considered a nuclear grade SiC/SiC composite composed of high purity, near-stoichiometric, and dense fibers and matrix. However, these composite materials have not been demonstrated to retain such fundamental properties as strength and dimensional stability under the high-dose irradiation typical of their application. The purpose of this work is to examine the high-dose irradiation effect of the nuclear grade SiC/SiC composite. Materials have been evaluated for dimensional stability and mechanical / thermophysical properties in a range of dose up to 40 displacement per atom in the High Flux Isotope Reactor.

FS2: Computational Design, Modeling, and Simulation of Ceramics and Composites

Characterization of New Materials, Interfaces and Grain Boundaries at Atomic Scale

Room: Coquina Salon D
Session Chairs: Wai-Yim Ching, University of Missouri-Kansas City; Jingyang Wang, Institute of Metal Research

8:00 AM

(ICACC-FS2-001-2011) Atomic-scale modelling of ceramic interfaces by aberration-corrected STEM and first principles calculations (Invited)

N. Shibata*, S. Findlay, T. Mizoguchi, The University of Tokyo, Japan; K. Matsunaga, Kyoto University, Japan; T. Yamamoto, Y. Ikuhara, The University of Tokyo, Japan

Understanding the atomic-scale structures of surfaces and interfaces is essential to control the functional properties of many advanced ceramic materials. Recent advances in electron microscopy techniques such as aberration-corrected scanning transmission electron microscopy (STEM) and high-voltage electron microscopy (HVEM) have become capable of directly characterizing localized atomic structures in ceramic materials, and open the possibility for understanding the atomic-scale mechanism of surface and interface related properties in ceramic materials, in conjunction with the recent advanced theoretical calculation techniques. In the present talk, we will review our recent atomic-scale studies on alumina grain boundaries and TiO2 surface and interfaces using aberration-corrected STEM and first principles calculations. We conclude that the combination of aberration-corrected STEM with first principles calculation is a very powerful method to understand complex structures of surfaces and interfaces and hence properties of ceramic materials.

8:30 AM

(ICACC-FS2-002-2011) Grain growth in perovskite ceramics (Invited)

M. J. Hoffmann*, M. Baeurer, M. Syha, D. Weygand, P. Gumbsch, KIT, Germany

Perovskite ceramics are widely used for electronic devices. In most applications the macroscopic electrical properties depend on the microstructure and the properties of the grain boundaries. However, the functional behaviour of the grain boundaries during service and the behaviour of the grain boundaries (and the bulk) during processing cannot be manipulated independently. In order to tailor both properties, a deeper understanding of the link between the local properties at interfaces and the global microstructural evolution is needed. Strontium titanate has been used as a model material to study grain growth in perovskite materials. It was found, that normal growth behaviour deviates from the expected Arrhenius type temperature dependency in the way that at two temperatures the mobility of the grain boundaries drops with rising temperature. This anomalous behaviour is very likely linked to changes in the relative boundary energies of the ceramic. In order to understand the basic mechanisms, grain growth has also been simulated with a 3D vertex dynamics model where features of the real material such inclination dependent boundary energy and boundary mobility were considered. The combined experimental and numerical approach is used to gain a deeper understanding of the influence of local grain boundary properties on the growth behaviour of a polycrystalline material.

9:00 AM

(ICACC-FS2-003-2011) Development and application of interatomic potentials for ultra high temperature ceramics (UHTC): ZrB2 and HfB2

J. Lawson*, NASA Ames Research Center, USA; M. S. Daw, Clemson University, USA; C. W. Bauschlicher, NASA Ames Research Center, USA

Ultra high temperature ceramics (UHTC) including ZrB2 and HfB2 are characterized by high melting point, good strength, and reasonable oxidation resistance. These materials are of interest for use as sharp leading edges for hypersonic vehicles among other applications. Progress in computational modeling of UHTCs has been limited in part due to the absence of suitable interatomic potentials. We present a Tersoff style parametrization of such potentials for ZrB2 and HfB2 appropriate for atomistic simulations. Parameters are fit to data generated from ab initio calculations. The accuracy of the potentials is assessed against further ab initio data. As a first non-trivial application, molecular dynamics simulations are performed to evaluate the thermal conductivity of single crystals and the thermal resistance of high symmetry grain boundaries.

9:20 AM

(ICACC-FS2-004-2011) Wear of Nanocrystalline Ceramics by Atomistic Simulations (Invited)

I. Szlufarska*, M. Mishra, University of Wisconsin, USA; Y. Mo, Massachusetts Institute of Technology, USA

Ceramics show outstanding mechanical properties such as high strength and high hardness over a wide range of temperatures and are stable in harsh environments. However, the low fracture toughness of ceramics limits their practical utility for instance as wear-resistance coatings. There have been several reports of improving the fracture strength of ceramics by reducing the grain sizes to nanometer regime. Choosing SiC as a model ceramic, we have performed large scale molecular dynamics (MD) simulations of wear in nanocrystalline (nc) SiC to understand the toughening mechanisms in the presence of grain boundaries and the effect of grain size on plasticity in ceramics.

Dislocation plasticity, grain boundary sliding and grain boundary fracture have been identified as the deformation mechanisms active during wear in nc-SiC whereas separate simulations of wear performed on single crystal SiC show only dislocation plasticity. We have quantified the contribution of each of these mechanisms to strain relaxation inside the deformation zone as a function of grain size and the depth of cut. Sliding at the grain boundaries can be controlled by dopants. To discuss the effect of doping on grain boundary sliding and overall mechanical response of the material, we will show results of large scale MD simulations of nanoindentation of ultrananocrystalline diamond (UNCD) with varying percentage of H atoms in the grain boundary regions.

10:00 AM

(ICACC-FS2-005-2011) Simulation of friction and wear processes in carbon tribocontacts (Invited)

P. Gumbsch*, KIT, Germany; L. Pastewka, M. Moseler, Fraunhofer IWM, Germany; G. Moras, KIT, Germany

Ceramic coatings are often used as protective coatings for tribologically loaded components. Modelling friction and wear processes in such coatings is still a great challenge. It has to be chemically accurate to correctly describe bond breaking events and must yet be suitable for engineering application which requires description of macroscopic materials degradation and materials. Our aim is to demonstrate on simple model systems the usefulness of modelling approaches in this context. I will describe our first approaches towards the simulation of wear processes of diamond and diamond-like carbon (DLC) films. Ab initio methods and simpler tight binding approaches are used to assess the relative importance of certain chemical changes or reactions. These methods also form the basis for the development of empirical potentials that can accurately represent bond breaking processes. They are then used for atomistic simulations of the immediate tribocontacts. Phase transitions and structural changes in these contacts are studied and found to be important for the understanding of the polishing of diamond and the wear of DLC.

10:30 AM

(ICACC-FS2-006-2011) Theoretical XANES/ELNES spectra of Si-K, Si-L, N-K, and O-K edges of an intergranular glassy film in a prismatic model of β-Si_3N_4 (Invited)

P. Rulis*, W. Ching, University of Missouri - Kansas City, USA

Recently, a prismatic model of the intergranular glassy films (IGFs) in β-Si_3N_4 was constructed using a multi-step simulation technique and a variety of its physical properties were investigated theoretically. The model has 907 atoms of which 679 atoms are in the bulk region and 228 atoms (72 Si, 32 N, and 124 O) are in the IGF region with a width of approximately 16.4 Å. In the present model, the majority of the Si atoms in the IGF are four-fold bonded to either 4 O or 3 O and 1 N and with a few Si atoms having 'defective structures'. Most N atoms are 3-fold bonded while O is 2-fold bonded, and there are no N-N or N-O or O-O pairs. Over the years, there have been many experimental investigations on the formation and nature of the atomic scale IGF structures including TEM based ELNES measurements. We have calculated the XANES/ELNES spectra of over 100 atoms within the IGF region of the model using the super-cell OLCAO method. The calculated spectra provide a large data base for meaningful statistical analysis. The calculated Si-K, Si-$L_{2,3}$, N-K, and O-K edges of the IGF atoms are divided into different groups according to their local bonding structures and their correlations to the structure are critically analyzed. The implication of these results will be discussed.

11:00 AM

(ICACC-FS2-007-2011) Kinetic Monte Carlo Simulation of Oxygen and Cation Diffusion in Yttria-Stabilized Zirconia (Invited)

B. Good*, NASA GRC, USA

Yttria-stabilized zirconia (YSZ) is of interest to the aerospace community, notably for its application as a thermal barrier coating for turbine engine components. In such an application, diffusion of both oxygen ions and cations is of concern. Oxygen diffusion can lead to deterioration of a coated part, and often necessitates an additional anti-oxidation coating. On the other hand, the high oxygen diffusivity of YSZ makes the material of interest for use as a solid-state electrolyte in fuel cells. Cation diffusion in YSZ is much slower than oxygen diffusion. However, such diffusion is a mechanism by which creep takes place, potentially affecting the mechanical integrity of the coating. The kinetic Monte Carlo (kMC) method offers a number of advantages compared with the more widely used molecular dynamics simulation method. In particular, kMC is much more efficient for the study of processes, such as diffusion, that involve infrequent events. We describe the results of kinetic Monte Carlo computer simulations of oxygen and cation diffusion in YSZ. Using diffusive energy barriers from the literature, we present results on the temperature dependence of oxygen and cation diffusivity, and on the dependence of the diffusivity on Y concentration and oxygen and cation sublattice vacancy concentrations. We also present preliminary results of the effect on diffusivity of Y ion clustering.

11:30 AM

(ICACC-FS2-008-2011) Computer Simulation of Radiation Effects in Ceramics and Composites (Invited)

R. Devanathan*, F. Gao, X. Sun, M. Khaleel, Pacific Northwest National Laboratory, USA

Advanced ceramics and ceramic-matrix composites that are radiation tolerant are needed for advanced fusion and fission reactors, and nuclear waste immobilization. Traditionally, the study of radiation and extreme environment effects in ceramics has relied heavily on experiments. With the ongoing development in leadership-class computers, models and algorithms, sophisticated computer simulation that is validated by experiment can provide valuable insights into fundamental mechanisms governing the radiation response of ceramics. This presentation will review the results of recent simulations of radiation effects in silicon carbide, zircon, xenotime, urania and glasses, including the effects of swift heavy ion irradiation. The role of interfacial processes in ceramic-ceramic composites will also be discussed. Factors that can improve the radiation tolerance of ceramics will be highlighted.

S1: Mechanical Behavior and Performance of Ceramics & Composites

Processing-Microstructure-Properties II

Room: Coquina Salon A
Session Chairs: Bikramjit Basu, IIT Kanpur; Wataru Nakao, Yokohama National University

1:30 PM

(ICACC-S1-064-2011) Microstructure and mechanical properties of pressureless sintered and HIPed silicon nitride ceramics

V. D. Krstic*, Queen's University, Canada; A. Bellosi, F. Bucciotti, ISTEC-CNR, Institute for Science and Technology of Ceramics, Italy; Z. Krstic, Queen's University, Canada; V. Medri, ISTEC-CNR, Institute for Science and Technology of Ceramics, Italy

Monolithic silicon nitride ceramics with yttria and nanometric alumina as sintering aids were developed with the aim to improve flexural strength and fracture toughness of the sintered bodies. The level of yttria and alumina was varied from 8 to 10wt%. The pressureless sintering was carried out at 1760°C for 1 h to reach closed porosity in all samples. The pressureless sintered samples were than HIPed under nitrogen gas pressure of 180 MPa at temperatures ranging between 1760°C and 1850°C. The hot pressing time was one hour. The room temperature hardness, toughness and flexural strength reached values of up to 16 GPa, 9 MPa.m1/2 and 1150 MPa, respectively. An increase in strength of up to 30% was measured after hot isostatic pressing compared to pressureless sintered materials. The correlation between

starting compositions, thermal treatments, microstructures and mechanical properties were investigated and discussed.

1:50 PM

(ICACC-S1-065-2011) Grain Boundary Control for Si3N4 Ceramics in the REO-MgO System

Z. Nawaz, Ceradyne Inc, USA; J. J. Swab, Army Research Labs, USA; B. Mikijelj*, Ceradyne Inc, USA

Properties of several hot pressed silicon nitride materials, based on the simultaneous additions of rare earth oxides and magnesia, were correlated with their microstructure and grain boundary phase characteristics using TEM. Differences in mechanical properties and grain boundary interfacial strengths were observed depending on the rare earth species employed. Results will be compared with similar systems investigated by other groups.

2:10 PM

(ICACC-S1-066-2011) DFT Model Of The Interface Between β-Si3N4 Grains And The Intergranular Glassy Film

J. Synowczynski*, J. A. Andzelm, J. J. Swab, Army Research Laboratory, USA

Silicon nitride based ceramics are attractive candidates for high temperature structural materials due to their higher melting temperatures and superior thermal shock resistance, erosion/corrosion resistance, and hardness when compared to steels. However, to date, attempts to exploit these properties for applications involving transient high temperature chemically-reactive erosive environments have failed due to their low tensile strength, low fracture toughness, and mechanical property variability. Recent experimental work by Becher has demonstrated that Si3N4 processed with rare earth dopants can achieve tensile strengths and fracture toughness values in excess of 1 GPa and 10 MPa*m1/2 respectively. According to high resolution scanning transmission electron microscopy (HRSTEM) these dopants segregate and order along the interface between the Si3N4 grains and the amorphous SiON intergranular film (IGF). The exact mechanism by which they improve the mechanical properties is not well understood. In this study, we develop a first principles Density Functional Theory (DFT) model for the interface between β-Si3N4 grains and the intergranular glassy films. We study the effect of over 30 dopants on the stability of the Si3N4 / IGF interface and identify a correlation between interface stability and measured fracture toughness values.

2:30 PM

(ICACC-S1-067-2011) In-situ development of carbon nanotubes containing silicon nitride nanocomposites

J. González-Julián*, Institute of Ceramics and Glass (CSIC), Spain; A. Datye, The University of Tennessee, USA; K. Wu, Florida International University, USA; M. Belmonte, Institute of Ceramics and Glass (CSIC), Spain

The main challenges for developing ceramics/carbon nanotubes (CNTs) nanocomposites are associated to the dispersion of CNTs within the matrix, the densification of the composite avoiding CNTs degradation and, the improvement of the matrix/nanotube interface. In this sense, a new method based on the in-situ CNTs growth on silicon nitride (Si3N4) powders and further densification using the spark plasma sintering (SPS) technique is proposed. CNTs were grown on Si3N4 powders by CVD at 750°C using a mixture of acetylene/hydrogen/argon and a cobalt precursor (0.5-5.0 wt.%) as catalyst. Then, CNTs containing compositions were SPSed at 1585°C. A complete characterization of the as-grown CNTs and the sintered composites was performed mainly using micro-Raman spectroscopy and scanning electron microscopy. Besides, elastic modulus and hardness of the specimens were determined. In contrast to ex-situ methods, where CNTs are added to a ceramic slurry, the in-situ process led to the development of ceramic powder compositions containing up to 22 vol.% of CNTs with an excellent nanotubes distribution within the matrix, which was kept after the densification stage. Besides, dense Si3N4/CNTs nanocomposites were obtained avoiding the CNTs degradation. Moreover, the in-situ process enhanced the mechanical properties compared to ex-situ materials, which is a consequence of their stronger matrix/nanotube interlock.

2:50 PM

(ICACC-S1-068-2011) The Effect of Sintering Techniques and Grain Size on the Mechanical and Optical Properties of Multiphase Ceramics

C. Hoo*, M. L. Mecartney, UC Irvine, USA

This study investigates the effect of conventional sintering, sinter forging and field assisted sintering at temperatures ranging from 1300°C – 1500°C on the densification and optical properties of multiphase ceramics. Results of sintering a three phase alumina – mullite – spinel composite for an alumina rich, spinel rich and equal volume composite will be presented. The VIS – IR transparency of each composition will be compared to single phase transparent materials and multiphase translucent ceramics. Relevant data on contamination, microstructure, and density will be correlated with the different processing techniques. Additional data will be presented on the hardness and fracture toughness of the composites.

3:30 PM

(ICACC-S1-069-2011) Potential use of crack-healing to improve thermal shock resistance of ceramic components

W. Nakao*, Yokohama National University, Japan

Availability of self-healing on the thermal shock resistance of ceramic components was investigated. Using gas quenching method, the crack-healed alumina- 18 vol% SiC composite, which has excellent self-healing ability, was applied to thermal shock of the arbitrary quenching rate. The procedure could give rise to the thermal stress fracture at high temperature. The critical quenching rate at thermal stress fracture of the healed specimen was found to be 6.47 K/s, corresponding to the thermal stress of 452.3 MPa. Alternatively, that of the cracked specimen was found to be 5.02 K/s, corresponding to the thermal stress of 350 MPa. From the obtained results, usage of self-healing was confirmed to improve extremely thermal shock resistance. The present result suggests that usage of self-healing gives a large advantage to design the high temperature ceramic components, because the mechanically reliable design and thermal shock resistance cannot coexist due to low thermal conductivity.

3:50 PM

(ICACC-S1-070-2011) Characteristics of coarser defects, strength and weibull modulus in dry-pressed ceramics

S. Tanaka*, S. Goi, R. Furushima, K. Uematsu, Nagaoka University of Technology, Japan

Coarser processing defects originate fracture and govern the strength and its variation of engineering ceramics. The Griffith equation relates the characteristics of coarse defects to the strength only with two parameters; defect size and fracture toughness. Strength and its fluctuations of ceramics should be explained by the characteristics of coarse defects, which were developed in the fabrication processing. The objective of this study is to explain strength and their fluctuations by the characteristics of coarse defects. The number density of coarser defects is assumed to be given by the power function, f=Ac^-n as in our previous study. The number density of coarser defects increases with increasing parameter A, and the distribution of are narrowed with increasing n. The strengths and Weibull modulus are simulated in detail by the assumed power functions of coarse defects and Griffith equation. Coarse defects in alumina and silicon nitride ceramics were characterized by the optical microscopy with thinned ceramics. There were many coarse defects originated from the interstices of granules in the pressed compact. The number distribution of coarser defects could be approximated by the power function as assumed above. The simulation of strength and its distribution agreed very well with the measured strengths and Weibull modulus.

4:10 PM

(ICACC-S1-071-2011) Properties of SiC ceramics prepared using wood particle based polymer composites

B. Muthiah*, A. Ganesan, Indian Institute of Technology Madras, India; B. Prasad V.V., Defense Metallurgical Research Laboratory, India

SiC ceramics were prepared from wood particle based polymer composites by pyrolysis and reactive silicon infiltration. Wood particles of two different size fractions were homogeneously mixed with pitch, phenolic resin and pitch-phenolic resin blend separately. The respective composites were made from these mixtures by compression molding process. These composite materials were carbonized to obtain porous carbon preforms and then converted into SiC ceramics by reaction infiltration with liquid silicon. Microstructure, phase compositions, and mechanical properties of the final SiC ceramics have been studied. The phases present in these SiC ceramics are β-SiC, silicon and carbon. The size of the wood particles and type of the polymer binder control the amount of these phases in the final SiC ceramics. SiC ceramics prepared using fine wood particles and pitch has very less amount of free carbon. Because of this, the SiC ceramics derived from pitch-fine wood particle composite shows better strength than other SiC ceramics.

4:30 PM

(ICACC-S1-072-2011) Designing near-zero thermal expansion ceramic composites by using β-eucryptite

A. Pelletant*, INSA-Lyon, MATEIS CNRS UMR5510, France; L. Blanchard, Thales Alenia Space, France; J. Chevalier, G. Fantozzi, H. Reveron, INSA-Lyon, MATEIS CNRS UMR5510, France

Near zero thermal expansion ceramic composites with high mechanical properties are attractive materials for industrial applications such as space optical structures, mirrors, or electronic. Designing these composites can be achieved by associating a material having a negative coefficient of thermal expansion or CTE (β-eucryptite) with another material having high mechanical properties and positive CTE (like alumina or zirconia). These kinds of composites are here processed through a solid route and sintered naturally at low temperatures in order to keep the β-eucryptite crystal structure. The negative CTE of β-eucryprite results from two phenomena. The first phenomenon is intrinsic and corresponds to a crystal lattice contraction of around $-0.4 \times 10^{-6}\ K^{-1}$. The second is extrinsic and is more linked to micro-cracks generation due to the anisotropic thermal expansion of the crystal lattice. Both combine into a highly negative CTE material ($-7.0 \times 10^{-6}\ K^{-1}$). When β-eucryptite is included in alumina or zirconia, the compressive stresses generated by the positive CTE oxide influence its dilatometric behaviour. An adjustable CTE can therefore be achieved in these ceramic composites, allowing the design of near-zero thermal expansion ceramic composites with high mechanical properties.

4:50 PM

(ICACC-S1-073-2011) High and low-energy activations of nano-zirconia based systems

S. Kulkov*, S. Buyakova, Institute of Strength Physics and Material Sciences RAS and Tomsk State University, Russian Federation

It was shown that during mechanical activation zirconia-based nanosystem was divided into two subsystems with the average size of structural elements differing by two orders of magnitude. The fraction of the quasi-amorphous (X-ray amorphous) phase therewith increases. It was shown the ceramic was made up of linear grain chains with high bond strength at grain boundaries; in so doing, along with strictly linear elasticity the matrix exhibits micromechanical instability under deformation. In this case, the attainable strain and ultimate stress of ceramics produced from such powders greatly exceed the values for coarse-grained ceramics with similar parameters of the porous structure. It was shown that microdamage accumulation has a threshold character and after local fracture the material is deformed by the previous law. There is direct correlation between macrostresses and local (meso-) parameters of strain distribution. The regions of uniform strain accumulation alternate with the regions where strains change abruptly, which leads first to local and then to macrofracture of the entire material.

5:10 PM

(ICACC-S1-074-2011) Preceramic-polymer-bonded SiC performs for high volume fraction SiCp/Al composites

K. Sujirote*, K. Dateraksa, S. Ngernbamrung, National Metal & Materials Technology Center, Thailand; R. McCuiston, King Mongkut's University of Technology Thonburi, Thailand; J. Wannasin, T. Sungkapun, cPrince of Songkla University, Thailand

Preceramic polymer polycarbosilane (PCS) and silicon carbide (SiC) powders were used as the starting materials for the fabrication of porous SiC ceramic preforms. Since the aim of these preforms was to make SiC/Al composite with high solid loading, maximum packing density of pressed compact was designed using Dinger-Funk distribution with an exponent of 0.37. Additional in-situ SiC from an organic–inorganic transformation during heat treatment process acted as the bonding material between SiC particles. The effect of the SiC powder:PCS ratio on the porosity and flexural strength of the porous SiC ceramics were investigated. Open porosity of the preforms varied from 30 to 45%, the pore diameter was approximately 1 micron. Fracture strength of the porous SiC ceramics was in the range of 20-30 MPa. No strength degradation was observed from thermal shock test at ΔT lower than 600^{o} C. An infiltrated SiCp/Al composite exhibited tensile and flexural strength of 206 MPa and 694 MPa, respectively.

5:30 PM

(ICACC-S1-075-2011) Pultrusion of chemically bonded phosphate ceramics composites

H. A. Colorado*, T. Hahn, C. Hiel, UCLA, USA

Chemically bonded phosphate ceramic (CBPCs) composites have been reinforced with both carbon and glass fibers by the pultrusion process at Composites Support and Solutions (CS&S). Unlike conventional ceramics, CBPCs were manufactured at room temperature becoming energetically inexpensive and environmentally benign [1, 2]. The CBPCs were obtained by mixing wollastonite powder with a phosphoric acid formulation through the Resonant Acoustic Mixing (RAM). Samples were tested under thermal shock and fire environments, and under three point bending tests. The structural characterization was performed by using x-ray micro tomography (CμT) and both optical and scannnig electron microscopy. Results showed a significant improvement in the mechanical properties and a good structural stability under thermal shock. Porosity measurements are also presented. The main goal in this paper is to enhance the bending strength of the CBPCs reinforced with glass and graphite fibers by a pultrusion process.

5:50 PM

(ICACC-S1-076-2011) The Influence of Production Conditions and Resin Systems on the Mechanical Properties of Kenaf Fiber Reinforced Thermoset Composites

R. Paskaramoorthy*, University of the Witwatersrand, South Africa

This paper focuses on the mechanical properties and water absorption characteristics of kenaf fibre reinforced thermoset composites manufactured by resin transfer moulding. Varying production conditions were considered as alternatives to fibre treatments, thereby potentially avoiding additional cost and complexity in the manufacturing process. Laminates were produced by altering various parameters including fibre moisture content, mould temperature and mould pressure following injection. Tensile, flexural, impact and water absorption tests were conducted. Production conditions were found to have insignificant effect on mechanical properties except for pressurisation which increased the tensile and flexural strengths and de-

creased water absorption at low fibre fractions. Examinations using a scanning electron microscope showed that all the laminates failed by fibre pull-out. The effect of different resin systems was considered. It is found that the laminates made of kenaf fibres and vinyl ester and epoxy resins have better tensile and flexural strengths than those made of a polyester resin. In addition, impact tests and SEM studies show that epoxy composite laminates fail by fibre fracture, polyester laminates fail by fibre pull-out and vinyl ester laminates fail by a combination of the two.

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

Multifunctional and Nanostructured Coating Systems

Room: Coquina Salon G
Session Chairs: Jeffrey Eldridge, NASA Glenn Research Center; Eric Jordan, University of Connecticut

1:30 PM

(ICACC-S2-059-2011) Damping Mechanisms in High Temperature Coatings (Invited)

D. R. Clarke*, A. Limarga, A. Shanian, Harvard University, USA

High temperature coatings have been developed for a variety of applications ranging from thermal management to abrasive sealing to controlling friction. There is also the potential to develop coatings to provide vibrational damping at elevated temperatures, temperatures above which polymeric materials are stable. Coatings made of defective oxides can provide both intrinsic and extrinsic damping mechanisms, for instance, point-defect rearrangement within the crystal structure, and frictional dissipation from microcracks and splat boundaries. Data on damping in oxides from a variety of publications in the literature, our own work and finite element computations is used to compare the effectiveness of different mechanisms at different temperatures. The finite element computations also provide an opportunity to design the optimum placement of coatings to suppress different modes of vibration.

2:00 PM

(ICACC-S2-060-2011) Atomic Layer Deposition of Nanostructured Ceramic Coatings (Invited)

J. Elam*, Argonne National Laboratory, USA

Atomic layer deposition (ALD) is a thin film growth technique that uses alternating, self-limiting chemical reactions to deposit materials in an atomic layer-by-layer fashion. Although this process is already used commercially for microelectronics manufacturing, ALD promises to have a much broader impact extending far beyond microelectronics. In particular, the capability to infiltrate and coat nanoporous substrates coupled with a broad palate of available materials make ALD a versatile technique for synthesizing nanostructured materials. At Argonne we are pursuing a variety of new applications for ALD including photovoltaics, catalysis, and energy storage. A central theme in these efforts is that we use ALD to apply precise, conformal coatings onto nanostructured scaffolds to impart the desired optical, electrical, or chemical properties to advance these technologies.

2:30 PM

(ICACC-S2-061-2011) Recent Developments in the Properties and Applications of Ultra-Nanocrystalline Diamond and Tungsten Carbide/Amorphous Hydrocarbon Nanocomposite Coatings (Invited)

G. L. Doll*, The Timken Company, USA

Carbon-based hard coatings have been traditionally referred to as diamond-like carbon or DLC although their physical properties may be very different from diamond. For example, DLC has been used to describe chemical vapor deposited diamond with properties similar to natural diamond, amorphous hydrocarbon materials with properties more similar to graphite, and a range of materials in between. Chemical vapor deposited diamond can have various degrees of crystallinity: microcrystalline, nanocrystalline, and ultra-nanocrystalline, which greatly affects their properties and their usage in applications. Ultra-nanocrystalline diamond is creating some exciting new opportunities for biological micro-electromechanical systems (MEMS). When transition metals are incorporated in amorphous carbon coatings, a nanocomposite material is formed consisting of nanocrystalline metal carbide precipitates in an amorphous hydrocarbon matrix. The tribological and mechanical properties of these nanocomposites make them very attractive as wear protecting and/or friction reducing coatings for mechanical components. This presentation reviews recent developments in the properties and applications of ultra-nanocrystalline diamond and tungsten carbide/amorphous hydrocarbon nanocomposite coatings.

3:20 PM

(ICACC-S2-062-2011) SiC nanowire-toughened SiC oxidation protective coating for carbon/carbon composites

Y. Chu, Q. Fu*, H. Li, K. Li, Northwestern Polytechnical University, China

To prevent carbon/carbon (C/C) composites from oxidation, a dense SiC nanowire-toughened SiC coating was prepared on them by a two-step technique composed of chemical vapor deposition (CVD) and pack cementation. Firstly, SiC nanowires were prepared on the surface of C/C composites by the first step CVD, and then SiC coating materials were infiltrated in the holes of SiC nanowire layer by the second pack cementation to form a dense coating. The morphologies and crystalline structures of the coatings were characterized by scanning electron microscopy (SEM) and X-ray diffraction. Observation of SEM confirms a relatively random-oriented distribution of SiC nanowires in the coating, which played an important role in decreasing the size of the cracks and improving the oxidation resistance of the coating. Oxidation test shows that, the weight loss of the SiC coated C/C sample without SiC nanowires was up to 7.00 % after oxidation at 1773 K for 20 h in air, while that of C/C composites with SiC coating toughened by SiC nanowires was only 2.68% after oxidation at 1773 K for 44 h in air.

3:40 PM

(ICACC-S2-063-2011) Finite element model characterization of nano-composite thermal and environmental barrier coatings

Y. Yamada*, Ohio Aerospace Institute, USA; D. Zhu, NASA Glenn Research Center, USA

Thermal and environmental barrier coatings have been applied for protecting Si based ceramic matrix composite components from high temperature environment in advanced gas turbine engines. It has been found that the delamination and lifetime of T/EBC systems generally depend on the initiation and propagation of surface cracks induced by the axial mechanical load in addition to severe thermal loads. In order to prevent T/EBC systems from surface cracking and subsequent delamination due to mechanical and thermal stresses, T/EBC systems reinforced with nano-composite architectures have showed promise to improve mechanical properties and provide a potential crack shielding mechanism such as crack bridging. In this study, a finite element model (FEM) was established to understand the potential beneficial effects of nano-compsoites systems such as SiC nanotube-reinforced oxide T/EBC systems.

4:00 PM

(ICACC-S2-064-2011) Super Dense TiO2 Films on Glass, FTO and Silicon Substrates Made by Dip Coating

J. Prochazka*, L. Kavan, M. Zukalova, JHI, Czech Republic; A. Poruba, Solartec, Inc., Czech Republic

Efforts to make TiO2 dense coatings from sol-gel precursors on glass and other substrates have to overcome many obstacles. In fact, thin films TiO2 made by the regular sol-gel methods always show some degree of undesirable porosity, cracks, lack of mechanical parameters

such as poor adhesion to the substrate, low abrasion and scratch resistance, reduced optical transparency and low density of the film. PVD and CVD methods are usually used to achieve good mechanical parameters. The sol-gel method described in this work provides super-dense TiO2 thin films on glass, FTO, silicone and other substrates. Mechanical and other characteristics of these films are excellent, exceeding the parameters of CVD and PVD made films. The films can be prepared at the temperature as low as 350°C.

4:20 PM

(ICACC-S2-065-2011) Conductive ternary ceramic nanocomposite Ti-C-based coatings as novel electrical contact materials

P. Eklund*, L. Hultman, Linkoping University, Sweden; U. Jansson, Uppsala University, Sweden

Nanocomposite Ti-C-based conductive ceramic coatings are of interest for such applications as electrical contacts, tribological coatings, and thermal barriers. Substrates such as Cu, Ni, Al, or steel are widely used and impose an upper limit on the synthesis temperature, often as low as 200 – 300 C. Here, we present an overview of our work on sputter-deposition, structure and properties of Ti-C-based multifunctional coatings as a function of substrate temperature between RT and 300 C. The films are nanocomposites comprised of nanocrystalline TiC (nc-TiC) in an amorphous matrix of, e.g., C and/or SiC depending on the choice of composition and additional elements. Typical hardness and E-modulus are 20 GPa and 290 GPa, respectively. The electrical resistivity was measured to 70 μΩcm – 300 μΩcm and can be controlled by tuning the matrix volume percentage and any additional elements. The mechanical behavior is ductile, with significant pile-up observed around the nanoindents – in contrast to the brittle ceramic TiC. This can be explained by rotation and gliding of nc-TiC grains in the amorphous matrix. Furthermore, such nanocomposite materials can minimize problems with wear and welding while retaining low contact resistance. Consequently, this type of novel coating with appropriate mechanical properties offers a solution to problems in many electrical applications.

4:40 PM

(ICACC-S2-066-2011) Effect of Thickness on Deformability and Fracture Behavior of Ultra-thin Al2O3 Layer Coated on Ductile Material

R. T. Doloksaribu*, R. Kitazawa, Y. Kagawa, The University of Tokyo, Japan

Ultra-thin Al2O3 layer, which thickness range was from 10 to 200 nm, has been coated on ductile thin substrates e.g. Al and polyimide, by atomic layer deposition (ALD) process using Trimethylaluminum (TMA) and H2O2 as starting materials. The coated materials were tensile-tested in ambient air at room temperature under various loading rates. During the tests, direct observation on deformation and fracture behavior of the coated layer was also done. Deformability of the coated layer was evaluated from initial cracking strain/stress of the layer during tensile test. After loading up to selected stress, fracture behavior of the layer was observed by optical microscope and SEM. It is found that first detectable cracking strain of the coated film depends on both the thickness and substrate materials, respectively. Multiple transverse cracking behavior, which follows after the initial cracking, also depends on the thickness and substrate material, respectively. Transverse crack usually stops within a width direction and it does not extend through entire sections. The distance between two neighboring transverse cracks depends on the thickness of the layer. Discussions are made on the thickness dependence of deformation and fracture behavior of the ultra-thin Al2O3 layer.

5:00 PM

(ICACC-S2-067-2011) Doped ZnO TCO Electrodes by Sol-Gel Deposition

G. Grader*, G. Shter, I. Winer, Technion-Israel Institute of Technology, Israel

An important component of thin-film PV cells is a Transparent Conducting Oxide (TCO) layer, which serves as a front electrode in the device. Doped ZnO is a superb material for TCO electrodes due to its excellent transparency, good conductivity, and low-cost. The sol-gel method is an effective way to fabricate high quality thin films, while providing an economical high deposition rate. The desired stoichiometry is controlled by the salts and solvents in the starting precursor solution. The purpose of this work is to study the effect of precursor solution composition on the film quality. We investigated the influence of different chelating agents (DEA and MEA) and different solvents on film's morphology, phase orientation, grain size and pore structure. We also examined the effect of the dopant type and concentration on the film's electrical and optical properties. The films showed a granular, porous structure with grain's diameter of 10-100 nm. The thickness of the layers ranged from 100 to 600 nm. Optimal transparency and resistivity were approximately 90 percent and 0.003 ohm cm, respectively. These results are state-of the art for sol-gel deposited ZnO films. The effect of the sol's composition of the film properties will be discussed.

S3: 8th International Symposium on Solid Oxide Fuel Cells (SOFC): Materials, Science and Technology

Interconnects

Room: Coquina Salon E
Session Chairs: Jeff Stevenson, Pacific Northwest National Laboratory; Ayyakkannu Manivannan, US DOE/NETL

1:30 PM

(ICACC-S3-061-2011) CroFer 22 APU in real SOFC stacks (Invited)

Q. Fang*, M. Heinrich, C. Wunderlich, staxera GmbH, Germany

Among the potential ferritic candidates for SOFC applications, CroFer 22 APU has been proven to be one of the best materials. However, bare CroFer 22 APU is still not sufficient to fulfill the lifetime requirement of 40,000 hours at relatively high working temperature (~850°C) of ESC stacks. The lifetime of CroFer 22 APU can be extended by different protective coatings. Previous work has shown that spinel coatings such as MnCoFe (MCF) and CuNiMn (CNM) can effectively retard the Cr evaporation and increase the durability of SOFC stacks. In order to compare the protective effects of MCF and CNM coatings on CroFer 22 APU under real operating conditions, two stacks with mixed coatings were built and tested. The stacks contained both uncoated layers as well as layers with MCF and CNM coating. The protective layers were also prepared by different coating techniques. Post mortem analysis (PMA) was performed after stack testing. Bipolar plate cross sections were investigated by SEM/EDX and the Cr content within the cathodes was determined by ICP-OES, which showed that MCF coating was more effective in Cr retarding than CNM coating. The MCF coated CroFer 22 APU bipolar plates and cells from other separated stacks after long term operation (>13,000h) were also analyzed by SEM/EDX and ICP-OES. Based on the obtained results, especially the oxide growth rate, a lifetime prediction of 0,5mm CroFer 22 APU sheet under SOFC working conditions is given.

2:00 PM

(ICACC-S3-062-2011) Effect of Metallic Interconnects Thickness on Its Long-Term Performance in SOFCs

W. Liu*, X. Sun, L. Stephens, M. Khaleel, PNNL, USA

Ferritic stainless steel has attracted a great deal of attention for its use as an interconnect in SOFCs because of its gas-tightness, low electrical resistivity, ease of fabrication, and cost-effectiveness. However, oxidation reaction of the metallic interconnects in a typical SOFC working environment is unavoidable. The growth stresses in the oxide scale and on the scale/substrate interface combined with the thermal stresses induced by thermal expansion coefficient mismatch between the oxide scale and the substrate may lead to scale

delamination/buckling and eventual spallation during stack cooling, which can lead to serious cell performance degradation. Therefore, it is crucial to investigate the effect of various geometric and mechanical factors on the reliability and durability of the metallic interconnect in SOFC operating environments. As a powerful contender of ferritic interconnects used in SOFC, its interfacial reliability of the oxide scale and SS 441 substrate is very important for its application. In this paper, we applied an integrated experimental/analytical methodology to explore the effect of the SS441 thickness used as interconnect in SOFC on the stability of the oxide scale. Experimental and modeling results show that the thickness of metallic interconnects has great influence on the long-term reliability of SS441 under SOFC operating conditions.

2:20 PM

(ICACC-S3-063-2011) Characterization of Complex Interfaces in Coated Metallic Interconnects

N. Magdefrau*, E. Sun, L. Chen, Y. John, United Technologies Research Center, USA; M. Aindow, University of Connecticut, USA

Recent publications have shown differences in the effectiveness of (Mn,Co)3O4 on Crofer 22 and Haynes 230 alloys. In order to elucidate this finding, detailed interfacial characterization using FIB/TEM has been carried out. This talk will highlight the initial findings and implications that they bring in developing an effective interconnect coating for long-term SOFC applications.

2:40 PM

(ICACC-S3-064-2011) Effect of Chromium Doping on the Crystal Structure, Electrical Conductivity and Thermal Expansion of Manganese Cobalt Spinel Oxides

Y. Liu*, K. Wang, J. Fergus, Auburn University, USA

Metallic interconnects have reduced the operating temperature and cost of solid oxide fuel cells, however their oxidation during operation and chromium volatilization can cause serious problems, such as chromium poisoning and cell degradation, so ceramic coatings have been developed as barriers to chromium and oxygen diffusion. Among them, $Mn_{1.5}Co_{1.5}O_4$ spinel has shown promising performance. To evaluate the long-term stability of the coating, the properties of the reaction layer formed between the spinel coating and the Cr_2O_3 scale on the alloy surface need to be characterized. In this work, the crystal structure, electrical conductivity and thermal expansion of several spinel samples, $(Mn,Co)_{3-x}Cr_xO_4$ ($0.5 \leq x \leq 2$) were determined. The crystal structure was determined using x-ray diffraction, electrical conductivity was measured by the 4-probe DC method and thermal expansion was tested from room temperature to 1273K. With increasing Cr the cubic crystal structure was stabilized, the electrical conductivity decreased and coefficient of thermal expansion also decreased. The decrease in electrical conductivity indicates that formation of the reaction layer, $(Mn,Co)_{3-x}Cr_xO_4$, may lead to an increase in electrical resistance of the spinel coating, which will increase the overall cell resistance.

3:20 PM

(ICACC-S3-065-2011) Optimized Spray MnCoO Spinel Coating for SOFC application with Design of Experiment Method

J. Choi*, J. W. Stevenson, M. Chou, Pacific Northwest National Laboratory, USA

Generally, ferritic stainless steel, which has low cost and good matching of thermal expansion coefficient with other components, is used as interconnect materials in building SOFC stacks. However, they produce Cr-containing volatile species at the high operating temperature. A conductive spinel coating has been developed for preventing cathode poisoning from these vaporized Cr-containing species and to provide an electrical conductive layer for building stacks. It is essential that the spinel coating be sufficiently dense to block the Cr-containing species volatilization. Therefore, it is important to develop an optimized process for fabricating the coatings. This paper will summarize development of an ultrasonic spray coating method and optimization of the process using design of experiment methodology with Taguchi and ANOVA analysis. Using spray parameters obtained from the DOE optimization, dense spinel layers with about 2-micrometer thickness have been fabricated. The results of this work demonstrate the possibility of automated mass production of dense conductive spinel coated interconnect materials.

3:40 PM

(ICACC-S3-066-2011) LiF as sintering aid for Co_2MnO_4 spinel used as protecting coating on stainless steel SOFC interconnectors

A. L. Prette*, V. M. Sglavo, University of Trento, Italy

Protective coatings are often deposited on SOFC interconnectors to avoid poisoning of cathode from chromium species that evaporate from stainless steel. Co_2MnO_4 spinel compounds are usually considered as protection barriers. Such ceramic sinters only at high temperatures (>1200°C) and this can be dangerous for the properties of the stainless steel interconnector. One of the major issue is therefore the creation of a compact and impermeable coating at relatively low temperatures in order to preserve the metal substrate. In the present work, Co_2MnO_4 spinel was sintered using lithium fluoride as sintering aid in order to decrease sintering temperature and increase densification rate and final density of the coating. The analysis was carried out on pressed pellets with different amount of sintering aid. Density evolution was correlated to temperature, morphology and composition of the spinel powders. It was found that 30% LiF within Co_2MnO_4 can decrease the sintering temperature of hundreds degrees. Dilatometry analyses was used to evaluate the sintering behavior and SEM was used to evaluate the microstructure as a function of different amounts of sintering aid. The performance of the coating against Cr evaporation was also analyzed.

4:00 PM

(ICACC-S3-067-2011) Next Generation Protective coatings for SOFC Interconnects

M. M. Seabaugh*, M. G. Beachy, S. Ibanez, R. Kimbrell, M. J. Day, G. Arkenberg, NexTech Materials, Ltd., USA

As solid oxide fuel cell technology enters product commercialization, the long-term stability of SOFC cells and stacks becomes critical to the commercial success of the industry. To maintain low stack and system costs, coatings for low cost metallic interconnect materials are required. These coatings must prevent chromium volatilization and uncontrolled oxide scale development during operation. Further, they must exhibit sufficient bulk conductivity to maintain low stack area specific resistance over the life of the stack. To fully exploit the cost advantages offered by metallic interconnect designs, it is essential that coating approaches be size-scalable and allow high volume throughput at low capital cost. NexTech has systematically developed cost-effective approaches to synthesizing and depositing oxide coatings through value-conscious materials processing and deposition processes. Recently, manganese cobalt spinel and alternative oxide coating synthesis and deposition has been demonstrated using production process designed to allow high throughput production. Evaluations have included the development of cost-effective materials synthesis at 100+ kg lot size, as well as materials deposition and firing approaches for components 625 cm2 and larger, with throughput at the laboratory scale of hundreds of parts per day.

4:20 PM

(ICACC-S3-068-2011) Development of low cost protection coatings for SOFC interconnect applications

G. Xia*, X. Li, J. D. Templeton, Z. Nie, J. W. Stevenson, Pacific Northwest National Laboratory, USA

Due to their low cost, high temperature oxidation resistance, comparable thermal expansion coefficient to adjacent components of

anode-supported planer SOFC stacks, chromia-forming ferritic stainless steels, such as AISI 441, are among the most promising candidate materials for interconnect applications. However, bare alloys cannot be directly used for interconnects because the rapid growth of chromia scale will lead to high internal electrical resistance and the migration of chromium species via this scale can cause cathode poisoning and cell performance degradation. To mitigate these issues for long term SOFC operation, protection coatings on ferritic stainless steel interconnects have been developed for years at PNNL. Manganese-cobalt spinels, particularly, Mn1.5Co1.5O4, are proven to be highly effective protection coating materials. Currently, considerable efforts have been devoted to the cost reduction for materials and process via investigating alternative precursors and compositions for interconnect coatings while maintain their protection effectiveness. Recent progress in this area will be summarized in this paper.

4:40 PM

(ICACC-S3-069-2011) Effects of micro-defects on gas tightness and electrical conductivity of Ca-doped LaCr2O3 coatings

K. Baik*, T. Jeong, C. Park, Chungnam National University, Republic of Korea

Ca-doped LaCr2O3 was deposited onto a NiO-YSZ anode by atmospheric plasma spraying for SOFC interconnector. The as-sprayed Ca-doped LaCr2O3 interconnector layer contained micro-defects such as microcracks and intersplat pores that were formed by a large thermal contraction of liquid splat during cooling, and subsequently reduced the gas tightness. Controlling feedstock powder characteristics allowed the minimization of micro-defects in the sprayed coating, which led to better electrical performance and gas tightness. Subsequent heat treatment at elevated temperatures effectively eliminated the intersplat pores and transformed from layered splat structure to equiaxed grain structure. The electrical conductivity of Ca-doped LaCr2O3 interconnect coating reached up to ~50 S/cm in air environment and ~2.0 S/cm in H2 reduction environment at 800oC.

5:00 PM

(ICACC-S3-070-2011) Cathode Contact Materials

M. C. Tucker*, L. Cheng, L. C. DeJonghe, LBNL, USA

Cathode contact materials (CCM) provide electrical contact and mechanical bonding between the SOFC cathode and interconnect. Stainless steel interconnects are preferred because of their low cost. This choice limits the processing temperature for cell-to-interconnect bonding to no more than 1000C and ideally less than 900C, to avoid excessive oxidation of the stainless steel. This processing limit puts a severe restriction on choice of CCM, as many candidate materials do not sinter at this low temperature. LBNL is now focusing on selection and development of appropriate CCM compositions to enable a highly conductive, strong cell-to-interconnect interface after sintering at 1000C or below. A list of candidate materials was selected from the cathode material literature. These materials were synthesized and screened for conductivity, sintering at 900-1000C, CTE, and reaction and adhesion with other cell components. The results of this screening suggest that LSCF, LSCuF, SSC, and LSC are the most promising compositions studied. The screening process, and ASR tests incorporating these materials will be presented.

5:20 PM

(ICACC-S3-071-2011) Development of Cathode/Interconnect Contact Materials at PNNL

G. Xia*, Z. Lu, L. Shari, J. D. Templeton, Z. Nie, J. W. Stevenson, Pacific Northwest National Laboratory, USA

Cathode/interconnect contact materials play an important role on the performance of a SOFC stack and have received increasing attentions recently. There are several basic requirements for contact materials in order to obtain low, stable interfacial contact resistance. The contact materials should be electrical conductive, robust, readily forming strong bonding with, and mechanically and chemically compatible to adjacent components-cathode and interconnect (including protection coatings). In addition, low materials and processing costs must be considered. PNNL is developing optimized cathode/interconnect contact materials using a variety of approaches. Recent progress in this area will be presented.

S5: Next Generation Bioceramics

Medical and Dental Applications of Bioceramics

Room: Ponce de Leon
Session Chair: Min Wang, The University of Hong Kong

1:30 PM

(ICACC-S5-021-2011) Spark Plasma Sintering of HA-Ti composite: in Vitro biomineralization and cell culture (Invited)

A. Kumar, S. Dhara, K. Biswas, B. Basu*, Indian Institute of Technology Kanpur, India

Hydroxyapatite (HA) is widely researched for its good biocompatibility property. However, poor mechanical property limits its wider application. Therefore particulate reinforced HA-Ti composite developed to improve the mechanical property, without compromising on biocompatibility property to any significant extent. The conventional sintering of HA-Ti with longer sintering duration leads to the formation of CaTiO3, TiO2, Ti2O, β-TCP and α-TCP. In the present work Spark Plasma Sintering conditions are optimized to restrict the sintering reactions, while achieving better combination of fracture toughness (≥ 1.5 MPa.m1/2) and flexural strength (> 100 MPa). The ability of a biomaterial to bind the natural bone in vivo predicted by apatite forming ability in Simulated Body Fluid (SBF). In this context, in vitro biomineralization test has been carried out in 2x modified Kokubo's SBF on pure HA, HA-5wt%Ti, HA-10wt%Ti and HA-20wt%Ti for 1 week to 6 weeks at 37oC and at pH 7.4. Right from first week, the formation of the apatite has been noticed that continues to grow up to 6 weeks. The culture of SaOS-2 cells on HA-20 wt%Ti composites, established good cellular proliferation with filopodia extension as well as extracellular matrix formation after 72 hours.

2:00 PM

(ICACC-S5-022-2011) Microbeam X-ray grain averaged residual stress in dental ceramics (Invited)

H. Bale, University of California, USA; M. Allahkarami, Oklahoma State University, USA; N. Tamura, Advanced Light Source, USA; J. C. Hanan*, Oklahoma State University, USA

Ceramic dental restorations consist of translucent porcelain and an underlying structural ceramic core. The maximum bite loads in service (<200 MPa, molars) are much below failure stresses. In spite of low stresses, ceramic dental restorations undergo failures in their first year. Zirconia is widely accepted for cores due to toughness, compatibility, and aesthetics. Its tetragonal-to-monoclinic phase transformation produces compressive residual stresses in the vicinity of concentrated tensile stresses. For complex dental crown geometries, eliminating residual stresses is not trivial. Moreover, techniques interpreting internal stress states are lacking. Microdiffraction using highly focused monochromatic X-ray beams provides residual stress. In addition, spatially resolved phase transformation maps in zirconia have now been demonstrated. Using synchrotron and laboratory X-rays, zirconia dental crowns subjected to impact fatigue were examined. Stresses in the tetragonal phase were based on measured stress-free lattice parameters. In the neighborhood of transforming grains, tetragonal grains showed compressive residual stresses. Tensile residual stresses of 0.5 GPa in the core with monoclinic transformation were observed. This advances understanding of residual stresses and phase transformations in failure and reliability of dental restorations and related bio-ceramics.

2:20 PM

(ICACC-S5-023-2011) Bioactive Glass Scaffolds for the Repair of Load-Bearing Bones (Invited)

M. N. Rahaman*, Missouri University of Science and Technology, USA

There is a need to develop new scaffolds to repair defects in load-bearing bones, such as segmental defects in long bones, using a method that is biocompatible and durable during the patient's lifetime. Bioactive glass is an attractive material for use in filling bone defects because of its widely recognized ability to support the growth of bone cells and to bond strongly with hard and soft tissue. However, porous three-dimensional scaffolds of bioactive glass prepared by conventional methods often lack the requisite mechanical properties for repairing load-bearing bones. In this work, we investigated methods such as unidirectional freezing of suspensions and freeze extrusion fabrication for the production of silicate (13-93) bioactive glass scaffolds with the requisite mechanical properties and microstructure for potential use in the repair of load-bearing bones. The mechanical response and in vitro performance of the scaffolds, as well as the ability of the scaffolds to support tissue infiltration in vivo, will be described.

2:40 PM

(ICACC-S5-024-2011) In situ Manufacture of Ceramic Coatings: Biomimicry of Leaf Surfaces (Invited)

J. A. Nychka*, J. E. Samad, University of Alberta, Canada

The natural world has many designs for a variety of problems associated with sustaining life. One such problem exists in plants, wherein leaf surfaces can be superhydrophobic to prevent becoming waterlogged lest they rot and cease to exchange gases through their stomata. While the biomimicry of plant surfaces has been reported throughout the literature the classes of materials generally do not include oxide ceramics due to their inherent hydrophilic nature. We report on new ceramic coatings which have a range of wettability (apparent contact angles of 24 to 128°) based on their structure, which is determined by processing conditions in the thermal oxidation of metallic alloy substrates. Applications include surgical tools, medical devices, implant coatings, and anti-corrosion coatings to name a few. An important distinction from existing hydrophilic and hydrophobic coatings is their thermal stability and chemical inertness, owing to the fact that they are comprised of oxide ceramics, such as alumina.

3:30 PM

(ICACC-S5-025-2011) On the potential of chemically bonded ceramics as biomaterials (Invited)

L. A. Hermansson*, Doxa AB, Sweden

The chemically bonded ceramics (CBC), also known as inorganic cements, are based on materials of the system CaO-Al2O3-P2O5-SiO2-H2O (CAPSH) comprising hydrated phosphates, aluminates and silicates. CBCs include body temperature formed materials with high potential as biomaterials. The possibility of tailor-making materials opens up for a number of different applications. The following product areas have been identified; dental cement, endodontic products, sealants, restoratives, and pastes for augmentation and implant coatings. The presentation will focus on chemistry and structural aspects and include 1) the cement phases, 2) the particle size of the cements, 3) the hydration temperature, 4) the environment (complementary ions), 5) processing agents, 6) inert additives, 7) the volume involved, and 8) compact density and the w/c ratio. The Ca-aluminate cements and also the Ca-silicate cements exhibit some inherent properties not so often taken into account. These deal with the huge water up take capacity of the cement. Another aspect is the fact that the hydrates after precipitation appear as nano-crystals in the size interval 20-50 nm. Another aspect seldom used is the fact that the cement yields open porosity, even if the porosity level is low. The pore channel size is estimated to be 1-2 nm. The nano-size pore system can favourably be used when the cement functions as a carrier for controlled drug delivery.

3:50 PM

(ICACC-S5-026-2011) Electrically Stimulated Enhancement of Cell Proliferation on Ferroelectric-Hydroxyapatite Composites

A. K. Dubey, S. D. Gupta, B. Basu*, Indian Institute of Technology Kanpur, India

The present contribution reports the effect of pulse electric field stimulation on cell-material interaction by analyzing cellular functionality and viability. After initial experiments on control disc, Hydroxyapatite (HAp) and HAp-40wt% BaTiO3 were used as model biomaterials. The enhancement of cell proliferation on the biomaterial surface was observed within a narrow window of field intensity/frequency/time duration of electrical stimulation. The cell proliferation was increased by up to 90%, 53% and 66% on control disc, HAp and HAp-40wt% BaTiO3, respectively at the optimal field strength of 666.7 mV/cm (166.7 mV/cm for HAp) and frequency of 100Hz with respect to the non-treated sample. The optimal field strength decreases with an increase in frequency (from 50 Hz to 150 Hz) or the time duration of electrical stimulation (5 min to 10 min at each stage). The presence of a piezoelectric phase (like BaTiO3) shifts the optimal voltage towards higher values as compared to pure HAp. At lower field intensities, the energy density is quite low and increases parabolically with field strength. There is no significant increase in the temperature of the medium due to the application of short duration pulsed electric field. The obtained experimental results led us to believe that electric field with appropriate strength and duration can enhance the cell-material interaction.

4:10 PM

(ICACC-S5-027-2011) Do cell culture solutions transform brushite into octacalcium phosphate? (Invited)

I. Mert, S. Mandel, A. Tas*, Yeditepe University, Turkey

This study was designed to investigate the brushite (dicalcium phosphate dihydrate, DCPD, CaHPO4x2H2O) powders soaked in DMEM (Dulbecco's Modified Eagle Medium) solutions at 36.5C. Two different DCPD powders were synthesized. The first of these DCPD powders was prepared by stirring calcite (CaCO3) powders in a NH4H2PO4 solution from 6 to 60 minutes at room temperature. These powders were found to consist of water lily-shaped crystals. The second type of DCPD powders had the flat-plate morphology. Both powders were separately tested in DMEM-immersion experiments. Monetite (DCPA, CaHPO4) powders were also synthesized with a unique water lily morphology by heating the water lily-shaped DCPD crystals at 200C for 2h. DCPD powders were found to transform into octacalcium phosphate (OCP, Ca8(HPO4)2(PO4)4x5H2O) upon soaking in DMEM solutions at 36.5C over a period of 24 h to 1 week. DCPD powders were known to transform into apatite when immersed in SBF solutions. This study found that DMEM solutions are able to convert DCPD into OCP, instead of apatite. CaP cements with DCPD as the product phase could therefore be expected to first transform into OCP (rather than apatite) upon immersion in physiological solutions. The current study also provided a method of synthesizing OCP powders at the human body temperature.

4:30 PM

(ICACC-S5-028-2011) Aging-free dental zirconia-based ceramics

N. A. Courtois*, INSA-Lyon MATEIS UMR 5510, France; E. Apel, C. Ritzberger, Ivoclar Vivadent AG, Liechtenstein; H. Reveron, INSA-Lyon MATEIS UMR 5510, France; V. Rheinberger, Ivoclar Vivadent AG, Liechtenstein; J. Chevalier, INSA-Lyon MATEIS UMR 5510, France; W. Höland, Ivoclar Vivadent AG, Liechtenstein

Yttria-doped tetragonal zirconia (Y-TZP) is today of major interest in biomedical applications. Its combination of strength, toughness and aesthetic makes it particularly suitable for dental restoration. Nevertheless, considering that ageing issue can not be totally overcome with Y-TZP, the purpose of this study is to investigate ceria-doped zirconia (Ce-TZP) as an alternative. Ce-TZP has a perfect resistance to ageing and exhibits high toughness values but improvements in strength are

still necessary. In order to achieve this goal, a composite approach is used, by adding various second phases belonging to the spinel-type aluminate family to a Ce-TZP matrix. Composite preparation includes either conventional processing method by mixing of commercial powders or an innovative one-step co-precipitation synthesis. The calcination of various co-precipitated composites is here studied, and the sintering ability is checked. Stability versus aging is investigated by XRD after autoclaving according to ISO standard. Biaxial flexural strength and toughness are measured. Well dispersed composites with submicron grain sizes are obtained with both preparation methods,. The resistance against aging of Ce-TZP/MgAl2O4 and Ce-TZP/LaMgAl11O19 is assessed and confirmed to be much better to Y-TZP tested in the same conditions. A biaxial flexural strength of 900MPa is reached in a Ce-TZP/MgAl2O4 composite.

4:50 PM

(ICACC-S5-029-2011) Fractographic Analysis of Broken Ceramic Dental Restorations

G. Quinn*, American dental association foundation, USA; K. Hoffman, American dental association foundation, USA

This presentation will provide new fractographic analyses of several in vivo fractured ceramic crowns and bridges made with modern dental restorative materials. It is part of an ongoing study to understand the mechanisms of fracture of such restorations. Recommendations for manufacturers, laboratories and clinicians will be made.

5:10 PM

(ICACC-S5-004-2011) Improving Biocompatibility by Nanoscale modification (Invited)

F. Rosei*, INRS, Canada

Modifying the nanoscale structure/chemistry of materials allows to optimize their properties [1]. Our strategy rests on creating nanopatterns that act as surface cues [2,3] and affect cell behavior. We developed a treatment of Ti-based materials that creates a unique nanostructured topography [4], showing that chemical oxidation is a general strategy for affecting biocompatibility [5]. Our treatment promotes the growth of certain cells while inhibiting that of others, without using growth factors. Nanostructured Ti surfaces selectively inhibit fibroblast growth [4] and promote osteogenic cell activity [6] in vitro. Controlling nanoscale features and functionalizing surfaces with molecular overlayers [7] will lead to a new generation of multifunctional biomaterials that selectively influence cell behavior at the host-biomaterial interface. Further enhancement of mechano-biocompatibility may be provided by coating with spider silk [8]. Enhancement of antibacterial properties using nanoscale strategies will also be discussed. [1] F Rosei, J Phys Cond Matt 16, 1373 (2004) [2] F Variola et al, Small 5, 996 (2009) [3] F Variola et al, Biomaterials 29, 1285 (2008) [4] F. Variola et al, Adv. Eng. Mater, 11, B227 (2009) [5] F Vetrone et al, Nanolett 9, 659 (2009) [6] L Richert et al, Adv Mater 20, 1488 (2008) [7] S Clair et al, J Chem Phys 128, 144705 (2008) [8] C Brown et al, submitted

S6: International Symposium on Ceramics for Electric Energy Generation, Storage, and Distribution

Thermoelectric Materials for Energy Harvesting

Room: Coquina Salon B

Session Chairs: George Nolas, University of South Florida; Fivos Drymiotis, Clemson University

1:30 PM

(ICACC-S6-001-2011) Bottom-Up Approach for the Synthesis of Thermoelectric Materials with Nano-Scale Domains* (Invited)

G. Nolas*, A. Datta, J. Paul, A. Popescu, L. Woods, University of South Florida, USA

A bottom-up approach in synthesizing thermoelectric nanocomposites that allows for nano-scale domains is described. The approach involved composition and size controlled syntheses of thermoelectric materials as nanocrystals by solution-phase processes followed by densification into bulk pellets by Spark Plasma Sintering (SPS). Synthesis approaches were selected based on the effectiveness of yielding organics free nanocrystals in large quantity. Densification of nanocrystals by SPS contributed to the uniform distribution of nano-scale domains in the bulk matrix material that also preserved nanostructuring. Doping of the nanocrystals allowed for modifications of the bulk carrier concentrations. Electronic and thermal transport properties of the nanocomposites were evaluated and indicated enhancement in the thermoelectric properties as compared to that of bulk materials. The bottom-up strategy was investigated in the context of research into cost-effective, scalable, and reproducible materials preparation approaches towards improving the thermoelectric properties of existing materials. *This work is supported by the U.S. Army Medical Research and Materiel Command under Grant No. W81XWH-07-1-0708 and the National Science Foundation under Grant Nos. CBET-0932526 and CMMI-0927637.

2:00 PM

(ICACC-S6-002-2011) Search for enhanced thermopower in perovskites

B. Dabrowski*, Northern Illinois University, USA

Transition metal oxides with thermopower enhanced by spin and orbital degrees of freedom may possibly lead to stable materials with large figure of merit. Electron doped SrMnO3 materials on either Mn or Sr sites behave in a similar manner, resistivity and thermopower rapidly decrease due to the introduction of itinerant charges for equivalent substitution levels. Measurements at 1000K showed that instead of theoretically predicted enhancement the thermopower is decreased. The thermopower of electron doped SrTiO3 materials satisfy Hikes description, however, no additional enhancement was observed. The hole doped cobaltites exhibit limited solubility for small Rare Earths RCoO3 perovskites, which have been predicted as the most attractive compounds for enhanced thermopower. The dependence of thermopower on charge doping and temperature appears to follow the extended Heikes formulation only at low doping and below 300 K, which indicate that Co3+ and Co4+ exist in several spin states beyond that range. Among all investigated compounds the largest ZT~0.3 values were observed for 3-8% Nb substituted SrTiO3 materials at 700K. Taking into account the decreased electrical conductivity in our polycrystalline samples, the ZT values found should be considered as the lower estimates of realistic values. Supported by the U.S. DOE-BES DE-AC02-06CH11357

2:20 PM

(ICACC-S6-003-2011) LSCoO-Mn ceramics as possible material for thermoelectric energy conversion

J. Rodriguez*, L. Moreno, Universidad Nacional de Colombia, Colombia

Thermoelectric properties of polycrystalline $La_{0.75}Sr_{0.25}Co_{1-x}Mn_xO_{3-\delta}$ ($0 \le x \le 0.12$) (LSCoO-Mn) compounds have been studied. The samples were grown by citrate sol-gel method, their transport properties were studied in the temperature range between 100 and 290K as a function of temperature and the manganese content. The Seebeck coefficient (S) is positive over the measured temperature range and its magnitude increases with the manganese content up to values close to 140 μV/K. The electrical resistivity (ρ) goes from metallic to semiconducting behavior as the Mn level increases, at room temperature ρ(T) exhibit values less than 2 mΩ-cm. From S(T) and ρ(T) data the thermoelectric power factor, PF was determined. This performance parameter reach maximum values around 30 $\mu W/K^2$-cm in the temperature range between 230K and room temperature. The observed behavior in the transport properties become these ceramics potential thermoelectric materials, which could be used in thermoelectric applications.

2:40 PM

(ICACC-S6-004-2011) Titanium oxide-based materials as potential high temperature thermoelectrics

M. Backhaus-Ricoult*, Corning Incorporated, USA

Search for high performance thermoelectric oxide materials is driven by the desire of waste heat recovery in various stationary and mobile applications. Titanium oxide-based composites show potential for such high temperature applications. In the current work, impact of intrinsic defects, dopants, planar defects, porosity, grain size and second phase particles on the thermoelectric properties of the titanium oxide-based materials are systematically investigated and interpreted in terms of carrier concentration, carrier mobility and lattice thermal conductivity. Materials are prepared by solid state reaction or precursor route, naturally fired or rapidly densified under pressure (SPS). Extensive microstructure characterization at the microscopic level was conducted to determine grain size and phase distribution. Spatially resolved spectroscopy allowed to assess the local electronic structure, oxidation states and interactions of titanium, oxygen and dopants and the valence band structure. The systematic analysis provides guidelines for driving the material to a high figure of merit and is illustrated by numerous examples.

3:20 PM

(ICACC-S6-005-2011) Structure and Thermoelectric behavior of Silver-Chalcogenide Based Composites (Invited)

F. Drymiotis*, S. Lindsey, Clemson University, USA; J. Lashley, Los Alamos National Laboratory, USA; T. Drye, J. Capps, B. Ma, Y. Wang, D. Rhodes, Q. R. Zhang, K. Modic, S. Cawthorne, T. Tritt, Clemson University, USA

We will be discussing the structure, microstructure and thermoelectric behavior of stoichiometric and doped PbTe-Ag2Se and AgSbTe2-Ag2Te composites. We have observed that reacting PbTe-Ag2Se in a 1:1 molar ratio forms a two phase composite consisting of a phase that crystallizes in the fcc cubic PbSe structure and a phase that crystallizes in the Ag2Te structure. By varying the Ag concentration, we can manipulate which variant of the Ag2Te structure stabilizes at room temperature and can consequently manipulate the electrical and thermal transport behavior of the composite and hence the thermoelectric performance. In the case of AgSbTe2-Ag2Se we have found that we also obtain a 2-phase composite, consisting of a phase that crystallizes in the AgSbTe2 rocksalt structure and a phase that crystallizes in the monoclinic α-Ag2Te structure. The temperature dependence of the thermal conductivity of Cu-doped AgSbTe2-Ag2Se is similar to that of amorphous solids. Additionally, the thermal conductivity,thermopower, and electrical resistivity are able to somewhat decouple due to the novel microstructure. Electrical and thermal transport measurements on the Cu-doped AgSbTe2-Ag2Se reveal that this system is a promising high-performance bulk thermoelectric material.

3:50 PM

(ICACC-S6-006-2011) Optimization of Electronic Entropy and Entropy Transport: A Novel Approach to High ZT Materials

D. M. Gruen*, P. Bruno, M. Mendelsohn, J. Routbort, D. Singh, Argonne National Lab., USA

This paper presents a review of recent work on a novel approach to high ZT materials based on the development of nanoensembles consisting of strongly interactive components.The aim is to create materials with 30-40% conversion efficiencies that are not resource limited and are environmentally benign. They must be thermally, mechanically and electrically stable at least up to temperatures of 1000K. Assuming high temperature operation and non-interacting carriers makes it likely that the thermopower can be expressed in terms of the entropy of mixing of carriers with electronic states. In the event, the governing equation entails a term consisting of the ratio of the density of carriers to the density of electronic states. In order to maximize the thermopower, this term should be as small as possible. Formidable problems are associated with achieving this condition and these will be discussed. Approaches to measuring the electronic entropy transport across ohmic boundaries in semiconductor/metal shell structures recently synthesized by us using spark plasma processing techniques will also be discussed.

4:10 PM

(ICACC-S6-007-2011) Synthesis, Structure and Thermoelectric Behavior of Ag2Se1-xTex

J. Capps*, D. Rhodes, Q. Zhang, F. Drymiotis, T. Tritt, Clemson University, USA

The binary silver chalcogenides display interesting thermoelectric behavior. However, additional research is required in order to assess their potential as thermoelectric materials. We will be discussing the synthesis, structure and high-temperature thermoelectric behavior of Ag2Se1-xTex in an effort to understand how disorder and phase competition affect thermoelectric performance.

4:30 PM

(ICACC-S6-008-2011) Thermoelectric Characterization of Beta Gallia Rutile Intergrowths

J. J. Grover, K. J. Scott, D. Edwards*, Alfred University, USA

Beta-gallia rutile intergrowths, which possess a natural superlattice structure, are being investigated as potential thermoelectric oxides. Powders were prepared as $(Ga_{0.75}In_{0.25})_4(Ti_ySn_{1-y})_5O_{16}$, $0 \leq y \leq 0.3$ using solid-state reaction and then sintered in air at 1400 ^oC for 96 hours to form polycrystalline samples. Impedance, four-point dc electrical conductivity and Seebeck coefficient were measured in situ from room temperature to 900 ^oC in air. The conductivity of the y=0 sample ranged from 10^{-7} S/cm at 300 ^oC to 10^{-3} S/cm at 900 ^oC, and exhibited an activation energy of 1.2 eV. In general, the conductivity of the samples decreased and the high-temperature activation energy increased with increasing values of y. Samples prepared with $y > 0$ exhibited an extrinsic as well as intrinsic conduction regime. The Seebeck coefficients of the samples were negative indicating n-type conduction. The Seebeck coefficient of the $y = 0$ sample range from -899 microV/K at 550 ^oC to -633 microV/K at 1000 ^oC. Assuming that thermal conductivity is on the order of 1 W/m-K, ZT is estimated to be ~10^{-3} at 1000 ^oC, which is lower than desired for thermoelectric applications. Strategies for improving ZT in beta-gallia rutile intergrowths will be discussed

4:50 PM

(ICACC-S6-009-2011) TG-DSC-MS Investigations on Thermoelectric and Semiconductor Materials

E. Post*, NETZSCH Gerätebau GmbH, Germany; B. Fidler, NETZSCH Instruments, USA

The components of thermoelectric materials and other compound semiconductors often have a relatively high vapor pressure at elevated temperatures. This limits the application temperature and can also cause difficulties with the preparation. The classical thermoelectrics such as PbTe, Bi2Te3, Bi2Te3/Sb2S3, PbSe1-xTex etc. consist of elements with considerable vapor pressure at higher temperatures. Even if the compounds themselves are thermally stable, evaporation of components could occur during preparation or exposure to high temperatures during operation. Other chalcopyrite- or defect chalcopyrite-structured semiconductor materials such as CuGaSe2 or ZnGeP2 are promising for sandwich solar cells due to their band gap range. Impurities or stoichiometric discrepancy can have a high impact on the electrical properties and the efficiency of the energy conversion. A very powerful tool for the characterization of the thermal stability of these kinds of materials is the STA-MS-Skimmer coupling which allows simultaneous monitoring of the mass change, energetics and evolved gaseous products. Because of the special construction, even highly condensable gases such as metal vapors can be detected under normal pressure conditions up to temperatures of 2000°C. In

this paper, the design and function of the Skimmer coupling is explained and measurement examples of the above-mentioned material groups are discussed.

5:10 PM

(ICACC-S6-010-2011) Titanium matrix composites reinforced with in-situ grown CNTs

M. Guzman*, V. Proano, A. Zaretski, Florida International University, USA; A. Datye, The University of Tennessee - Knoxville, USA; K. H. Wu, Florida International University, USA; H. T. Lin, Oak Ridge National Laboratory, USA

Titanium matrix composites have been used in fighter engines and turbo fan engines for decades. The continuous need for faster speeds and higher efficiency has necessitated the development of composites with better thermal and mechanical properties. The development of Titanium – Carbon Nanotube (CNT) composites could provide sufficient improvements for implementation in the aerospace industry. Ti-CNT composites have had limited success due to agglomeration and nonuniform distribution of CNTs in the matrix which led to the formation of large micron sized Titanium Carbide (TiC) particles on the grain boundaries. In-situ formation of TiC during consolidation due to the reaction between Carbon and Titanium has the potential to enhance the mechanical properties of the composite. In-situ growth of CNTs on Titanium powder and its effect on the microstructure, mechanical and thermal properties of Titanium matrix composites fabricated by Spark Plasma Sintering (SPS) is studied in this research.

5:30 PM

(ICACC-S6-011-2011) Analysis of capacitance-voltage characteristics of ferroelectric spray deposited KNO3: PVA composite films

N. Dabra, J. S. Hundal*, Baba Farid College of engineering and Technology, India

The composite films of ferroelectric potassium nitrate (KNO3): poly (vinyl alcohol) (PVA) with different weight percentages of KNO3 have been prepared at 200°C. The capacitance voltage (C-V) characteristics of all the composite films exhibit butterfly features that supports the presence of a ferroelectric phase in the composite films. The composite films of KNO3: PVA containing equal proportions of KNO3 and PVA gave highest value of the capacitance ~ 0.21 nf at coercive field. Differential dielectric constant versus electric field curves were recorded for each composite film. The field emission scanning electron microscopy (FE-SEM) and atomic force microscopy (AFM) have been employed to study the surface morphology of the composite films.

S7: 5th International Symposium on Nanostructured Materials and Nanotechnology: Development and Applications

Synthesis, Functionalization and Processing of Nanostructured Materials I

Room: Coquina Salon C
Session Chairs: Gunnar Westin, Uppsala University; Kathy Lu, Virginia Polytechnic Institute and State University

1:30 PM

(ICACC-S7-048-2011) Raman analysis of selected willemite/olivine (CoxZn2-xSiO4, 0 ≤ x ≤ 2) nanoparticles synthesized by an epoxide-assisted sol-gel method (Invited)

L. Mduduzi Cele*, Tshwane University of Technology, South Africa

Raman spectra of selected willemite/Olivine CoxZn2-xSiO4 nanoparticles synthesized by an epoxide assisted sol-gel method are reported. Powder diffraction (XRD) and Scanning Electron Microscopy (SEM) are used as complementary analysis methods. Many technological applications require materials with large surface area and small particle size [1]. Hongtao Cui et al have shown that a clear homogeneous gels of SiO2-MO (metal ions having a formal charge of +2) can be formed at specific reaction conditions in the synthesis of doped willemite nanoparticles using an epoxide assisted sol-gel procedure [2,3]. This method is used in this work, to synthesize a series of Willemite/Olivine nanoparticles with small particle size and minimal aggregation for analysis by Raman spectroscopy. The Raman spectra of the selected solid solutions indicate a persistence of the olivine structure past the midpoint Co/Zn concentration ratio, [Co2+]:[Zn2+]=1:1 to about [Co2+]:[Zn2+]=0.75:1.25. These results are confirmed by XRD studies and are discussed in terms of the Crystal Field Stabilization Energy (CFSE) and other factors. Applications of these nanoparticles are also discussed.

2:00 PM

(ICACC-S7-049-2011) Microwave-assisted Synthesis & Characterization of Tin Oxide Coated Carbon Nanotubes

S. C. Motshekga*, S. Sinha Ray, S. Pillai, Council for Scientific and Industrial Research, South Africa; S. C. Motshekga, University of Johannesburg, South Africa

Multi-walled carbon nanotubes (MWCNTs) coated with tin oxide (SnO2) nanocomposites were synthesized by microwave irradiation method. This technique is of recent interest for its rapid volumetric heating, higher reaction rate, reducing reaction time, uniform surface decoration and smaller particle size. Detail characterization of the SnO2-decorated MWCNTs nanocomposites were performed by using transmission electron microscope, X-ray diffractometer and Raman spectroscopy. Results showed the uniform distribution of SnO2 nanoparticles on the MWCNTs surfaces'. Such observations indicate that microwave irradiation is an efficient method for the synthesis of nano-structured materials.

2:20 PM

(ICACC-S7-051-2011) Controlling of ZnO Precipitation by Polymers

M. Oner*, B. Akin, Yildiz Technical University, Turkey

Zinc oxide (ZnO) is material that has attracted intensive research effort for its unique properties and versatile applications in transparent electronics, piezoelectric devices, chemical sensors, catalysts, pigments, varistors and gas sensors. ZnO has been prepared by different methods such as laser vaporization, pyrolysis and chemical vapor deposition. But many of these methods usually require high temperature. ZnO has been prepared by wet chemistry, including precipitation from aqueous solutions of zinc salts, hydrothermal and sol-gel processes. Among these methods, the low cost and simplicity of aqueous precipitation make this approach the most attractive, for possible commercial applications. In this work, ZnO nanoparticles were produced by hydrolysis of zinc nitrate in the presence of polymers in aqueous solution. The effects of various polymers such as biodegradable, environmentally friendly polysaccharide-based polycarboxylate, carboxymethyl inulin (CMI), latex particles and vinylsulfonic acid homopolymer on morphology and crystal size distribution were studied in aqueous media. Latex is an aqueous microemulsion based on styrene-acrylic copolymer. The influence of reaction parameters such as temperature, and additive concentration on crystallinity, crystal size and morphology of the obtained product was investigated by X-ray diffraction (XRD), BET and Scanning electron microscopy (SEM) and particle sizer.

2:40 PM

(ICACC-S7-052-2011) Understanding Effect of Surface Morphology during Focused Ion Beam Guided Anodization (Invited)

K. Lu*, B. Chen, Z. Tian, Virginia Polytechnic Institute and State University, USA

Growth of porous anodic alumina on non-flat aluminum surfaces has been investigated by focused ion beam guided anodization. When

the depth of the focused ion beam patterned features is small, the anodized nanopores grow perpendicular to the aluminum surfaces; the anodized nanopores terminate and bend at the boundary of the inclined aluminum surfaces. Branching of a single nanopore into two new ones under the concave surfaces has been observed, which is different from creation of branched nanopores through anodization voltage decrease. When the depth of the focused ion beam patterned nanopores is large, anodized nanopores grow parallel to each other but not perpendicular to the aluminum surfaces.

3:30 PM

(ICACC-S7-053-2011) Microwave Assisted Synthesis and Characterization of Silver/Gold Nanoparticles Loaded Carbon nanotubes

C. E. Maepa*, S. Pillai, S. Sinha Ray, Council of Science and Industrial Research, South Africa

Microwave assisted synthesis of nanostructured materials has recently shown remarkable advantages over the conventional synthesis routes such as rapid volumetric heating, high reaction rate, reduced particle size, homogeneous and narrow size distribution of particles. In this work, we report a comparison between conventional and microwave assisted loading of silver/gold (Ag/Au) nanoparticles on the surface oxidised multi-walled carbon nanotubes (MWCNTs). Both wet impregnation and deposition precipitation methods were used as the conventional methods for the preparation of the Ag/Au-MWCNT heterostructures. The synthesized heterostructures were Characterized using high-resolution scanning and transmission electron microscopy, X-ray Diffraction, Raman, UV-Visible and Photoluminescence Spectroscopes. Results showed that microwave assisted- synthesis method produced much better distribution and property enhancement on Ag/Au-MWCNT nanocomposites when compared to the conventional methods.

3:50 PM

(ICACC-S7-054-2011) Structure and Mechanical Properties of Superhard Nanocomposite Coatings on Ti -Hf-Si-N Base

A. D. Pogrebnjak*, Sumy Institute for Surface Modification, Ukraine; V. Beresnev, Sumy State University, Ukraine; M. Kaverin, Sumy Institute for Surface Modification, Ukraine; P. Zukovski, Lublin University of Technology, Poland; F. Komarov, Belgorod State University, Russian Federation; N. Makhmudov, Samarkand Branch of Tashkent University of Information, Uzbekistan; D. Kolesnikovl, Belarus State University, Belarus; M. Il'yashenko, S. Danilchenko, V. Baidak, A. Dem'yanenko, Kharkov National University, Ukraine; P. Konarski, Lublin University of Technology, Poland

Using vacuum-arc deposition with HF discharge, superhard coatings Hf-Ti-Si-N of 1.2 to 2.7μm thickness, 46 to 62GPa hardness, and high values of elastic modulus reaching 480 to 630GPa, were fabricated. For coating deposition, we employed a composite sintered cathode Hf-Ti-Si, leaking-in N into the source chamber. We found that multiple changes of physical-chemical and mechanical properties depended essentially on potential, which was fed to a substrate, rather than pressure of Ar/N mixture fed to reaction chamber. Using RBS, EDS with SEM, XRD,SIMS, GD-MS,X-ray tensometry (α-sin2ψ-method), AFM, STM, measurements of nanohardness and cylinder-plane wear tests, we investigated structure, properties, and stress of the coatings. Grain size of nanocomposite coatings was determined using XRD and TEM, which demonstrated 6.8 to 15.6nm range. Phase composition of the coating was determined using X-ray diffraction and transmission electron diffraction and was the following nc-(Ti,N), nc-(HfSi) and α-Hf5Si4. Hf, Ti, and Si concentration varied depending on condensation (deposition) conditions.

4:10 PM

(ICACC-S7-055-2011) Inductively-Coupled Plasma Synthesis of Nanopowders for Optical Applications

C. Haines*, US Army ARDEC, USA; R. Sadangi, Rutgers University, USA; D. Martin, D. Kapoor, US Army ARDEC, USA; B. Kear, Rutgers University, USA

Nanostructured oxides represent a new class of optical materials with the potential to match the transparency of single crystals whilst exhibiting enhanced mechanical/thermal properties due to their ultrafine grain size. In order to realize such materials, high quality starting powders are essential. These powders must be small in size (< 50 nm), non-agglomerated, and free of impurities (both intrinsic and extrinsic). In this paper, we report on the synthesis of high purity, high surface area nanopowders via inductively-coupled plasma (ICP) inert gas condensation. The rapid quenching rates (>10^6K/sec) inherent in the process allow for ultrafine powders of nearly any composition, frequently *metastable* in nature due to the Gibbs-Thomson effect. We will discuss the effects of processing parameters on the particle size, degree of metastability, and purity of the powders. Initial sintering results via Field-Assisted Sintering Technology (FAST) will also be discussed.

4:30 PM

(ICACC-S7-056-2011) Easy synthesis of a nanostructured hybrid with nanoparticles and carbon nanotubes

S. Moon*, Japan Aerospace Exploration Agengcy, Japan; T. Sekino, Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University, Japan; T. Ogasawara, Japan Aerospace Exploration Agengcy, Japan

Carbon nanotubes (CNTs) have been considered for many applications because of their extraordinary physical, chemical, and mechanical properties. To extend their application even further, researchers are investigating the application of nanoparticles (NPs)—including metallic, semiconducting, and insulating nanoparticles—onto CNT surfaces to extend the range of applications to energy conversion and sensing devices. Much research has been carried out on synthesis methods, process optimization, fabrication, and functional analysis for NP–CNT hybrid materials. In previous researches, to synthesize CNT–NP nanohybrids, the CNT surfaces are usually functionalized by harsh oxidative processes, such as refluxing in HNO3. While these surface functionalizations provide the efficient anchoring of different NPs, they tend to considerably degrade the mechanical and electronic performance of the nanotubes because of the introduction of a large number of defects. Therefore, the development of a facile fabrication method to realize nanostructured hybrids having the intrinsic properties of CNTs can enhance the availability of NP–CNT systems for future devices. In this research, we focus on the development of a novel, facile fabrication method for various NP–CNT hybrid arrays. Interactions between the capping molecules on the NPs and the surface of the CNT will be discussed.

4:50 PM

(ICACC-S7-057-2011) Synthesis of Nano-Size TiB2 Powders Using Carbon Coated Precursors

R. Dudukuri, R. Koc*, J. Mawdsley, D. Carter, Southern Illinois University at Carbondale, USA

This research deals with the production and properties of titanium diboride (TiB¬2¬¬) from novel carbon coated precursors. This work provides information on using different boron sources and their effect on the resulting powders of TiB¬2. The process has two steps in which the titanium containing oxide powders were first coated with carbon by cracking of a hydrocarbon gas, propylene (C3H6) and then, mixed with boron carbide or boric acid powders in a stoichiometric ratio. These precursors were treated at temperatures in the range of 1200-1400o C for 2 h in flowing Argon atmosphere to synthesize TiB2. The process utilizes a carbothermic reduction reaction of novel carbon coated precursor that has potential of producing high-quality powders (sub-micrometer and high purity). Single phase TiB¬2 powders produced were compared with commercially available titanium diboride, obtained from boron carbide and boric acid containing carbon coated precursor. *This research was supported under Contract No: DE-AC02-06CH11357, U.S. Department of Energy and the University of Chicago Argonne, LLC, representing Argonne National Laboratory.

5:10 PM

(ICACC-S7-058-2011) ZnO nanowire asters: growth and characterization

M. Ladanov*, G. Matthews, M. Ram, A. Kumar, University of South Florida, USA

Recently, ZnO nanostructures have attracted a great deal of interest due to their optical, piezoelectric, electrical and biocompatible properties, and have been used in solar cells, nanogenerators, sensors and biosensors. ZnO nanowires have shown interesting properties in combination with biological system. Apart from their electrical and optical properties, ZnO nanostructures could be used for the mechanical reinforcement of existing biomimetic scaffolds such as collagen and/or other biodegradable polymers. Under this work, a cheap and comparatively facile hydrothermal growth method for the bulk production of ZnO nanostructures exhibiting an aster-like geometry. has been demonstrated. Based on the obtained results, the novel nanostructured ZnO nanowires could be used as reinforced material to biopolymer (collagen). We have observed that aster shape presented an increased surface area, could provide a means for enhancing the stabilization of the gels and\or polymers. With controllable growth the method allows the geometry of presented nanostructures to be tuned for maximal coupling between the two phases of composite and increased mechanical strength.

5:30 PM

(ICACC-S7-059-2011) Synthesis of Nano-sized CaB_6 using Carbon Coated Precursors

N. A. Siddiqui*, R. Koc, Southern Illinois University Carbondale, USA; J. Mawdsley, D. Carter, Argonne National Laboratory, USA

Calcium Hexaboride has been successfully synthesized at the laboratory scale using carbon coated precursors. Carbon coating is performed via pyrolysis of propylene at 550°C in a coating reactor. Various sets of precursors have been prepared where the starting materials include calcium carbonate, a source of boron which may be boric acid or boron carbide, and carbon black. An effort has been made to study the effects of various amounts of coatings on different combinations of starting materials to form the precursor material, and characterize the CaB_6 formed following the carbothermal reduction of these carbon coated powders under continuous argon flow at a maximum temperature of 1600°C with a holding time of 4 hours. XRD analysis shows that single phase CaB_6 can be successfully formed using carbon coated precursors while employing either boron carbide or boric acid as the boron source. TEM imaging and BET surface area measurements clearly indicate that carbon coated precursors provides high quality CaB_6 powders with finer particles and uniform morphology. The results and discussion provide emphasis on approaches for preparing carbon coated precursors depending on the boron source.

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

Thermal Stability

Room: Coquina Salon H

Session Chairs: Nina Lane, Drexel University; Jie Zhang, Materials Chemistry, RWTH-Aachen University

1:30 PM

(ICACC-S12-028-2011) High-temperature Phase Stability of α-Ta_4AlC_3

N. J. Lane*, Drexel University, USA; P. Eklund, J. Lu, L. Hultman, Linköping University, Sweden; M. Barsoum, Drexel University, USA

Of the experimentally identified 413 MAX materials, Ta_4AlC_3 has been shown to exist both as α-Ta_4AlC_3, with Ti_4AlN_3-like stacking sequence, and β-Ta_4AlC_3, in which the Ta_{II} and C_{II} atom positions are shifted resulting in a detwinning and loss of the normal characteristic zigzag stacking of the MAX phases. Based on the first principles studies, it has been suggested that a polymorphic phase transition is thermodynamically favorable at 1600 °C. Herein, we investigate the dependence of this phase transformation on temperature alone by heating cold-pressed α-Ta4AlC3 powders to temperatures of 1450 °C, 1550 °C, 1600 °C, and 1700 °C. The α-Ta4AlC3 samples were stable with no indications of any α-β transformation, as shown by the presence of the strong characteristic X-ray diffraction peaks of α as well as the characteristic zigzag stacking observed in transmission electron microscopy. Other factors that may affect the stability of the polymorphs including vacancies, impurities, and pressure will be discussed.

1:50 PM

(ICACC-S12-029-2011) High-Temperature Thermal Stability of Ternary Nitrides: A Comparative Diffraction Study

I. Low*, Curtin University of Technology, Australia; E. Wu, Institute of Metals Research, Chinese Academy of Science, China; W. Pang, Curtin University of Technology, Australia

The susceptibility of Ti2AlN and Ti4AlN3 to high-temperature thermal dissociation in a dynamic environment of high-vacuum has been investigated using in-situ neutron diffraction. In high vacuum, these MAX phases decomposed above 1400°C through the sublimation of Al and possibly Ti elements, forming a surface coating of TiNx ($0.5 \leq x \leq 0.75$). The kinetics of isothermal phase decomposition was modelled using the Avrami equation and the Avrami exponent (n) of isothermal decomposition of Ti2AlN and Ti4AlN3 was determined to be 0.62 and 0.18 respectively. The apparent activation energies of decomposition in both phases have also been determined and compared. The characteristics of thermal stability and phase transitions in Ti2AlN and Ti4AlN3 are compared and discussed.

2:10 PM

(ICACC-S12-030-2011) Additive Effects on the Thermal Properties of ZrB2

M. Thompson*, W. G. Fahrenholtz, G. Hilmas, Missouri University of Science and Technology, USA

Zirconium diboride (ZrB2) ceramics were densified by hot pressing with different additives. Carbon, B4C, and TiB2 were employed to form a grain boundary phase, isolated particles, and solid solutions, respectively. In previous studies, these additives have been used to remove oxygen impurities, improve strength, and/or form solid solutions. The focus of this study was to investigate the effect of these different types of additives on the thermal properties of the ceramics. Microstructural information including grain size, grain boundary compositions, and second phase distributions were characterized. Thermal conductivity was characterized as a function of temperature. Existing models including effective medium theories developed by Bruggeman and Maxwell were then utilized to understand the effects of grain boundaries, isolated particles, or solid solutions on thermal conductiivty. Electrical conductivity measurements were also used to separate the electron contribution of thermal conductivity from the phonon component, which allow for utilization of models for electron and phonon contributions such as brick layer or Bloch-Gruneisen models to further describe the effects of grain boundaries, isolated particles, or solid solutions on thermal conductivity.

2:30 PM

(ICACC-S12-031-2011) Effect of Various Additives on the Oxidation Behavior of HfB_2-SiC Based Ultra High Temperature Ceramics between 1600 and 2100 °C

C. Carney*, T. Parthasarathy, UES, Inc., USA; M. Cinnibulk, Wright Patterson Air Force Base, USA

Hafnium diboride (HfB_2) alloyed with silicon carbide (SiC) has been proposed as a material for use at ultra high temperatures in excess of

1400 °C in air. However, use temperatures of ultra high temperature ceramic (UHTCs) are expected to exceed 1800 °C and it is at these temperatures that HfB_2-SiC begins rapid oxidation. In an attempt to decrease oxidation, various additives including W, La, Ce, Nd, La, Y, Er, and Yb were mixed with HfB_2-SiC-based UHTCs in the form of carbides or borides. The oxidation resistance of these compounds was tested between 1600 and 2100 °C. Additives such as Y stabilized the tetragonal phase of the resulting hafnia (HfO_2) below temperatures observed for the binary HfB_2-SiC compound, while additives such as W promoted densification in the HfO_2 scale. All of the tested rare earth elements reacted with either one or both of the HfO_2 and the protective silica scale giving rise to complex oxidation scales. Y, Nd, La, and W have shown comparable or improved oxidation resistance near 1600 °C, while W decreased the oxidation scale thickness of the exposed samples at 1800 °C and above.

2:50 PM

(ICACC-S12-032-2011) Effect of Nb, Mo and W Additives on Densification and Oxidation Behavior of Zirconium Diboride

M. Kazemzadeh Dehdashti*, W. G. Fahrenholtz, G. E. Hilmas, Missouri University of Science and Technology, USA

The effect of metal additives on densification and oxidation behavior of pressureless sintered ZrB_2 ultra-high temperature ceramics was investigated. Nb, Mo and W were added as 4, 6 and 8 mol% individually or in combination. B_4C and/or C were also added as densification aids for either attrition milled or as-received milled ZrB2 powders. The powders were attrition milled using zirconia media to avoid adding additional metallic species into the system as contaminants. The results indicated that attrition milled ZrB_2 has improved densification behavior (>97% after sintering at 2000°C) compared with as-received milled ZrB_2 (<88% after sintering at 2150°C), with the same amount of additives, due to reduction in particle size. The amount of zirconia that entered the system due to attrition milling was measured and a sufficient amount of B_4C was added to convert it to ZrB_2 during sintering. The effects of temperature and holding time on oxidation behavior were studied by measuring mass gain and scale thickness after heating the sintered ceramics in air. Microstructures and chemistries of reaction layers were characterized using scanning electron microscopy, energy dispersive spectroscopy and X-ray diffraction.

Joining and Novel Processing

Room: Coquina Salon H
Session Chairs: Jeremy Watts, Missouri University of Science and Technology; Young-Hoon Seong, Korea Advanced Institute of Science and Technology

3:30 PM

(ICACC-S12-033-2011) Characterization of Fusion Welded ZrB_2-Based Composites

H. J. Brown-Shaklee*, J. Watts, W. G. Fahrenholtz, G. Hilmas, Missouri S&T, USA

Gas tungsten arc welding was used to produce fusion joints in ZrB_2-SiC composites. Joints ranged in quality from highly porous with interconnected macro-pores to fully dense with no visible porosity. Microstructure evaluation revealed that all joints contained a mixture of a submicron eutectic microstructure with interspersed ZrB_2 grains whose size and morphology varied with the temperature gradient in the weld. Complete melting at the top of the ZrB_2-SiC fusion zone was observed whereas only partial melting was evident below the topmost 100 μm. Strengths of butt-joints ranged from ~100 MPa for highly porous welds to >160 MPa for dense welds. The characteristic 6-H SiC Raman peak at 789.2 cm^{-1} was shifted to 793 cm^{-1} in the parent material indicating that the SiC was under compressive stress outside the fusion zone. Recrystallization of SiC to other polytypes within the heat affected and fusion zones was characterized using Raman spectroscopy.

3:50 PM

(ICACC-S12-034-2011) Joining Ultra-High Temperature Ceramics using Refractory Metal Braze Compositions

M. Di Prima*, W. Pinc, University of Arizona, USA; Z. Wing, Advanced Ceramics Manufacturing, USA; E. Corral, University of Arizona, USA

The development of next generation aerospace vehicles will require the use of novel joining methods for ultra-high temperature ceramics (UHTCs) to be used in application as thermal protection system materials. Currently, there are limited approaches to join UHTCs that result in high temperature resistance and reliable mechanical properties at the joint. Therefore, our novel approach uses spark plasma sintering in order to create highly refractory and ductile joints for UHTCs. We are using a refractory metal braze that is rich in zirconium in order to join ZrB2-SiC composites at temperatures greater than 1800 °C. Investigations into the oxidation resistance of the joint up to, 1600 °C, and preliminary mechanical properties of the joined UHTCs will be presented.

4:10 PM

(ICACC-S12-035-2011) Joining Ultra-High Temperature Ceramics Using Boron Rich Braze Materials

W. Pinc*, M. Di Prima, University of Arizona, USA; Z. Wing, Advanced Ceramics Manufacturing, USA; E. Corral, University of Arizona, USA

Novel methods for joining ultra-high temperature ceramics (UHTCs) are necessary in order to meet the extreme thermal protection requirements of next generation aerospace vehicles. However, there are limited materials and approaches that satisfy the requirement at the joint, which are refractoriness and mechanical strength that are equal to that of the UHTCs. Therefore, our novel approach focuses on processing superior high-temperature resistance joints using spark plasma sintering methods. The focus on this presentation will discuss joining ZrB_2-SiC composites at temperatures greater than 2000 °C, using a boron rich braze material. Investigations into the oxidation resistance of the joint, in air, up to, 1600 °C, and preliminary room temperature mechanical properties will be discussed.

4:30 PM

(ICACC-S12-036-2011) Application of ZrSi2 as a precursor for introducing fine SiC within ZrB2 matrix

S. Lee*, S. Song, H. Kim, KIMS, Republic of Korea

ZrB2 - SiC composites were fabricated using ZrB2, ZrSi2, B4C and C as starting materials. A mixture of SiC and ZrB2 particles finer than 400 nm in size was obtained as a result of reactions between ZrSi2, B4C and C during heating using spark plasma sintering. Dense ZrB2 containing fine SiC could be obtained as a result. Dense ZrB2 - SiC composites having 97% in relative density could be obtained after sintering at 1500oC. 4- point bending strength of ZrB2 with and without fine SiC was 460 and 600MPa after sintering at 1500oC for 30min.

4:50 PM

(ICACC-S12-037-2011) A Novel Method to Fabricate Ceramic Composites with Aligned Fiber Phases

M. Acosta*, R. W. Trice, J. P. Youngblood, Purdue University, USA

A novel ceramic composite fabrication method that affords alignment of a reinforcing high aspect ratio phase is being investigated. In this process, ceramic loaded gels are produced by adding solid phases (>50vol.%) in aqueous suspensions containing water soluble polymers (~1-7vol.%) to control the rheological behavior. During casting, cylindrical foam molds are dipped in the ceramic loaded suspension and rotated to align fibers. Parallel plate rheometry was used to characterize the effect of the polymer content and powder amount on forming. Initial studies using alumina and alumina/carbon fiber suspensions revealed that suspensions containing PVP (with molecular weights of 1,300,000gr/mol and 55,000gr/mol) as a viscosity modifier follow a Herschel-Bulkley fluid behavior with yield stresses >50Pa,

consistencies ranging between ~1Pa-s^n and 35Pa-s^n, and flow indices <1. Furthermore, suspensions showed to be thixotropic over a wide range of shear rates (<600 s^-1). Green bodies have been fabricated with up to 10 vol. % fiber loading. Future studies will involve applying the same principals of fabrication to different matrix/fiber composite systems such as alumina/alumina fiber composites and UHTCs such as ZrB2 with SiC fibers. Strength and toughness measurements will be made in the composites fabricated to understand the role of the process parameters in the final microstructure and mechanical properties.

5:10 PM

(ICACC-S12-038-2011) Densification of Metal Matrix Composites Comprised of Open-Cell Ceramic Foam Infiltrated with Refractory Metal Powder

E. J. Faierson*, K. V. Logan, Virginia Polytechnic Institute and State University-National Institute of Aerospace, USA

Tungsten has many desirable properties for high-temperature, extreme-environment applications, some of which include: high melting point (3422° C), low coefficient of thermal expansion (4.5 [|#8226#|] 10^{-6} K^{-1}), and good mechanical properties at elevated temperatures. Tungsten alloys are good candidate materials for fuel encapsulation in nuclear thermal propulsion reactors and first wall materials in fusion reactors. This study investigated the infiltration of commercially available silicon carbide and tantalum carbide open-cell foams with tungsten powder. Tantalum carbide has one of the highest melting points of known materials (3880° C). Vibration, vacuum, and isostatic pressure were utilized to infiltrate the foams with the tungsten powder. Infiltration of the foam was quantified through mass measurements and pycnometry data. The infiltrated foam was densified through vacuum sintering. Microstructural analysis was conducted on the foam prior to infiltration and on the composite after sintering.

5:30 PM

(ICACC-S12-039-2011) Thermomechanical Properties and Characterization of Heat Treated ZrB_2-SiC Composites

E. W. Neuman*, G. E. Hilmas, W. G. Faherenholtz, Missouri University of Science and Technology, USA

Mechanical properties of hot pressed, heat treated zirconium diboride – silicon carbide (ZrB_2-SiC) composites were tested at room temperature and at elevated temperatures. ZrB_2-SiC composites with 30vol% SiC as a dispersed particulate phase were hot pressed to full density at 1950°C under an applied pressure of 32MPa in a flowing argon atmosphere. The hot pressed billets were machined to ASTM standard test bars with the tensile surface polished to 1um. The test bars were heat treated at temperatures in the 1300 to 1600°C range for times up to 100 hours in an argon atmosphere. Young's modulus, Vickers' and Knoop hardness, fracture toughness (chevron notch), and four-point bend strength were measured for the as processed and heat treated samples. Four-point bend tests, and fracture toughness from room temperature to 1600°C were performed in air. A 40% increase in retained strength at 1600°C has been demonstrated for samples heat treated at 1400°C for 50 hours compared to the as processed material. X-ray diffraction was performed to identify secondary phases. Raman spectroscopy was used to characterize the residual stresses. The influence of microstructure on the mechanical properties will be discussed.

5:50 PM

(ICACC-S12-040-2011) Isothermal Oxidation of Ti_2GeC in Air

B. Anasori*, Y. Elraheb, M. W. Barsoum, Drexel university, USA

The isothermal oxidation kinetics and morphology of the oxide phases that form after oxidation in ambient air of bulk Ti_2GeC was studied in air in the 500-800°C temperature range for the first time. After an incubation time of the order of 50 h, during which the weight gain was minimal, the reaction kinetics at 700 °C became linear. The oxidation product was a single layer of a rutile-based $(Ti_{1-y}Ge_y)O_2$ solid solution with $y < 0.1$. The presence of the cracks after the incubation period is believed to have led to significantly higher oxidation rates as compared to other rutile-forming ternary carbides, such as Ti_3GeC_2. The oxidation occurred mostly by the inward diffusion of oxygen through the rutile-based layer. Pure Ge was also observed at the oxide/carbide interface.

FS1: Geopolymers and Other Inorganic Polymers

Synthesis and Processing

Room: Coquina Salon F
Session Chair: Waltraud Kriven, University of Illinois at Urbana-Champaign

1:30 PM

(ICACC-FS1-001-2011) Production of geopolymers from untreated kaolinite (Invited)

H. Rahier*, M. Esaifan, J. Wastiels, Vrije Universiteit Brussel, Belgium; F. Slaty, I. Aldabsheh, H. Khoury, University of Jordan, Jordan

The purpose of this study is to use local raw materials with a low energy impact to produce construction materials. Since some years research is going on in Jordan to produce construction materials, starting from local raw materials. Geopolymers have the benefit that they have a smaller environmental impact than concrete, but also the main raw material, for instance kaolinite, is often locally available. To minimize the production cost, the kaolinite will be used as such and thus not be dehydroxylated. The aim of this research is to -find out which local raw materials can be used -optimize the production (composition, curing) -find out how to do the production in the field -make a water reservoir for water harvesting The proposed raw materials are kaoline, bentonite, tripoli, porcelanite, diatomite, silica sand, granite, zeolitic tuff, scoria (tuff) and basalt. The reactivity of these materials was tested by measuring how fast they dissolve in NaOH solutions. With kaolinite specimens with compressive strength of 41 MPa under dry conditions and 23 MPa under wet conditions were obtained. Since the materials will be used for the construction of water ponds, the durability of these specimens was tested (dry/wet, acid attack, ASR). Also these materials exhibit good mechanical performance upon heating to 600 °C, opening a possibility for use under elevated temperatures.

2:00 PM

(ICACC-FS1-002-2011) The Effect of Addition of Pozzolanic Tuff on Geopolymers (Invited)

H. N. Khoury*, F. Slaty, I. Aldabsheh,, University of Jordan, Jordan; H. Rahier, Vrije Universiteit, Belgium; M. Esaifan, Vrije Universiteit, Belgium; J. Wastiels, Vrije Universiteit, Belgium

New geopolymerized materials are developed in Jordan using local materials and alkali solutions. The geopolymerization process is achieved by activating the raw kaolinite with alkaline sodium hydroxide solution. Silica sand is added as filler to improve the workability of the mixture. The new geopolymer was cured at temperatures under 80 °C for 24 hr. The produced geopolymers proved to be highly durable under different physical and chemical conditions. The products gave a high unconfined compressive strength values higher than 45 MPa for dry conditions. Crystalline sodium aluminum silicate phases dominated mainly by Na-zeolites are responsible for the high compressive strength. The effect of pozzolanic tuff on the physical and chemical properties of the geopolymers is investigated in this work. The results indicated that the addition of 50% pozzolanic tuff gave the maximum compressive strength after 14 days curing time under dry and wet conditions. The high strength, heat resistance, low production cost, low energy consumption, and low CO2 emissions suit the use of the geopolymers as a green construction material.

2:30 PM

(ICACC-FS1-003-2011) Bottom ash-based geopolymer materials: mechanical and environmental properties (Invited)

R. Onori, A. Polettini, R. Pomi, University of Rome "La Sapienza", Italy; J. Will, A. Hoppe, A. Boccaccini*, University of Erlangen-Nuremberg, Germany

Geopolymers, also referred to as inorganic polymers, are alumino-silicate materials having the potential of being used in a number of applications, e.g. as structural and non-structural materials, concrete products, reagents for waste and wastewater treatment, structural ceramics, fire resistant composites, etc.. Although geopolymers are traditionally produced through alkali activation of naturally occurring alumino-silicates, the results of several studies published in the last ten years have shown that industrial residues with high silicon and aluminium contents may be considered as suitable source materials for the production of inorganic polymers. The present study was aimed at assessing the feasibility of geopolymer synthesis using bottom ash from municipal waste incinerator as the source of Si- and Al- containing phases. Alkaline activation at mildly elevated temperatures was used to force a rearrangement of the alumino-silicate matrix resulting in the production of a geopolymeric material. Incinerator bottom ash was selected as a potential candidate for the process since it is known to be composed of amorphous and vitreous phases, the most abundant constituents being Ca, Si and Al minerals.

3:20 PM

(ICACC-FS1-004-2011) Microwave Processing of Geopolymers and Evolved Glass-Ceramic Composites

T. A. Gubb*, H. S. Shulman, M. L. Fall, Ceralink, Inc., USA; W. M. Kriven, University of Illinois at Urbana-Champaign, USA

An investigation into the effects of thermal treatments of geopolymers using microwave and Microwave Assist Technology™ was conducted. Historically, geopolymers have undergone conventional heat treatment to produce the glass-ceramic phase transitions. However, due to the well known benefits of microwave heating and sintering, this method is being explored as a high-efficiency alternative. Multiple geopolymer compositions (alumina-silicate, Na/K charge balanced, reinforced and unreinforced) were microwave heated to 500C and 1400C for dehydration and glass-ceramic formation respectively. Varying fiber reinforcement materials were substituted to determine an appropriate composite for direct microwave heating. Analysis and results include cost (efficiency), microstructural characterization, thermal, chemical, and mechanical properties will be presented.

3:40 PM

(ICACC-FS1-005-2011) Geopolymerization of Rice Hull Ash and Red Mud and Its Potential for Civil Infrastructure Applications

J. He*, G. Zhang, Louisiana State University, USA

This work presents the results of a study on reusing rice hull ash (RHA), a major waste from burning rice hull, and red mud (RM), an abundant alumina refinery waste produced by the Bayer process, as raw materials for the production of geopolymers. A range of parameters in the geopolymerization reaction, consisting of RHA to RM ratio, RHA with different particle size, sodium hydroxide solution to solid mixture (including RHA and RM) ratio, and variable concentrations of sodium hydroxide solution, were examined to understand the extent and degree of geopolymerization of RHA and RM and their influence on the mechanical properties of the end products – RHA&RM-based geopolymers. The process of geopolymerization was confirmed by the composition of the final products analyzed by X-ray diffraction. Also, the results of unconfined compression testing indicate that the compressive strength of RHA&RM-based geopolymers is comparable with certain Portland cements. In addition, the utilization of RHA&RM-based geopolymers also bring both environmental and economic advantages in practice. Thus, the findings suggest that these two wastes, RHA and RM, can be reused to make geopolymers that are a viable cementitious material, which can find applications in civil infrastructure constructions.

Porosity in Geopolymers

Room: Coquina Salon F

Session Chair: Tammy Metroke, Air Force Research Laboratory

4:00 PM

(ICACC-FS1-015-2011) Porosity Control of Geomaterial Foams at Low Temperature (Invited)

J. Henon, A. Alzina, J. Absi, D. Smith, S. Rossignol, S. Delair*, Gemh, France

The problem linked to carbon emissions highlighted new materials as an alternative to cement: geopolymers. At low temperature (<100°C) their manufacturing emits six times less CO2. Previous works at the laboratory were realized to synthesize and improve a geomaterial from clays, alkali silicate and alkali hydroxide. The addition of silica fume as a porogen agen involved to a final inorganic foam with a geopolymer matrix. An interesting aspect of this foam is an efficient thermal conductivity leading some isolating properties. The mechanisms involved in the formation of the porous structure are based on the competition between a dihydrogen production and a polymerization responsible of the hardening: the gas bubbles are trapped inside the material. The purpose of this study is to control the porosity, dealing with the viscosity, the polycondensation reaction, external parameters, and to establish kinetic relations. Several parameters like temperature, drying steps, sample shaping, alkali type, were tested to establish the best conditions to perform the foam porosity. All these data are necessary to investigate a model (Salome/Code-Aster software) which can identify the impact of the manufacturing process of the material on its efficient thermal conductivity. This study evidenced the possibility to perform fine porosity foam working at 45°C with a large surface exchange.

4:30 PM

(ICACC-FS1-006-2011) Geomaterial Foam as Moisture Sensor (Invited)

E. Prud'homme*, P. Michaud, GEMH-ENSCI, France; E. Joussein, GRESE, France; S. Rossignol, GEMH-ENSCI, France

Geopolymers are amorphous three-dimensional alumino-silicate binder materials which may be synthesized at slightly elevated temperature by alkaline activation of alumino-silicates. This kind of material displays insulating properties and efficient thermal behavior, which allows considering their use in building area. However, building materials are currently exposed to weathering effect such as humidity and heat variations. In this condition, a geomaterial with moisture sensor properties will be very attractive. The aim of this work deals with the preparation of macro-porous or quasi-dense geomaterials based on alkaline silicate, alkaline hydroxide, metakaolin and industrial waste. Natures of alkaline element, presence of porosity and addition of industrial waste have an impact on the moisture sensor properties of geomaterials. To compare material performances in terms of bulk and porosity, two studies have been done. In first approach, samples were kept in oven at different humidity atmosphere. Weight, shrinkage, FTIR and SEM measurements are performed in order to evaluate material behavior and especially microstructure. In order to test the material durability in water, samples are immersed numerous times in various solutions. Alteration was evaluated by titration, ICP and FTIR, which put in evidence the formation of protective gel at the surface. This behavior is very attractive and gives an opportunity to be used as a moisture sensor.

5:00 PM

(ICACC-FS1-007-2011) Inorganic Polymers to Make Porous Ceramics used for Environmental Bioremediation (Invited)

J. Schorr*, R. Helferich, S. Sengupta, MetaMateria Technologies, USA

Lightweight ceramics, bonded with inorganic polymers, having controlled open porosity are molded into simple or complex shapes for use in bioremediation cleanup and other applications. Flexibility exists in adjusting the composition of the porous ceramic. Bonding is typically through inorganic hydrogels. Parts are strong but sintering can be used to create a stronger ceramic bond. A wide range of compositions and geometries are made, with pore sizes typically ranging

from sub-micron to 250 microns or larger. High surface area makes these inorganic porous ceramics a very versatile platform for growing large colonies of biological films used for waste gas and waste water cleanup. Examples will be described. The open, hierarchal porosity provides relatively high flow of gas or water into or through the porous material with a low pressure drop, which is desirable for bioremediation applications where either aerobic or anoxic conditions exist.

5:30 PM

(ICACC-FS1-008-2011) Effect of Water Addition to Maintain Workability on Properties of Geopolymers Derived from Metakaolin or Fly Ash

T. Metroke*, J. Eichler, Universal Technology Corporation, USA; M. I. Hammons, M. V. Henley, Air Force Research Laboratory, USA

The effect of addition of approximately 1–5 wt. % water to the geopolymer paste to maintain workability during mixing on the compressive strength and structural properties of geopolymers derived from metakaolin (MK) or fly ash (FA) were determined. After curing at 90°C, compressive strength, gel composition, gel conversion, and porosity were determined as a function of water addition. The results of this study indicate that additional water results in an increase in compressive strength of approximately 17–31% for MK-based and 28–100% for FA-based geopolymers. ATR–FTIR analysis of the materials showed that the additional water resulted in an increase in the Si–O–Si bonding character in the gel formed. An increase in the width of the pore size distribution was observed by nitrogen adsorption porosimetry to include pore structures due to Si–O–Si bonding, especially for FA-based geopolymers. The results of this study suggest that the increase in strength is related to a combination of (a) the increase in Si–O–Si content gel formed via homocondensation of hydrolyzed silicate oligomers and (b) an increase in bulk water content in the gel.

FS2: Computational Design, Modeling, and Simulation of Ceramics and Composites

Prediction/Simulation of Crystal Structure and Properties

Room: Coquina Salon D

Session Chairs: Hans Seifert, Technical University of Freiberg; Brain Good, NASA GRC

1:30 PM

(ICACC-FS2-009-2011) First principles calculations of LISICON-based solid electrolytes for all-solid-state Li-ion batteries (Invited)

A. Kuwabara*, Japan Fine Ceramics Center, Japan; Y. Koyama, Kyoto University, Japan; H. Moriwake, Japan Fine Ceramics Center, Japan; K. Nobuhara, Toyota Motor Corporation, Japan; I. Tanaka, Kyoto University, Japan

A combination of high accuracy first-principles cluster expansion calculations and Monte Carlo simulations have been used to examine the structure of LISICON solid-state fast ionic conductors, Li4-2xZnxGeO4, in order to quantitatively evaluate the spatial relationship between dopants and conducting ions. Several compositions with different Li/Zn ratios were examined by systematically changing the positions of Li and Zn ions within the crystal. The plane-wave-based Projector Augmented Wave (PAW) method was used for the first-principles calculations. Based on the small difference in energies between many different configurations, including the most stable structure, for each composition, it is concluded that dopant ordering does not occur, and that the Zn ions are randomly distributed throughout the crystal. The cluster expansion method was applied to the results from first-principles calculations of Li2ZnGeO4 and Li4GeO4. Interaction parameters obtained from the cluster expansion were used in Metropolis Monte Carlo simulations of Li2ZnGeO4. At low temperatures, structures in which Li and Zn are aligned in columns were stable, corresponding to an ordered phase. As the temperature was increased, Li ions were able to exchange positions because of the increased internal energy.

2:00 PM

(ICACC-FS2-010-2011) Ab-Initio Modeling of Perovskite Solid Oxide Fuel Cell Cathodes: Surfaces, Strains, and Oxygen Reduction Kinetics (Invited)

D. Morgan*, Y. Lee, University of Wisconsin - Madison, USA; J. Rossmeisl, J. Kleis, Technical University of Denmark, Denmark

Understanding how interfaces, surfaces, and strain effects can alter defect and ionic transport properties of oxides is an area of increasing research interest in solid state ionics. Furthermore, the connection between basic defect thermokinetics and surface catalytic ability is a critical issue in development of solid oxide fuel cell (SOFC) cathodes. In this talk we demonstrate how ab-initio modeling of bulk, surfaces and strain effects can be used to predict defect chemistry and catalytic ability. We show that defect energies change dramatically from bulk values near surfaces and these changes can be understood in terms of a simple model based on defect charge and local oxidation level. We also show how strain can alter defect formation energies and integrate these results into a strain dependent thermodynamic defect model for (La,Sr)CoO3 thin films. Finally, we relate basic defect energetic to SOFC cathode catalytic ability through a simple descriptor approach.

2:30 PM

(ICACC-FS2-011-2011) First-principles predictions of crystal structures and properties of hard materials (Invited)

C. Jiang*, Central South University, China; Z. Lin, Y. Zhao, Los Alamos National Laboratory, USA

Diamond is the hardest material known to date. However, applications of diamond are limited by its poor resistance to oxidation as well as reaction with ferrous alloys. Great efforts have been made to search for hard materials with better thermal and chemical stabilities than pure diamond. Recently, two novel hard materials, diamond-like BC5 and orthorhombic Ta2N3, have been successfully synthesized under high pressure and high temperature conditions. In this work, we perform first-principles calculations based on density functional theory to predict the crystal structures and properties of those two compounds. Interestingly, for diamond-like BC5, there is only a very small energy difference between the most stable ordered configuration and the fully disordered state, suggesting that the synthesized BC5 is likely to be disordered. For Ta2N3, our random structure search, which samples the potential energy surface in an unbiased manner, discovers a tetragonal structure that is more stable than the experimentally observed orthorhombic structure under ambient conditions. Orthorhombic Ta2N3, however, remains the thermodynamically stable phase at pressures above 7.7GPa. Surprisingly, perfect orthorhombic Ta2N3 is found to be mechanically unstable due to a negative shear modulus c66. Our calculations indicate that minor oxygen impurity plays a key role in stabilizing the orthorhombic Ta2N3 lattice.

3:10 PM

(ICACC-FS2-012-2011) Understanding defect chemistry through first-principles calculations and thermodynamic modeling (Invited)

Z. K. Liu*, Pennsylvania State University, USA

This presentation will provide an overview of our efforts in developing computational approaches for understanding and modeling defects in complex oxides through first-principles calculations based on the density functional theory (DFT) and thermodynamic modeling based on the CALPHAD method [1]. DFT based first-principles calculations require only knowledge of the atomic species and crystal structure to define the energetics of a structure, and hence are predictive in nature. The effects of temperature and pressure on electronic structures and total energy can be efficiently taken into account by phonon density of states and electron density of states. We recently

developed a mixed-space approach to first-principles calculations of phonon frequencies for polar materials [2]. The CALPHAD method is for modeling thermodynamic properties of multicomponent systems by integrating experimental phase equilibrium and thermochemical data. It begins with the development of models and the evaluation of parameters of unary and binary systems, followed by ternary and multi-component systems. The combination of first-principles calculations and CALPHAD modeling enables us to treat multiple defects with high concentrations in complex oxides.

3:40 PM

(ICACC-FS2-013-2011) Glasses with temperature and/or pressure independent elastic moduli (Invited)

L. Huang*, F. Yuan, Rensselaer Polytechnic Institute, USA

Based on a charge-transfer three-body potential, our molecular dynamics simulations showed that "intermediate" glasses with temperature and/or pressure independent elastic moduli can be obtained through either chemical modifications or pressure-quenching. By preparing glass using pressure-quenching routes, we can tune its structure and properties in a controllable way. With increasing of quenching pressure, the thermo-mechanical anomalies of silica rich glasses gradually diminish and eventually disappear. By controlling the pressure under which the initial glass was quenched, we can obtain silica glass with zero pressure/temperature dependent mechanical properties. Such glass shows very interesting behaviors in contact mechanics. Pressure quenched glasses have permanently "densified" characteristics, with density, elastic moduli and hardness increase dramatically, and behave opposite to the normally processed glasses under thermal and mechanical probes.

4:00 PM

(ICACC-FS2-014-2011) Elastic and mechanical properties of doped Hydroxyapatite (HAP)Crystals

S. Aryal*, W. Ching, UMKC, USA; K. Matsunaga, Kyoto University, Japan

Hydroxyapatite (HAP) is an important bioceramic which constitutes the mineral components of bones and hard tissues in mammals.It is bioactive and is used as bioceramic coatings and bone fillers. HAP readily absorbs impurities so stoichiometric HAP is not common. The change in the mechanical properties of impurity-doped HAP is a subject of considerable importance. Using ab initio method we have calculated the elastic and bulk properties of stoichiometric HAP with one impurity ion (Ba, Cd, Cu, Mg, Ni, Sr, and Zn) in the 2x2x2 hexagonal supercell of 384 atoms at either the Ca-1 or Ca-2 site, and also a model with one vacancy at the Ca-1 site. In general, substitution at the Ca-2 site increases the mechanical strength especially the shear and Young's modulus. For the vacancy model, the bulk modulus, the shear modulus and the Young's modules increased by 0.56%, 0.89% and 0.84% respectively over the pure HAP. For impurity substitutions, only Cd, Mg and Sr substitutions at Ca-2 show consistent increase in all three moduli while the Cu substitution at the Ca-1 site shows large decrease in shear modulus (-3.54%), Young's modulus (-2.87%) and a modest increase in the bulk modulus (+0.95%). The effect of defect and impurities on the elastic constants, the overall mechanical strength in HAP and their implications will be presented and discussed.

4:20 PM

(ICACC-FS2-015-2011) Modelling the Effects of Thermal Stress Cycling in Refractory Systems

A. A. Pandhari*, The University of British Columbia, Canada, Canada

In pyrometallurgical reactors, the thermal stress field of the refractories changes when heat transfer conditions at the hot-face change. Changing heat transfer conditions is routine in batch processes involving distinct charge-tap-rotation events. In many reactors, processing conditions are such that cooling is generally less aggressive than heating, which can be very aggressive, for example, charging of a ladle with liquid steel at 1600 °C. Rapid heating or cooling can lead to thermal spalling of the hot-face. It is suggested that 'thermally induced refractory cracking' is often the primary cause of in-service refractory failure but quantitative support for this is lacking. The current work focuses on quantifying thermal stress in the bulk refractory under processing conditions common to extractive metallurgical operations and in particular, conditions that may induce failure of the refractory. For this purpose, the finite element software, ABAQUS, will provide the platform for development of a thermomechanical model of refractory subjected to industrially relevant heating and cooling conditions. Simulation results suggest that the heated refractory at 1150 °C, when cooled, generates significant tensile thermal stresses. Even with the air cooling, the magnitude of these stresses is comparable to the tensile modulus of rupture indicating a high probability of refractory thermal cracking.

4:40 PM

(ICACC-FS2-016-2011) Ab initio investigation of H-bonding and O K-edge XANES spectra in bulk water

L. Liang*, P. Rulis, UMKC, USA; L. Ouyang, Tennessee State University, USA; W. Ching, UMKC, USA

Water is one of the most intriguing substances on earth. The network structure which mainly determined by the intermolecular hydrogen bond interactions has attracted large efforts from both experimental and theoretical sides. We have studied a periodic model of bulk water (a = 21.6641Å and density: 1g/cc) with 340 H_2O molecules using a combination of different ab initio simulation packages. The electronic structure, bond order (BO) values and X-ray absorption near edge structure (XANES) spectra are obtained. Based on the BO values, the 340 molecules are categorized into four groups according to their HB numbers (2-5). The average HBs per molecule is 3.85 in support of the tetrahedral network. The intra- and inter-molecular structural parameters are then analyzed in accordance with the four groups. The calculated total O K-edge spectra correctly reproduce four peak features observed in the experiments. The decomposition of the spectra into the four groups confirms that the pre-peak is caused by the broken-bonded O and there exist large fluctuations on other spectral features of individual water molecules.

5:00 PM

(ICACC-FS2-017-2011) Comparative study of XANES spectra of different phases of elemental boron

L. Wang*, P. Rulis, W. Ching, UMKC, USA

Elemental boron has very complex structures with more than 16 different allotropes. Among of them, α- and β-boron are thermodynamically most stable. α-phase, tetragonal phase, γ-phase and β-phase are the primary phases of boron. XANES, as one of techniques of X-ray absorption spectra (XAS), is an important experimental tool to explore local environment(e.g., octahedral, tetrahedral coordination) and subtle geometrical distortions. We have calculated the XANES spectra of every nonequivalent site of B phases (α-B_{12}, β-B_{106}, t-B_{50} and γ-B_{28}) using the supercell-OLCAO method. The result for α-B_{12} agrees with the experimental data very well. The XANES spectra of γ-B_{28}, t -B_{50} and β-B_{106} are the predicated spectra to be confirmed by experimental measurements. We further analyze our calculated spectra by grouping the spectra based on different geometrical configurations (icosahedra, single boron, boron pair, icosahedra clusters, etc.). The decomposed XANES spectra for each crystal are very different and show the influence of the local environment and distortions in affecting their spectral features.

5:20 PM

(ICACC-FS2-018-2011) Computational study of wave propagation in second-order nonlinear piezoelectric media

D. Hopkins*, G. Gazonas, Army Research Laboratory, USA

In this paper, we present computational results for the response of piezoelectric materials with 6mm symmetry when subjected to shock loads and large electric fields. The governing equations are based on a

second-order theory of piezoelectricity for the 6mm crystal class formulated in a Lagrangian reference frame. These equations represent the fully coupled nonlinear multiphysics response. Numerical solutions of these equations are first validated using analytical solutions for wave propagation in linear piezoelectric media. The effects of the nonlinear coupling introduced by higher order elastic, dielectric and piezoelectric coupling coefficients are then examined. It is shown that inclusion of the higher order terms predicts a reduction in the peak stress induced in the material. Also, the wave speed is shown to be lower than the bar velocity predicted by linear piezoelectricity. Possible application of these effects in tailoring the stress response of this class of piezoelectric material is discussed.

5:40 PM

(ICACC-FS2-019-2011) Degradation of Si3N4 Glow Plugs in Air – Experiment and Modeling

H. Karimi Sharif*, C. Oprea, T. Troczynski, The University of British Columbia, Canada; C. Blair, A. Welch, Westport Innovations Inc., Canada

Si3N4-based ceramic heaters ("Glow Plugs" GP) are evaluated as an ignition source in natural gas and hydrogen combustion engines. In this work GPs were aged in an electric rig in ambient air. The heat was produced by passing DC electric current through a pair of resistors embedded in the Si3N4 insulator, resulting in GP steady-state temperature of up to about 1500C. The resulting compositional change within the Si3N4 insulator under the influence of the electric field has been investigated by Scanning Electron Microscopy (SEM/EDX). It is shown that the electric field causes the sintering aid cation (Ytterbium ions Yb3+) to redistribute in alignment with the electric field lines. A model is proposed to describe the electric field effects on long-term degradation of Si3N4 ceramic insulators (GPs) at elevated temperatures. The model solves Poisson's equation for electrostatic analysis of the heater, coupled with time-dependent Nernst-Planck equation for diffusion/migration analysis of sintering additive cations (Yb3+) within the ceramic heater. The model was verified against SEM micrographs taken from cross section of aged silicon nitride heaters. It is proposed that the model may have implications in a wide range of disciplines from semiconductor/insulator technology to biological and medical physics.

Friday, January 28, 2011

S1: Mechanical Behavior and Performance of Ceramics & Composites

Joining

Room: Coquina Salon A
Session Chair: Monica Ferraris, Politecnico di Torino

8:00 AM

(ICACC-S1-077-2011) Torsion tests for joined ceramics and composites

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

Results of an experimental investigation on epoxy-joined SiC and alumina tested in shear and apparent shear mode by several different configurations will be presented. Ceramics have been joined by an epoxy adhesive (AV119), which is a model brittle joining material chosen to obtain several joined samples in a reasonable time. Advantages and disadvantages of each configuration are discussed and compared to results obtained with the same epoxy-joined carbon/carbon composites, tested by the same tests. Torsion test seems to be one of the most appropriate test for the determination of the shear strength of joined ceramics as well as joined CMCs. Torsion tests are proposed in some ASTM standards [ASTM F734-95 (2006) , ASTM F1362-09] but none of them is directly applicable to joined ceramics; these two standards have been adapted to joined SiC, by preparing butt-joined cylinders, tubes, and hourglass-shaped samples.

8:20 AM

(ICACC-S1-079-2011) Mechanical strength of silicon-based joints using elementary and structural experiments

G. Roux*, O. Gillia, L. Nguyen, V. Chaumat, Commissariat à l'Energie Atomique et aux Energies Alternatives, France

BraSiC® silicon based brazing technology for ceramics and ceramic matrix composites (CMC) is advantageously used for applications in optical mirror for space, in high temperature heat exchangers and in chemical reactors. Mechanical properties of the joint must be measured in assembly configuration, due to residual stresses induced by brazing process, principally due to elastic and thermal expansion incompatibilities between the braze and base materials wich conduce to a strong effect on failure strength in a brazed ceramic assembly. Joint thickness and temperature influence this stress field, conducing to well known dependences of such parameters in terms of mechanical strengths of that kind of assembly. This phenomenon is brought to light by numerical simulations, using classical rupture criterions. Elementary assemblies (for example 3 or 4 point bending tests specimens) are useful for model parameters identification, but final validation for industrial use involves most often a more geometrical and mechanical realistic experiment, like for example small scale prototypes or representative mock-ups, with sometimes complex loading like pressure or torsion ones. These experiments allow to validate failure prediction model with non-elementary loading. So, a review of different experiments performed on brazed assemblies at CEA/LITEN is presented and analyzed.

8:40 AM

(ICACC-S1-080-2011) Characterization of ceramic SiO2 nanopaste for microreactors shaping

D. Kata*, M. Wozniak, P. Izak, AGH University of Science and Technology, Poland; T. Graule, EMPA Swiss Federal Laboratories for materials Testing and Research, Switzerland; J. Lis, AGH University of Science and Technology, Poland

Screen printing and Rapid Prototyping methods of forming ceramic pastes hold great potential when it comes to manufacturing microreactors and SOFCs. The paper presents data gathered by studying rheological properties of freshly obtained pastes mainly intended for use in Rapid Prototyping. The pastes were prepared as non-aqueous colloidal solutions of OX50 Aerosil nanosilica dispersed in Butenediol Monacrylate BDMA monomer. Silica can be used in microreactor manufacturing process due to its ability to withstand high temperatures and its resistance to aggressive environmental conditions. The research was aimed at obtaining pastes that have the highest possible solid phase content. Rheological properties like viscosity as a function of shear rate, thixotropy and rheological model of pastes created on the basis of Aerosil OX50 (with 20-40 vol. % of solid phase) were measured using a rotary viscosimeter. Such pastes have proven adequate for 2D and 3D printing.

Tribological Properties of Ceramics and Composites

Room: Coquina Salon A
Session Chairs: Monica Ferraris, Politecnico di Torino; Oyelayo Ajayi, Argonne National Laboratory

9:40 AM

(ICACC-S1-081-2011) Friction performance of carbon fibre reinforced silicon carbide composites under wet conditions

G. Bian, A. Swarbrick, C. Ji, H. Wu*, Loughborough University, United Kingdom

It is generally recognised that carbon fibre reinforced silicon carbide composite should be one of the best materials for rotors of friction brakes that have been widely used in almost all sorts of road vehicles. The typical gains by using this type of composite include significant weight saving, ability to function at higher temperature, and longevity due to extremely low wear rate, comparing to the most commonly used grey cast iron or steels. However, we have recently

noticed that environmental conditions during braking could have an unexpected impact on the friction performance of brakes consisting of such composite rotors, which could become a troublesome factor for brake designers to use this composite with confidence. In this study, we experimentally simulated the effect of water on the loss and recovery of the friction coefficient for composites with different microstructures, as well as the influence of different pad materials. The post-braking surfaces at different stages were further analysed with microscopy techniques; by using the experimental outcomes, we are able to reconstruct possible mechanisms for the change of friction performance under wet conditions.

10:00 AM

(ICACC-S1-082-2011) An experimental study on the effects of SiC on the mechanical and wear properties of Cr3C2-NiCr cermets

A. Ozer*, Y. K. Tur, Gebze Institute of Technology, Turkey; W. M. Kriven, University of Illinois at Urbana-Champaign, USA

Cr3C2-NiCr type cermets have been used in cutting industry since World War II for their relatively low sintering temperatures and relatively low densities. Their high corrosion resistance at high speeds and temperatures increases interest to these materials. In this study, the powder mixture of 75wt% Cr3C2-25wt% NiCr with a Ni-Cr ratio of 4/1 was produced as master composite at four different sintering temperatures for investigating its microstructure, transverse rupture strength, microhardness and wear properties. ZrO2 in two different crystal structures (3 mol % yttria stabilized tetragonal, 8 mol % yttria stabilized cubic) and SiC were added as reinforcements to study their effect on mechanical and wear properties of Cr3C2-NiCr cermets. SEM and EDX analysis performed for identifying microstructures indicated that full densification occurs at 1350°C for master cermets. As the relative density increases, an increase in the microhardness, transverse rupture strength of cermets was also observed. Pin on disc type wear tests were performed to characterize the wear properties of cermets.

10:20 AM

(ICACC-S1-083-2011) Increasing the operating pressure of gasoline injection pumps via ceramic sliding systems

C. Pfister*, H. Kubach, U. Spicher, Karlsruhe Institute of Technology, Germany

Spray-guided gasoline direct injection (GDI) shows strong potential to reduce both fuel consumption and pollutant emissions of modern combustion engines. This concept can be significantly improved by increasing the fuel injection pressure. Higher pressures lead to smaller droplets being injected into the combustion chamber, thus accelerating mixture formation. The materials used in the sliding systems of modern gasoline pumps wear severely at injection pressures above 20 MPa, whereas laboratory tests show substantial improvements in the performance of GDI engines at higher pressures. The use of ceramic parts in the sliding systems of the fuel pump should help to overcome these difficulties. As part of the Collaborative Research Centre "High performance sliding and friction systems based on advanced ceramics", investigations have been performed at the Karlsruhe Institute of Technology on a high-pressure pump built with ceramic sliding systems. The pump is fitted with several sensors to assess the performance of the sliding parts. The investigations performed within this project demonstrate great potential to increase injection pressures in GDI engines by using advanced ceramics in the sliding systems of the high-pressure gasoline pump.

10:40 AM

(ICACC-S1-084-2011) Co-continuous ceramic-foam/aluminum interpenetrating composites for wear resistance applications

J. Liu*, J. Binner, R. Higginson, C. Munnings, Loughborough University, United Kingdom

Metal-ceramic interpenetrating composites (IPCs) consist of 3D-continuous matrices of discrete metal and ceramic phases. The goal is to develop superior multifunctional properties compared with traditional MMCs with a view to using these composites in applications including wear resistance, electrical components and light weight structural parts in industries including aerospace, automotive and defence amongst others. In this project, a pressureless infiltration technique was used to produce IPCs by infiltrating molten aluminum alloys into a range of ceramic foams produced from alumina, mullite, spinel and silicon carbide. One goal was to investigate the different processing conditions required by the different aluminum alloy-ceramic systems; the spinel-based IPCs yielded the fastest infiltration at the lowest processing temperature. One of the features of the process route is the quality of the bonding between the metal and ceramic phases; the origin of this bonding was determined. Physical and mechanical properties, including coefficient of thermal expansion, wear resistance and hardness, of different IPC systems have all been characterized. The effects of the composition, microstructure and density of the ceramic foam on the performance were determined. It was found that the ceramic foam-based IPCs were twice as wear resistant as MMCs made by adding ceramic powders into alloys.

11:00 AM

(ICACC-S1-085-2011) Fiction and Wear Behaviors of Al_2O_3-15wt% ZrO_2-Solid Lubricants Nanocomposites at Temperature up to 600 °C

S. Kim, S. Lee*, Sun Moon University, Republic of Korea

Ceramics are important materials for high temperature applications such as components in advanced engines and gas turbines, and wear-resistant components. In recent years, high temperature low friction materials are important for application of eco-friendly and energy saving, etc. Energy loss in vehicles is roughly 10 % of energy input consumed by friction. Also, high temperature low friction materials based on nanocomposites were performed using several sintering processing and thermal spray coating method. The purpose of this work is to use the pulse electric current sintering (PECS) technique in order make self-lubricating Al_2O_3-15wt% ZrO_2-solid lubricants nanocomposites with better mechanical properties. Solid lubricants such as fluorides (CaF_2, and BaF_2), sulfides (MoS_2, and WS_2), and others (h-BN, and graphite) were used. Friction and wear behaviors of PECSed Al_2O_3-15wt% ZrO_2 nanocomposites at temperature up to 600 °C were investigated.

11:20 AM

(ICACC-S1-086-2011) Fretting fatigue of engineering ceramic with variable friction loads

C. Woerner*, K. Lang, Institut fuer Werkstoffkunde 1, Germany

Rollers made of ceramic are very well suitable for hot rolling of high-strength steels. During the shaping process the ceramic rollers are highly loaded. The appearing complex loading is caused by a cyclic loading from the rotation of the rollers and high Hertzian stresses connected with friction, caused by the contact between the rollers and the rolling stock during the shaping process. To investigate the lifetime behaviour of potential roller materials fretting fatigue tests are carried out in a modified four-point-bending unit, where a fretting pad is pressed on to the tensile side of the bending bar and oscillated. In the test series, the loading types of the fretting pad were varied. The materials alumina (F99,7 by Friatec), as model material and silicon-nitride (SL200BG by CeramTec) are investigated. Alumina shows a high damage at high friction loads and very low damage at low frictional loads. However, silicon-nitride shows a high damage even at low friction loads and a very high damage at high friction loads. The results show, that ceramics are heavily damaged by fretting fatigue loading. The main damaging effect at alumina is abrasive wear caused by the fretting pad. However, in silicon-nitride crack initiation and/or activation is more effective than wear. This explains the higher sensitivity of the investigated silicon-nitride to fretting fatigue.

S6: International Symposium on Ceramics for Electric Energy Generation, Storage, and Distribution

Materials for Energy Storage and Technologies

Room: Coquina Salon B
Session Chairs: Fatih Dogan, Missouri University of Science and Technology; Tseung Yuen Tseng, National Chiao Tung University

8:00 AM

(ICACC-S6-012-2011) Nanostructured Ceramic Dielectrics for High Energy Density Capacitors (Invited)

F. Dogan*, Missouri University of Science and Technology, USA

TiO2 ceramics with a grain size ranging from 150nm to 5μm were processed at various sintering temperatures, atmospheres and dopants. Microstructural development of the samples was characterized by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), X-ray Photoelectron Spectroscopy (XPS) and Transmission Electron Microscopy (TEM) techniques. Dielectric properties; such as dielectric constant, dielectric loss, polarization-electric field relationship and dielectric breakdown strength were measured using samples with acceptor and donor type dopants. Correlation between microstructural development and dielectric properties was interpreted through analysis of the results obtained by impedance spectroscopy measurements. It was found that nanostructured TiO2 ceramics exhibit lower leakage current, lower dielectric loss, higher breakdown strength as compared to coarse grained materials. Dielectric properties of TiO2 ceramics were significantly affected by dopants, sintering atmosphere and cooling rate during sintering. Results show that nanostructured TiO2 dielectrics, sintered under optimized sintering conditions, are promising dielectric materials for high energy density capacitors.

8:30 AM

(ICACC-S6-013-2011) Fabrication of Manganese Oxide-Carbon Nanotube Nanocomposite Supercapacitors and Their Properties (Invited)

T. Tseng*, National Chiao Tung University, Taiwan

The synthesis of an nanocomposite supercapacitor electrode based on nanosized manganese oxide and carbon nanotube by using electrophoretic deposition method is reported. X-ray diffraction, scanning electron microscope, transmission electron microscope, and X-ray photoelectron spectroscopy are employed to characterize the structure, surface morphology, microstrucure, and composition of the supercapacitors. The electrochemical properties measurements including cyclic voltammetry, stability test, and impedance measurement are also carried out in 0.1M Na2SO4 aqueous solution. The supercapacitor shows very high specific capacitance value of 600 F/g at a scanning rate of 100 mV/s. It remains about 80% of the original capacitance value after 6000 cycles. The supercapacitor exhibits a good reversibility and cycling stability. The correlation of the electrochemical properties with microstructure and composition of the nanocomposites are also provided.

9:00 AM

(ICACC-S6-014-2011) Nano-Engineering of Phase Separable Inclusions in High Performance YBCO Thick Films for Coated Conductors

T. G. Holesinger*, D. M. Feldmann, F. J. Baca, B. Maiorov, J. Y. Coulter, L. Civale, Los Alamos National Laboratory, USA

High critical current densities (Jc) in YBa2Cu3Oy (YBCO) coated conductors depend directly upon the connectivity and defect density within the films. Hence, one needs to develop methodologies for controllably introducing defect structures that are sufficient for tailoring the superconducting properties while, on the other hand, maintaining high critical current and uniformity over lengths exceeding a kilometer. A number of defect structures have been shown to be effective flux pinning centers, among them the ubiquitous Y2O3 and the general class of double-perovskites, A2BB*O6 where A = Ba and B can incorporate a wide range of elements. For this talk, we will present our results for B = Y, Zr, Nb, Sn, and Ru. Through changes in composition and targeted sets of additions, we show that it is possible to significantly reduce detrimental defects while precisely controlling the types and densities pinning defects within films, leading to enhanced performance in thick YBCO films. Jc values (SF, 75.6K) of 5 MA/cm2 (1000 A/cm-w) have been reached in 2 micron thick films. Flux pinning forces of 32.3 and 122 GN/m3 (75.5 and 65K, respectively) have been obtained in a 0.5 micron YBCO film with Ba2YNbOy additions.

9:20 AM

(ICACC-S6-015-2011) Ceramic Processing for Dense Magnesium Diboride

C. J. Dancer*, R. I. Todd, C. M. Grovenor, University of Oxford, United Kingdom

There is little consensus in the literature on the processing requirements to produce high quality MgB_2 material with low impurity content and high density. We have carried out a range of processing procedures to establish key parameters for ex situ production of dense MgB_2 by examining the effect of modifying the characteristics of the starting powder and the processing parameters during heat treatment. MgB_2 bulk material was produced from as-purchased and modified powders by pressureless heat-treatment under Ar gas and pressure-assisted methods (spark plasma sintering or hot pressing) under vacuum or Ar gas. Porosity, impurity content, hardness, grain size and magnetization were measured. Our results indicate that densification and applied pressure are strongly correlated, while the effect of temperature is less significant. The optimum processing environment (inert gas or vacuum) was dependent on the technique used. These results indicate that pressure-assisted heat-treatment is required in order to produce dense bulk MgB_2. A positive correlation between magnetization critical current density and bulk density was observed for magnesium diboride bulks up to around 90% density. Above this level other microstructural processes such as grain growth begin to influence the critical current density, suggesting that full elimination of porosity is not necessary to obtain good superconducting performance.

10:00 AM

(ICACC-S6-016-2011) Effect of Double Doping on crystal structure and electrical conductivity of W-containing Bi_2O_3 solid electrolyte (Invited)

C. Hsieh, C. Liu, C. Ni, K. Fung*, National Cheng Kung University, Taiwan

WO_3-doped Bi_2O_3 was found to be a stable Bi_2O_3-based system compared to commonly known Y_2O_3-doped Bi_2O_3 (YSB). However, the electrical conductivity of WO_3-doped Bi_2O_3 is significantly lower than that of YSB. The structure and electrical conductivity of doubly doped systems formulated as $(CaO)_x(WO_3)_{0.15}(BiO_{1.5})_{0.85-x}$ and $(YO_{1.5})_x(WO_3)_{0.15}(BiO_{1.5})_{0.85-x}$ (x =0, 0.1, 0.2 and 0.3) were investigated. The as-sintered $(W_{0.15}Bi_{0.85})_2O_{3.45}$ (15W) and $(Ca_{0.1}W_{0.15}Bi_{0.75})_2O_{3.35}$ (10CaWBi) formed a superstructure consisting of 10 enlarged cubic fluorite subcells. The substitution of Y^{3+} ion (0.1019 nm) for Bi^{3+} ion (0.117 nm) reduced the average cationic radius. Therefore, the as-sintered $(Y_{0.1}W_{0.15}Bi_{0.75})_2O_{3.45}$ (10YWBi) exhibited a single cubic structure that is isostructural with δ-Bi_2O_3. For 10YWBi, the cubic structure is more symmetric than the tetragonal structure of 15W. Thus, the conductivity is 2.38×10^{-2} S cm^{-1} at 700°C and slightly higher than that of 15W. The highest conductivity in $(CaO)_x(WO_3)_{0.15}(BiO_{1.5})_{0.85-x}$ system is 2.4×10^{-2} S cm^{-1} at 700°C for x = 0.1. This value is higher than that of Ca-free 15W and 10YWBi. The enhanced ionic conduction in 10CaWBi may be attributed to the higher anion vacancy concentration.

10:30 AM

(ICACC-S6-017-2011) Influence of mineral dust on SiC solar absorbers

M. J. Schmucker*, P. Schwarzbözl, German Aerospace Center (DLR), Germany

Ubiquitous mineral dusts may deposit on hot surfaces of porous ceramic structures used as volumetric absorbers in concentrating solar power systems. A test rig was designed for accelerated investigations of dust deposition effects and possible reactions between mineral compounds and SiSiC absorber samples. Two different bulk compositions of mineral dust were tested: Arizona road dust (SAE J726) composition (70wt.% SiO_2, 15 % Al_2O_3, 8% Fe_2O_3, 4 % CaO, 2 Na_2O, 1 % MgO) and a lime-rich composition (40wt.% SiO_2, 12 % Al_2O_3, 7% Fe_2O_3, 33 % CaO, 1% Na_2O, 1% K_2O, 6 % MgO). By charging honeycomb absorber samples with aerosols of specific inorganic dust the following effects were investigated: -Degree of particle adherence on SiC absorber samples as a function of temperature -Plugging of air channels -Alteration of optical properties, namely solar absorption and related thermal efficiency -Sintering of powders and reactions between powders and SiC surfaces to asses temperature limits of possible dust removing by simple mechanical methods. Preliminary experiments reveal that dust adhesion and sintering is more pronounced if mineral powders are employed instead of synthetic oxide powders of similar particle size. Thus, for realistic tests powder admixtures consisting of clay, quartz, calcite and dolomite were employed.

10:50 AM

(ICACC-S6-018-2011) Effect of sintering temperature on microstructure and dielectric properties of Cr2O3 doped CCTO (CaCu3Ti4O12) ceramics

M. Mishra*, V. Koutu, T. D. Senguttuvan, National Physical Laboratory, India

One weight percent Cromium doped calcium-copper-titanate (Cr2O3-doped CCTO) ceramics was prepared by solid-state reaction method. These samples were sintered at temperatures 1100 C, 1150 C, and 1200 C. Samples sintered at 1200 C showed a well defined helical grain growth. The average grain size of Cr2O3-doped CCTO increased with increase in sintering temperature. XRD patterns of these samples showed a diffraction profile similar to the body-centered cubic perovskite structure. An extra cuprite phase was observed in pure CCTO powder. The dielectric properties of Cr2O3 -doped CCTO materials improved with increasing sintering temperature and tan δ decreased with increase in sintering temperature.

11:10 AM

(ICACC-S6-019-2011) Dielectric Property of Polymer-Derided SiAlCN Ceramics

G. Shao*, L. An, university of central florida, USA

Fully dense polymer-derived SiAlCN ceramics were prepared at different pyrolysis temperatures in flowing nitrogen. The structures and compositions of the obtained materials were analyzed. The dielectric properties of the materials were characterized using Agilent impedance analyzer. It was found that the dielectric constant increased with increasing the pyrolysis temperature. The high dielectric constant of the materials is attributed to two mechanisms.

11:30 AM

(ICACC-S6-020-2011) Electric Properties of Ceramics with Different Compositions

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

Polymer-derived SiCN ceramics with different structures and compositions were prepared by using the precursors synthesized by reaction of Ceraset with different amount of PVN. The structures and compositions of the obtained materials were characterized by element analysis, NMR and EPR. The electronic and dielectric behavior of the materials was measured at room temperature. The relationship between the structures/compositions and the properties of these materials are discussed.

S7: 5th International Symposium on Nanostructured Materials and Nanotechnology: Development and Applications

Synthesis, Functionalization and Processing of Nanostructured Materials II

Room: Coquina Salon C
Session Chairs: Sean Li, The University of New South Wales; Francois Ribot, Universite Pierre et Marie Curie

8:00 AM

(ICACC-S7-060-2011) Nanoengineered Hydroxyapatite Nanorod Reinforced Poly (vinyl alcohol) Composite (Invited)

V. Rajendran*, N. Meenakshisundaram, M. Rajkumar, K. S. Rangasamy College of Technology, India

Hydroxyapatite (HAp, Ca10(PO4)6(OH)2) has a high affinity for natural tissue insitu engineering and can be molded to fill spaces created by physical damages in bones and or teeth. However, HAp shows poor mechanical properties such as low elasticity and high brittleness. Tailoring of nanophase crystalline hydroxyapatite with biocompatible polymeric matrix leads to the nanocompoiste which provides high flexibility, mechanical strength and biocompatible to mimic the natural bone. Therefore, a great attention has been paid on the development of novel bio-inspired HAp/polymer composites to mimic the natural hard tissues. A molecular control on the morphology, crystallite size, crystallinity, microhardness and resorabability of the HAp and their chemical bond interaction with polymeric matrix is needful in the biomaterials research. In this present study, pure HAp and HAp/poly (vinyl alcohol) (PVA) composites were prepared by tuning the PVA concentration. The particle size and surface morphology of prepared composite powder was studied by transmission electron microscopy (TEM). The phase identification was performed by powder X-ray diffraction (XRD) analysis. The characteristics peaks of the pure HAp and HAp/PVA composites were confirmed by FTIR analysis. Bioresorbability testing of the pure HAp and HAp/PVA nanocomposites was conducted by treating the specimen under simulated body fluids (SBF).

8:30 AM

(ICACC-S7-061-2011) Enhancement of magnetic properties in rare earth and cobalt codoped ZnO thin films for spintronic applications (Invited)

S. Li*, The University of New South Wales, Australia

Spin-polarized materials, which allow spin-polarized carriers to be efficiently injected, transported and manipulated in semiconductor hetero-structures, are essential for the realization of new spin-based multifunctional devices. In this work, a new ZnO based spintronic material was developed using rare earth elements and Co codoping technology. The codoped material with optimized stoichiometric atomic ratio has 3 times higher saturated magnetization than the materials doped with either rare earth element or Co only. The appearance of strong magnetoresistance in the codoped materials indicates that the rare earth elements may play an important role to construct the spin polarization network. Further investigation shows that the orbital spin of electrons induced by the rare earth ions in the materials are responsible for the superior magnetic properties. The individual magnetic moment contributed by the rare earth element and Co, which were characterized by X-ray magnetic circular dichrosim, is used to reveal the mechanism behind the intensive enhancement of electron spin polarization. In addition, x-ray absorption spectroscopy was also employed to obtain atomic-scale structural and chemical

state information including the unoccupied electronic states for the individual doped atoms.

9:00 AM

(ICACC-S7-062-2011) Transformation and Phase Determination of Y2O3 Subject to High Pressure Processing

J. Al-Sharab*, B. H. Kear, S. Duetsch, S. D. Tse, Rutgers University, USA

Yttrium oxide (Y2O3) forms the major constituent of current mid-IR (2-8μm) optical materials owing to its excellent optical and mechanical properties. In order to obtain functional Y2O3 material with high strength and excellent optical transmission, grain size should be <200nm. However, current processings require high sintering (>1500C) temperature which will result in larger grains > 2000 nm. In this research, we describe a reversible phase transformation process where a fully dense polycrystalline Y2O3 directly converted into nanocrystalline state. The process involves a forward transformation from cubic-to-monoclinic under a high pressure and a backward transformation from monoclinic-to-cubic under a lower pressure. An example is given of a reduction in grain size of cubic-Y2O3 from 300 μm to 0.1 μm in a single pressure-induced reversible phase transformation at 1000C. All processed samples were subject to atomic scale characterization in order to correlate structure with optical and mechanical properties. Further work is underway to establish the optimal processing parameters to achieve the finest possible nano-grain size in the fully transformed material.

9:20 AM

(ICACC-S7-063-2011) Preparation of Strongly Emitting Small Silica Beads with Multiple Quantum Dots and their Surface Modification

N. Murase*, M. Ando, National Institute of Advanced Industrial Science & Technology (AIST), Japan

Incorporation of colloidal quantum dots (QDs) into silica glass matrices has led to a more robust structure against environment. However, it is a big challenge to maintain the initial photoluminescence (PL) properties of the QDs after the incorporation. Hitherto, we have created several types of sol-gel derived silica glass impregnated with emitting QDs. During the research, we found out glass does not only protect and disperse QDs, but also plays active roles by creating new structures with innovative optical properties. In this presentation, we will focus the preparation of small silica beads impregnated with multiple QDs, and their surface modification for bioapplications. Surface of hydrophobic CdSe/ZnS QDs was gradually silanized using partially hydrolyzed tetraethyl orthosilicate (TEOS), and subsequently transferred to water phase. Partially hydrolyzed 3-mercaptopropyltrimethoxysilane regulates the assembly of QDs in water phase. For surface modification of the assembly, we have used pre-hydrolyzed TEOS and carboxyethylsilanetriol sodium (CES). Transmission electron microscope image revealed that the resulting beads had 25 dispersed NCs on average in silica beads with ca 50 nm in diameter. The typical PL efficiency was 30%, while their initial value in colloidal solution was 35%.

10:00 AM

(ICACC-S7-064-2011) Carbon nitride nanotubes prepared by simple chemical vapour deposition (Invited)

K. Ramesh*, Indian Institute of Science, India

Nanostructured carbon nitride films were prepared by pyrolysis assisted chemical vapour deposition. The precursor Azabenzimidazole was taken in a quartz tube and evaporated at zone 1 of a homebuilt two zone furnace. The dense vapours enter the pyrolysis zone (zone 2) kept at a desired temperature and deposit on the quartz substrates. Nanotubes of 30 nm diameter and 3μ length were observed for samples prepared at 775 °C. The samples prepared at 800 °C shows the formation of nanoparticles of carbon nitride. The FTIR spectrum of the prepared samples shows peaks at 1272 cm-1 (C–N stretching) and 1591 cm^{-1} (C=N) confirms the bonding of nitrogen with carbon. Raman D and G peaks, are observed at 1385 cm^{-1} and 1576 cm^{-1} respectively. XPS core level spectra of C 1s and N 1s show the formation of π bonding between carbon and nitrogen atoms. The size of the nano crystals estimated from the SEM images and XRD is ~100 nm. In some regions of the sample a maximum of 57 atom % of nitrogen was observed which is very close to the stoichiometric ratio of C3N4.

10:30 AM

(ICACC-S7-015-2011) A New Possibility for Microstructural Investigation of Clay-based Polymer Nanocomposite by Focused-Ion-Beam Tomography

S. Sinha Ray*, Council for Scientific and Industrial Research, South Africa

This presentation will show that the focused ion beam (FIB)-tomography as a high-resolution three-dimensional (3D) technique to study the morphology of polymer/clay nanocomposites. To establish the structure-property relationship of such composite material, it is very important to visualize the 3D-structure and distribution of clay particles in the polymer matrix. The sequential two-dimensional sectioning by FIB, followed by imaging of dispersed silicate layers using high-resolution scanning electron microscope, and computer reconstruction can show the degree of dispersion of silicate layers in 3D-space.

10:50 AM

(ICACC-S7-066-2011) Synthesis of Nano-size TiB2 Powders Using Carbon Coated Precursors

R. Duddukuri*, R. Koc, Southern Illinois University,Carbondale, USA; J. Mawdsley, D. Carter, Argonne National Laboratory, USA

This research deals with the production and properties of titanium diboride (TiB2) from novel carbon coated precursors. This work provides information on using different boron sources and their effect on the resulting powders of TiB2.The process has two steps in which the oxide powders were first coated with carbon by cracking of a hydrocarbon gas, propylene (C3H6) and then, mixed with boron carbide and boric acid powders in a stoichiometric ratio. These precursors were treated at temperatures in the range of 1200-14000 C for 2 h in flowing Argon atmosphere to synthesize TiB2.The process utilizes a carbothermic reduction reaction of novel carbon coated precursor that has potential of producing high-quality powders (sub-micrometer and high purity). Single phase TiB2 powders produced were compared with commercially available titanium diboride, obtained from boron carbide & boric acid containing carbon coated precursor.

11:10 AM

(ICACC-S7-067-2011) Probing, in suspension, the ligands on the surface on gold nanoparticles by DOSY NMR

F. Ribot*, H. Ben Sassi, L. Van Lokeren, Universite Pierre et Marie Curie, France

Nanoparticles (NPs) are one of the main pillars on which nanotechnologies have grown during the last years. Their bottom up syntheses often used organic capping molecules, that can interact with the surface of NPs to control the size, morphology, and stability. Different ligands can also be introduced later on to make the NPs compatible with the application medium or add functionality. Accordingly, a good knowledge of the interactions, in suspension, between NPs and the molecules used to prepare and functionalize them is of great interest to rationalize and improve their synthesis and their use. Pulsed field gradient NMR is a method which, in addition to common chemical shifts and scalar couplings, give access to the diffusion coefficients of the various species in a mixture. This technique, also known as DOSY (Diffusion Ordered Spectroscopy) NMR, affords a way to distinguish free molecules from those interacting with the surface of NPs, according to their different diffusion behaviors. This approach has been applied to suspensions of gold NPs (diam. ~10 nm) stabilized by various ligands (thiol, phosphine, amine) and has in-

deed allowed to differentiate and quantify free and bound capping molecules. Moreover, the relative affinity of different capping molecules has been probed on gold NPs stabilized by a mixture of two ligands, taking advantage of the selectivity of NMR.

11:30 AM

(ICACC-S7-068-2011) High Temperature Diffraction Study of In-Situ Formation of TiO2 Photocatalysts

I. Low*, Curtin University of Technology, Australia; V. De La Prida, Universidad de Oviedo, Spain

The solar photoelectrochemical water splitting for hydrogen fuel generation is an attractive CO2-neutral way to convert renewable solar energy into clean and sustainable chemical fuel energy which is storable and transportable. Since photocatalytic reactions mainly take place on the surface of the catalyst, a high surface-to-volume ratio is of great significance for increasing the decomposition rate. Very high photocatalytic activity has already been demonstrated for nanostructured TiO2 with various morphologies such as: nano-powders, nano-rods, nano-wires, nano-fibers, nano-belts, nano-tubes, and thin films. Although a lot of progress has been achieved in these forms of TiO2, the poor recuperability and reutilization limitation for nano-powders and processing difficulty for nano-fibres or nano-tubes are still challenges for their commercial applications. Here we report the characterisation of in-situ formation of TiO2 in as-anoodized Ti-metal and Ti3AlC2 at elevated temperature. The direct growth of aligned TiO2 nanostructures on the Ti or MAX-phase substrate has promising potential for photoelectrochemical applications.

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

Structural Stability under Extreme Environments

Room: Coquina Salon H

Session Chairs: James Zimmermann, Corning Incorporated; Pankaj Sarin, University of Illinois at Urbana-Champaign

8:00 AM

(ICACC-S12-041-2011) Behavior of MAX-phase thin films under 150-240 keV ion irradiation

M. Bugnet, Institut PPRIME, France; P. Eklund, Linköping University, Sweden; A. Declemy, M. Beaufort, Institut PPRIME, France; J. A. Hinks, S. E. Donnely, University of Salford, United Kingdom; V. Mauchamp, P. Guerin, M. Marteau, F. Pailloux, T. Cabioc'h*, M. Jaouen, Institut PPRIME, 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. In this study, the behavior under room temperature low energy Ar^{++} irradiation of Ti_2AlN and Ti_3AlC_2 was investigated in (Ti,Al)N/Ti_2AlN multilayers and in a Ti_3AlC_2 epitaxial thin film (Ar 150 and 240 keV, respectively). Their behaviors under irradiation, with fluences ranging from 1.5×10^{13} up to 10^{15} $Ar.cm^{-2}$, were studied using X-ray diffraction and Transmission Electron Microscopy (image, diffraction, electron energy-loss spectroscopy). Expansion along the c axis of the hexagonal lattice is evidenced in both compounds. For Ti_2AlN, a conservation of the (0006) and a progressive disappearance of the (0002) and (0004) diffraction peaks for increasing doses are observed. Concerning Ti_3AlC_2, a partial phase transformation to Ti_3AlC occurs as the fluence increases. One does not observe any amorphization of these two MAX phases, even for the highest dose (corresponding to 5 dpa). From these observations, the resistance to ion irradiation induced damages in Ti_2AlN and Ti_3AlC_2 will be discussed.

8:20 AM

(ICACC-S12-042-2011) Microstructural investigation of HfB_2-based ceramics after ultra high temperature testing with a defocused laser beam

D. J. Daniel*, E. Zapata Solvas, Imperial College London, United Kingdom; E. Sanchez Gonzalez, Universidad de Extremadura, Spain; P. Brown, Defence Science and Technology Laboratory, United Kingdom; W. E. Lee, Imperial College London, United Kingdom

Dense (~99% of theoretical density) Hf -based ultra high temperature ceramics (UHTCs) including HfB_2, 20 vol.% SiC reinforced HfB_2 (HS20) and 2 wt.% La_2O_3 added HS20 were fabricated by spark plasma sintering (SPS). Oxidation studies were carried out in air for the sintered UHTCs using a defocused laser (DFL) beam for 30 – 120 sec at two different heat fluxes, 8.2 MW/m^2 and 15 MW/m^2. Microstructural characterisation of the exposed surfaces and cross-sections of UHTCs after oxidation was carried out using FEG-SEM, TEM and FIB-SIMS. A wide range of microstructural features were observed, including needles, nanofibres and lamellae. Some surfaces were characterised by dendritic and eutectic morphologies. A complex array of mechanisms involving solid, liquid and vapour phases led to formation of these various morphologies including melting, oxidation, volatilisation and liquid flow. Cross-sections of exposed surfaces of DFL-tested samples revealed that they behaved differently when exposed to the two different heat fluxes in terms of surface damage, oxidation layer thickness and chemical composition of top exposed and intermediate layers. 2 wt.% La_2O_3 added HS20 had better survivability in terms of oxidation attack at high heat flux.

8:40 AM

(ICACC-S12-043-2011) Fabrication and plasma wind tunnel testing of UHTC structures (Invited)

F. Monteverde*, L. Silvestroni, D. Sciti, ISTEC-CNR, Italy; R. Savino, M. De Stefano Fumo, University of Naples "Federico II", Italy

The ultra-high-temperature ceramics (UHTCs) are currently the most studied key enabling technology for thermal protection structures (TPS) like wing leading edges, surface control components to be applied in the next generations of space vehicles flying at hypersonic speed or/and re-entering the Earth's atmosphere. They are characterized by sharp profiles to increase performances and maneuvrability.In the present contribution, technological demonstrators with a sharp profile were produced in the system ZrB2-SiC by hot-pressing and further shaping by EDM/mechanical machining. SiC was introduced in the form of particulate or short fibres.In both cases, the dynamic response to oxidation of such pointed UHTC demonstrators was studied under aero-thermal heating using a high enthalpy supersonic flow of a N2/O2 gas mixture in plasma wind tunnel. Microstructural features of the reaction scale developed upon oxidation were analyzed and correlated to test conditions through Computational Fluid Dynamics simulations. The significant heat flux and temperature gradients of the sample's surface exposed to the highly energized N2/O2 gas stream led to the formation and evolution of distinct layered oxide sub-scales. The outputs of CFD simulations, that are essential to model the test conditions of the free-stream and boundary layer, matched the in-situ determinations and material evolution during arc-jet testing.

9:10 AM

(ICACC-S12-044-2011) High Temperature Oxidation Test of ZrB_2-based UHTCs by Oxyacetylene Flame

Y. Seong*, S. Lee, D. Kim, Korea Advanced Institute of Science and Technology, Republic of Korea

Ultra high temperature ceramics (UHTC) include some refractory metal diborides that were historically studied and interests in ZrB_2-based ceramics have increased significantly in recent years because of

the drive to produce thermal protection systems and other components for hypersonic aerospace vehicles. However, reports on the oxidation and ablation behaviors of ZrB_2-based ceramics under simulated atmospheric re-entry conditions are limited and the characterizations are still not well understood because its oxide scale is complex, and it is difficult to achieve temperatures above 2000°C rapidly. In this study, ZrB_2-based ceramics were prepared by hot-pressing at 1900°C for 2hrs under 32 MPa and the high temperature oxidation behavior of the specimens was investigated using oxyacetylene flame. The temperature of the oxidation specimens was around 2200°C and the mass and linear oxidation rate plots with time variation were obtained. The mechanical properties test (flexural strength, toughness and hardness) of ZrB_2-based ceramics was performed to investigate the effects of high temperature oxidation on mechanical properties. The effects of SiC addition on microstructure, oxidation behavior of ZrB_2-based ceramics were also investigated. Finally, the oxidation mechanism of ZrB_2-based ceramics will be discussed using volatility diagram.

FS1: Geopolymers and Other Inorganic Polymers

Properties and Composites

Room: Coquina Salon F
Session Chair: Miladin Radovic, Texas A&M University

8:00 AM

(ICACC-FS1-009-2011) Flexural properties of pure and modified geopolymer matrix/ unidirectional fibers reinforced composites (Invited)

O. Bortnovsky*, P. Bezucha, Research Institute of Inorganic Chemistry, Czech Republic; D. Tran, D. Kroisova, P. Hajkova, Technical University of Liberec, Czech Republic

Detailed studies of novel geopolymer composites reinforced with unidirectional fibers showed that the simple evaluation of tests on flexural properties of ceramic composites in accordance with American and European standards provides effective values of flexural strength and, respectively, elasticity modulus E^* that are size dependent. By means of testing within a wide scale of specimen height H to length L ratio, it is possible, however, to obtain extrapolated flexural elastic modulus E and shear modulus G that can be considered as size independent material characteristics, following the procedure referred to plastic matrix composites. Analogously the evaluation of size independent values of flexural strength σ_m was done. To the difference from any strictly fixed test parameters, testing with differentiated H/L ratios provides more comprehensive information on the character of the composite, and is therefore recommendable especially in the development of new types of fiber-matrix pairs. Geopolymer matrix modification with minor amount (up to 1 %) of organic and inorganic additives brings a considerable effect on the target mechanical and utility parameters. Application of organic additives generally leads to enhanced stiffness and improved machining of composites. Application of inorganic additives improves the mechanical properties at ordinary and high temperature.

8:30 AM

(ICACC-FS1-010-2011) Mechanical Properties of Chopped Fiber Reinforced Geopolymer Composites as a Function of Temperature (Invited)

T. P. Dietz, W. M. Kriven*, University of Illinois at Urbana-Champaign, USA

The properties, microstructure, and processing of potassium or cesium-based geopolymer ($M_2O \cdot Al_2O_3 \cdot 4SiO_2 \cdot 11H_2O$) composites made with chopped fibers have been systematically studied. Geopolymers were manufactured at ambient temperature and cured in polymer molds in a constant temperature oven at 50 °C. The effects of varying weight percentages of fibers, processing conditions and heat treatments (i.e., annealing time to effect dehydration or crystallization) were examined by comparing the strengths and Weibull statistics of each sample with thoe of pure geopolymer. As an example, the effect of chopped basalt fibers of lengths of 1/2 or 1 inch increased the strength of bend bars broken in a three point flexure tested as a function of temperature to 1500 deg. C

9:00 AM

(ICACC-FS1-011-2011) Thermal Properties of Metakaolin Based Geopolymers

M. Lizcano*, Texas A&M University, USA; K. Lozano, University of Texas Pan American, USA; M. Radovic, Texas A&M University, USA

The thermal properties of alkaline activated geopolymers have been investigated. The metakaolin-based geopolymers were prepared by mechanically mixing metakaolin and alkaline silicate aqueous solutions to obtain samples with Si/Al atomic ratios ranging from 1.25 to 2.5 and M/Al atomic ratios equal to 1 where M is the alkaline metal ion. Geopolymer samples were cured in a laboratory oven for 24 hour at 80 oC in the sealed conditions. Structural characterization of the samples was carried out using X-Ray Diffraction (XRD) and Nuclear Magnetic Resonance (NMR). Thermal analysis was carried using Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA), Thermomechanical Analysis (TMA), and Thermal Constant Analysis (TCA) in the 25 to 1000 oC temperature range. Results of this study suggest that changes of thermal conductivity, heat capacity, and thermal expansion with temperature, depend on Si/Al ratio and porosity of the samples. In addition, it was found that the water release during first heating effect significantly thermal properties of geopolymers. Relationship between thermal properties of geopolymers and their structure and composition is discussed in more detail in this paper.

9:20 AM

(ICACC-FS1-012-2011) Synthesis and thermal properties of fly-ash based geopolymer pastes and mortars

C. Panagiotopoulou*, A. Asprogerakas, G. Kakali, S. Tsivilis, N.T.U.A, Greece

The present work deals with the synergetic effect of selected synthesis parameters on the compressive strength development of fly ash-based geopolymers. In addition, the thermal behavior of fly ash-based geopolymer pastes and mortars is also studied. The experimental consists of two parts: The geopolymer synthesis using the Taguchi experimental designing model which involved the variation of three control factors in three levels: i) 0.8≤R/Al≤1.2, ii) 0≤Na/(Na+K)≤1.0 and iii) 1≤[Si]/R2O≤2.0. The synthesis of two series of geopolymer specimens using the optimum synthesis (resulted from the first part) and sand/fly ash ratios 0 and 1. The specimens were exposed to temperatures up to 800○C. The dimensional and mass changes caused by the thermal treatment were studied, while the integrity of the samples was evaluated on the basis of pulse velocity measurements before and after the thermal exposure. In all cases, the compressive strength of the specimens was measured, and the structural changes were investigated by means of XRD, FTIR and SEM. The optimal synthesis conditions for Greek fly ash geopolymers were R/Al=1.0, Na/(Na+K)=1.0 and [Si]/R2O=1.0, while the factor having the highest impact on the development of compressive strength was the [Si]/R2O ratio. The thermal behavior of geopolymer pastes and mortars is also discussed.

10:00 AM

(ICACC-FS1-013-2011) Mechanical Response of Discontinuous Filament PVA Fiber Reinforced Geopolymers (Invited)

B. Varela*, J. W. Rogers, Rochester Institute of Technology, USA

The use of several types of fibers has been widely used to reinforce brittle materials. The use of fibers add the benefit of ductility, flexural and impact strength to the brittle matrix. Geopolymers are an emerging new class of ceramic materials with great potential in several industries. Fibers such as glass, carbon, boron and natural fibers,

among others, have been explore as reinforcement for geopolymers and reported in the scientific literature. The high alkalinity of the paste can hinder the range of possible fibers to use however, Polyvinyl Alcohol fibers proved to be stable under this conditions and to provide reinforcement to the geopolymer matrix. This work presents results from compressive and three point bending tests in an F type fly ash geopolymer when volume fraction substitution is the range of 0.5% to 1.5%. Results shown better enhancement in the ductility of the geopolymer after 28 days when 5mm long PVA fibers were used.

10:30 AM

(ICACC-FS1-014-2011) Effect of External and Internal Calcium in Synthetic Fly Ash on Geopolymer Properties (Invited)

K. Somna*, W. Bumrongjaroen, W. Gong, I. Muller, Catholic University of America, USA

The effect of external and internal calcium on the geopolymer formation was investigated. The specimen with external calcium was obtained by adding Ca(OH)2 to the geopolymer made with synthetic fly ash with low calcium content. The specimen with internal calcium was prepared by using synthetic fly ash with high calcium content in the geopolymer mix. Synthetic fly ash was used instead of real fly ash to control the glass composition in fly ash and to avoid the effect of calcium from mineral phases. Synthetic fly ash glasses with low and high calcium content were prepared from lab grade chemical oxide as a starting material for geopolymer matrices. The fly ash glass was ground and then mixed with NaOH solution and silica fume. The products were characterized by FTIR and DTA techniques to study the polymerization of the gel. The presence of calcium composite gel was determined by the difference in FTIR pattern before and after acid leaching which is specific for calcium composite gel. The leachate was analyzed by ICP to determine the gel composition and Ca/Si. The compressive strength of geopolymer was investigated to study the contribution of these gels to the strength of the geopolymer.

Phosphate-Based Inorganic Polymers

Room: Coquina Salon F
Session Chair: Hubert Rahier, Vrije Universiteit Brussel

11:00 AM

(ICACC-FS1-015-2011) Phosphate Geopolymeric Materials (Invited)

A. Wagh*, Consultant, USA

Chemically bonded phosphate ceramics/cements (Ceramicrete for Mg-phosphate compositions) are room temperature-setting inorganic materials with high strength, low porosity, and good durability. These characteristics are similar to alumino-silicate geopolymers. Studying their structure this author speculated that they may be a class of geopolymers in the annual meeting of the American Ceramic Society in 2004. Subsequently, Joseph Davidovits in his book on Geopolymers (2008) proposed chemistry and structure of phosphate and phospho-silicate geopolymers based on compositions developed in Argonne. His analysis gives key understanding of the amorphous phase found in these materials that is responsible for their high strength and dense structure. We propose here that the micro structure of phospho-silicate geoplymers consists of a network of crystalline phosphate structures connected by phospho-silicate geopolymeric amorphous materials. Evidence is provided with X-ray diffraction studies, micro structural studies and strength properties. We also propose an interesting argument for further research that because of content of phosphates in Nile delta, possibly phospho-silicates might have also contributed to the binding structure of the rocks used in Egyptian pyramids.

11:30 AM

(ICACC-FS1-016-2011) Development of Phosphate Grout Formulations for Placement in Closed-Out Reactors (Invited)

Y. Yusufoglu*, R. Ganga, D. Singh, Argonne National Laboratory, USA

As part of the D&D activity at Savannah River Site, a grout formulation with neutral pH is required to fill the aluminum cooling tubes in closed-out reactors to prevent spread to contamination. High pH cement is expected to be corrosive to the aluminum tubes. Chemically bonded phosphate ceramics are identified as a potential candidate because of their low pH as compared to portland cement based formulations. In this presentation, we will discuss the different phosphate ceramic-based formulations developed and evaluated to meet the requirements for grout placement as identified by the end user. Specific properties tailored were flow characteristics of the grout, gel time, compressive strength build up, and the temperature rise during the grout setting. Results on the evaluations will be presented.

FS2: Computational Design, Modeling, and Simulation of Ceramics and Composites

Novel Simulation Methods for Materials Processing and Performance

Room: Coquina Salon D
Session Chairs: Peter Gumbsch, KIT; Z. Liu, Pennsylvania State University

8:00 AM

(ICACC-FS2-020-2011) Thermodynamic Modeling in Zirconia-base Systems for Thermal Barrier Coatings (Invited)

H. J. Seifert*, M. Kriegel, O. Fabrichnaya, Technical University of Freiberg, Germany

A thermodynamic database for thermal barrier coating applications is presented. Analytical descriptions for the Gibbs energies of stoichiometric and solution phases in the system ZrO2-Y2O3-Al2O3-RE2O3 (RE = La, Nd, Sm, Gd, Yb) were developed. Sublattice models described in the Compound Energy Formalism were used to take into account the crystal structures and site occupancies of various species on Wyckoff positions. Reciprocal phase reactions determined a reasonable number of adjustable model parameters. To adjust these parameters experimental thermodynamic and phase diagram data were used. The data from thermal analysis and scanning electron microscopy (SEM) with EDX provided information on the character of phase transformations and solid solution ranges as a function of temperature. Enthalpies of formation and heat capacities of aluminates and pyrochlore phases were measured by high temperature calorimetry. These data were also used for dataset development. Based on the analytical descriptions various thermodynamic functions and extrapolated phase diagrams were calculated. The relevance of these data is discussed for materials of interest for thermal barrier coating applications.

8:30 AM

(ICACC-FS2-021-2011) Developing High-Performance Materials in Clean Power Systems: An Integrated Computational and Experimental Approach (Invited)

M. Gao*, D. Tafen, K. Wu, R. Hu, V. Jain, O. Dogan, J. Hawk, National Energy Technology Lab, USA; M. Widom, Carnegie Mellon University, USA

In order to reduce harmful environmental mission from coal-fired power plants, National Energy Technology Lab has developed various technologies to improve the efficiency in power generation. Accordingly there are urgent needs to design high-performance materials for these new technologies. For example, high-temperature structural alloys based on Cr and Nb for land based power plant components to be used in oxy- or hydrogen combustion turbines; multicomponent CuPd-based crystalline alloys and non-Pd amorphous alloys for hydrogen separation in water gas shift and steam reforming reactions

for efficient conversion of methane to hydrogen. We have adopted an approach that integrates computer simulations with critical experiments to accelerate new materials design. Balancing structure-property relationship require delicate tradeoffs and compromises by manipulating alloy system and composition, microstructure, coatings, and materials processing. During this talk, we will present ongoing research effort implementing this approach to design high-performance materials, using combination of computer simulation techniques such as first principles density functional theory calculations, Molecular Dynamics simulations, CALPHAD modeling, mesoscale microstructure simulations using phase field, and mechanical property simulations using discrete FFT and OOF.

9:00 AM

(ICACC-FS2-022-2011) Materials Design for Low Thermal Conductivity Ceramics (Invited)

J. Wang*, Y. Zhou, Shenyang National Laboratory for Materials Science, Institute of Metal Research, China

Searching new low thermal conductivity materials alternative to the commercialized yttria-stabilized zirconia (YSZ) is a 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 theory for predicting high-temperature thermal conductivity. The present presentation showed that identifying new low thermal conductivity materials can be accomplished by two steps: firstly, first-principles calculations of equilibrium crystal structure, elastic modulus, as well as the average sound velocity; and secondly making theoretical prediction of minimum high-temperature thermal conductivity using the David Clark's model for insulating materials. Based on the theoretical investigations, we highlighted some ternary Y-Si-O silicates, ternary Y-Al-O aluminates, and quaternary Y-Si-O-N oxynitrides with very low theoretical minimum thermal conductivity. Thereafter, theoretical predictions are validated in experiments after new breakthroughs in synthesizing these candidates in dense and bulk forms.

9:20 AM

(ICACC-FS2-023-2011) Ab initio Calculation of Electrical Conductivity in Metals

Y. Mo*, P. Rulis, W. Ching, University of Missouri-Kansas City, USA

Electrical conductivity in metals and alloys is an important physical quantity for many of their applications. We present a method to calculate the temperature-dependent electrical conductivity $\sigma(T)$ in metals and alloys based on Kubo-Greenwood formula with the momentum matrix elements explicitly included. An accurate evaluation of intra-band transitions across a narrow region near the Fermi level is used to obtain $\sigma(0)$. The Orthogonalized Linear Combination of Atomic Obitals (OLCAO) method is used to obtain the electronic structure and wave functions in a large supercell to account for the intra-band transitions with sufficient statistics to reduce fluctuation. The temperature-dependent DC conductivity $\sigma(T)$ is then calculated from $\sigma(0)$ using the Fermi distribution function. The above method has been applied to pure metals Al, Fe, and Ni with $\sigma(0)$ values within a factor of 10 of the experimental data. The discrepancy could be related to the fluctuations associated with insufficient size of the supercell or the k points in the calculation. Additional test results and its extension to alloy systems will be presented.

10:00 AM

(ICACC-FS2-024-2011) Electronic structure, bonding, and spectroscopic properties of two new lithium nitridosilicates: Advocate for the effective ab initio OLCAO method (Invited)

W. Ching*, P. Rulis, University of Missouri-Kansas City, USA

Recently, two new three dimensional quaternary lithium alkaline earth nitridosilicate crystals Li2CaSi2N4 and Li2SrSi2N4 were synthesized at 900C [1]. The crystal parameters were fully determined by x-ray diffraction. Both have a complex cubic structure (space group Pa-3 and Z=12) with 108 atoms in the unit cell. The electronic structure, interatomic bonding, optical properties, and core level spectroscopic XANES/ELNES in the form of Li-K, Ca-K, Ca-L2,3, Sr-K, Sr-L2,3, Si-K, Si-L2,3, and N-K for all crystallographic nonequivalent sites were calculated using the ab initio linear combination of the atomic orbitals (OLCAO) method. Both are large gap semiconductors with a direct band gap of 3.48 eV and slightly different refractive indices of 2.05 and 2.12 respectively. The XANES/ELNES spectra for the two nonequivalent Ca(Sr) sites and the two N sites show noticeable differences, reflecting the dependence on local environment. The calculated Li-K edge is in good agreement with the measure EELS spectrum [1]. All the above results were obtained in less than two calendar days which demonstrates the efficiency and accuracy of the OLCAO method for studying fundamental properties of complex crystals. [1] M. Zeuner, S. Pagano, S. Hug, P. Pust, S. Schmiechen C. Sheu and W. Schnick, Eur. J. of Inorganic Chemistry (in press).

10:30 AM

(ICACC-FS2-025-2011) Development of Grain Boundary "Phase" Diagrams as a New Materials Science Tool (Invited)

J. Luo*, Clemson University, USA

Impurity-based, nanometer-thick, interfacial films have been widely observed, where they often control the microstructural evolution and materials properties [Crit. Rev. Solid State Mater. Sci. 32, 67 (2007)]. A series of HRTEM studies revealed that impurity-based, quasi-liquid, intergranular films can be thermodynamically stabilized well below the bulk solidus lines in ceramic materials such as Bi2O3-doped ZnO [J. Am. Ceram. Soc. 82, 916 (1999)] and refractory alloys such as Ni-doped W [Acta Mater. 55, 3131 (2007)] and Ni-doped Mo [APL 94, 251908 (2009)]. Enhanced mass transport in such liquid-like grain boundaries explained a long-standing mystery regarding the mechanism of "solid-state activated sintering". We propose a long-range scientific goal of developing grain boundary "phase" diagrams as a new materials science tool [APL 92, 101902 (2008); Curr. Opin. Solid State Mater. Sci. 12, 81 (2008)]. Most recent results on Mo-Ni and Mo-Si-B based alloys will be presented. Important lessons can be learnt via studying analogous phenomena at free surfaces [Annu. Rev. Mater. Res. 38, 227 (2008)]. Like free surfaces, first-order and continuous transitions can occur at grain boundaries [APL 95, 071911 (2009)], resulting the formation of discrete grain boundary complexions [see Prof. Martin Harmer's Sosman lecture feature article, J. Am. Ceram. Soc. 93, 301 (2010)].

11:00 AM

(ICACC-FS2-026-2011) Optimal elastic design of CFCs by microstructure modeling using semi-analytical methods

R. Piat*, G. Stasiuk, S. Dietrich, J. Gebert, Karlsruhe Institute of Technology, Germany; I. Tsukrov, University of New Hampshire, USA; T. Böhlke, A. Wanner, K. Weidenmann, Karlsruhe Institute of Technology, Germany

The aim of the proposed studies is development of the carbon/carbon composite with prescribed elastic properties. To achieve this, a microstructure optimisation problem for estimation of the microstructure with prescribed stiffness is formulated. The design variables of the posed problem are the local fibers distribution, pyrolytic carbon texture in the matrix and porosity. The volume fractions of the fibers and pores in the whole microstructure are fixed. Material properties of the local microstructure of the composite are calculated using virtual models. The semi-analytical homogenization procedures were used for development of these models. Modeling results are compared with elastic properties obtained experimentally by tension and compression test and ultrasonic studies of the bulk material. The numerical model predicting elastic properties of the material with the highest accuracy was identified and utilized for calculation of the optimal microstructure. Results of the microstructure optimization are verified by some model problems (e. g., for material

with maximal Young Modulus in one direction). Approaches to design microstructure for complicated loading cases are proposed.

11:20 AM

(ICACC-FS2-027-2011) Effects of Architecture on the Failure of Woven CMCs Via the Multiscale Generalized Method of Cells

K. Liu*, Arizona State University, USA; S. M. Arnold, NASA Glenn Research Center, USA; L. Necefer, University of Kansas, USA; A. Chattopadhyay, Arizona State University, USA

It is well known that failure of material is a locally driven event. In the case of ceramic matrix composites, significant variations in the microstructure of the composite exist and their significance on both deformation and life response need be assessed. In the present work, the effects of these architectural parameters and material scatter of woven ceramic composite properties at both the macro (woven RUC) and structural scale will be studied to assess their sensitivity at each length scale. The Multiscale Generalized Method of Cells methodology is used to determine the overall deformation response, proportional elastic limit (first meso cracking), and failure under both tensile and in-plane shear loading conditions. The macroscale responses investigated the effect of these parameters on a single RUC (five harness satin) of the weave fabric; whereas the structural response considered multiple RUCs with a random combination of various macroscale RUCs. Results show that at the macroscale, architectural effects can present a wide variation in responses, but the influence of these same effects at the structural scale are reduced. Material scatter effects implemented at the microscale also show little variation at the macro scale.

11:40 AM

(ICACC-FS2-028-2011) Characterization of non uniform veneer layer thickness distribution on curved substrate Zirconia ceramics using X-ray micro-tomography

M. Allahkarami*, J. C. Hanan, Oklahoma State University (OSU), USA

The fabrication process of bi-layer ceramics requires a temperature change from sintering to room temperature. Residual stresses created as a result of thermal expansion coefficient mismatch may be sufficiently large to influence failure. Theoretical models predict residual stress as a function layer thickness. The geometry changes during the firing process. In a case of complex geometries like dental crowns, micro-X-ray tomography is a unique non destructive technique for layer thickness measurement. A method of developing a finite mesh model of real components involving complex geometries has been developed through the use of X-ray micro-tomography. This method computes minimum distance between two triangulated surfaces constructed from tomography data. For each vertex of one surface it computes the closest point on the other surface. The veneer layer thickness distribution was combined with residual stress curves advancing our understanding of the lower limit threshold of thickness in dental restoration design. An important observation is the significant range in residual stress in the veneer top surface from a tensile stress of 80 MPa to a compressive stress of -70 MPa as the thickness increased to 0.5 mm.

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