

## TABLE OF CONTENTS

### **SPECIAL SECTION: Environmentally Benign Materials**

#### **Introduction: Green Materials and Green Processes**

J. Szekely, R. Laudise

#### **New Opportunities for Metals Extraction and Waste Treatment by Electrochemical Processing in Molten Salts**

D.R. Sadoway

#### **Environmentally Benign Vacuum Deposition with Air to Vacuum to Air Technology**

K.L. Barth, W.S. Sampath

#### **Morphology of Instability of the Wetting Tips of Eutectic SnBi, Eutectic SnPb, and Pure Sn on Cu**

H.K. Kim, H.K. Liou, K.N. Tu

#### **A Silver-Tin Alternative to Dental Amalgams**

M.P. Dariel, U. Admon, D.S. Lashmore, M. Ratzker, A. Giuseppetti, F.C. Eichmiller

#### **Aerosol Synthesis of AlN by Nitridation of Aluminum Vapor and Clusters**

S.E. Pratsinis, G. Wang, S. Panda, T. Guiton, A.W. Weimer

#### **Biocompatible Whiskers with Controlled Morphology and Stoichiometry**

W. Suchanek, H. Suda, M. Yashima, M. Kakihana, M. Yoshimura

#### **Design of Highly CO<sub>2</sub>-Soluble Chelating Agents for Carbon Dioxide Extraction of Heavy Metals**

A.V. Yazdi, E.J. Beckman

#### **A Process Engineering Approach to Remedy an Environmental Problem of Fugitive Lead Emissions during Lead Refining**

L. Wang, A.E. Morris

#### **Monoclinic ZrO<sub>2</sub> and Its Supported Materials Co/Ni/ZrO<sub>2</sub> for N<sub>2</sub>O Decomposition**

H.C. Zeng, J. Lin, W.K. Teo, J.C. Wu, K.L. Tan

#### **Development of Copper-on-Alumina Catalytic Materials for the Cleanup of Flue Gas and the Disposal of Diluted Ammonium Sulphate Solutions**

G. Centi, B.K. Hodnett, P. Jaeger, C. Macken, M. Marella, G. Paparatto, S. Perathoner

#### **Activated Carbon for Control of Nitrogen Oxide Emissions**

A.M. Rubel, M.L. Stewart, J.M. Stencel

### **ARTICLES**

#### **Indentation Induced Deformation and Microcracking of Highly Textured Superconducting (Bi,Pb)<sub>2</sub>Sr<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> Ceramic**

W. Lo, A.M. Campbell, J. Luo, R. Stevens

#### **Cluster/Dislocation Interactions in Dilute Aluminum Based Solid Solutions**

C.L. Rohrer

#### **Monte Carlo Simulations of Long Range Order Kinetics in B2 Phases**

K. Yaldram, V. Pierron-Bohnes, M.C. Cadeville, M.A. Khan

#### **A Study of the Ultrasonic Technique Applied in Fabrication of SiC Fiber Reinforced Aluminum Composites**

J. Pan, D.M. Yang, X.F. Yin, H. Fukunaga

#### **Fabrication, Microstructure, and Mechanical Properties of TaC Particulate and SiC Fiber-Reinforced Lithia-Alumina-Silica Composites**

H-H. Shin, R. Kirchain, R.F. Speyer

#### **Fiber Strength Utilization in Carbon/Carbon Composites: Part II. Extended Studies with Pitch- and Pan-Based Fibers**

R.J. Zaldivar, G.S. Rellick, J.M. Yang

#### **Modification of the Surface Properties of Carbon Fibers via the Catalytic Growth of Carbon Nanofibers**

W.B. Downs, R.T.K. Baker

#### **Change of the Critical Thickness in the Preferred Orientation of TiN Films**

U.C. Oh, J.H. Je, J.Y. Lee

#### **Kinetics of the Reactive Spreading of Molten Aluminum on Ceramic Surfaces**

D.A. Weirauch, Jr., W.M. Balaba, A.J. Perrotta

#### **Investigation of SiC-AlN System: Part I. Microstructure and Solid Solution**

J-L. Huang, J-M. Jih

#### **Mechanical Solid State Reaction for Synthesis of β-SiC Powders**

M.S. El-Eskandarany, K. Sumiyama, K. Suzuki

#### **Chemistry, Microstructure, and Electrical Properties at Interfaces between Thin Films of Titanium and Alpha (6H) Silicon Carbide (0001)**

L.M. Porter, R.F. Davis, J.S. Bow, M.J. Kim, R.W. Carpenter, R.C. Glass

#### **Epitaxial Growth of PbTiO<sub>3</sub> Thin Films on (001) SrTiO<sub>3</sub> from Solution Precursors**

A. Seifert, F.F. Lange, J.S. Speck

#### **Synthesis and Characterization of TiO<sub>2</sub> Thin Films on Organic Self-Assembled Monolayers: Part I. Film Formation from Aqueous Solutions**

H. Shin, R.J. Collins, M.R. De Guire, A.H. Heuer, C.N. Sukenik

#### **Synthesis and Characterization of TiO<sub>2</sub> Thin Films on Organic Self-Assembled Monolayers: Part II. Film Formation via an Organometallic Route**

H. Shin, R.J. Collins, M.R. De Guire, A.H. Heuer, C.N. Sukenik

#### **Fabrication of Sr<sub>2</sub>Nb<sub>2</sub>O<sub>7</sub> Thin Films by Sol-Gel Processing**

A.V. Prasadarao, U. Selvaraj, S. Komarneni

#### **Structures and Electrical Properties of Barium Strontium Titanate Thin Films Grown by Multi-Ion-Beam Reactive Sputtering Technique**

C-J. Peng, S.B. Krupanidhi

#### **Synthesis of β-Sialon from Coals or Natural Graphite**

F.J. Narciso, A. Linares-Solano, F. Rodríguez-Reinoso

#### **Effects of Radiation on SiC-Based Nicalon Fibers**

L.L. Snead, M. Osborne, K.L. More

#### **A Combustion Synthesis Process for Synthesizing Nanocrystalline Zirconia Powders**

K.R. Venkatachari, D. Huang, S.P. Ostrander, W.A. Schulze, G.C. Stangle

#### **Preparation of Nanocrystalline Yttria-Stabilized Zirconia**

K.R. Venkatachari, D. Huang, S.P. Ostrander, W.A. Schulze, G.C. Stangle

#### **Influence of Yttria Content on the Preparation of Nanocrystalline Yttria-Doped Zirconia**

D. Huang, K.R. Venkatachari, G.C. Stangle

#### **A Novel Process for Combustion Synthesis of AlN Powder**

W-C. Lee, C-L. Tu, C-Y. Weng, S-L. Chung

#### **Kinetics of Hydrogen Desorption from Palladium and Ruthenium-Palladium Foils**

A.L. Cabrera, E. Morales L., J.N. Armor

## ABSTRACTS

**SPECIAL SECTION: Environmentally Benign Materials****Introduction: Green Materials and Green Processes**J. Szekely\*, R. Laudise<sup>†</sup>(\*Massachusetts Institute of Technology, <sup>†</sup>AT&T Bell Laboratories)

The societal concern about the environment is worldwide, and in more recent times, this has been translated into concrete action in terms of governmental regulations, citizen initiatives, and voluntary action by industry. The major strategies up until now have been command and control, regulate and remediate. Law, public policy, management, and science and technology have all focused on the end results of the chain of events, and have until very recently paid but minimal attention to root causes. It has to be recognized that, directly or indirectly, materials play a key role in the majority of our environmental problems, be it gaseous emissions from automobiles, or the waste streams resulting from metals production. Many of the residues in urban wastes are all closely related to materials issues. The containment and processing of various waste or pollutant streams also poses a whole range of materials issues.

Order No.: JA503-001

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**New Opportunities for Metals Extraction and Waste Treatment by Electrochemical Processing in Molten Salts**

D.R. Sadoway

(Massachusetts Institute of Technology)

Molten salt electrolysis is a proven technology for the extraction of metals—all the world's primary aluminum is produced in this manner. The unique properties of molten salts also make them excellent media in which to treat a variety of forms of waste. Of special note in this regard is electrolysis in molten oxides, a concept put forward by the author, initially as a "clean technology" for producing primary metal. However, in the context of waste treatment, electrolysis in molten oxides is a process offering the prospect of changing the valence of dissolved heavy metals while making pure oxygen gas as the main by-product. Laboratory tests conducted at a temperature of 1550°C on chromate sludge dissolved in a melt composed of Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, CaO, and MgO have confirmed electrochemical production of oxygen on a carbon-free anode.

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**Environmentally Benign Vacuum Deposition with Air to Vacuum to Air Technology**

K.L. Barth, W.S. Sampath

(Colorado State University)

The deposition of thin films and coatings frequently results in the generation of toxic waste, volatile organic compounds or large amounts of waste water and sludge. Vapor deposition in vacuum offers a more environmentally benign alternative, but is not prevalent outside of the microelectronics industry due to economic reasons. However, vacuum coating could be more widely accepted, and could potentially replace non-vacuum deposition methods, if either the cycle time or costs associated with vacuum coating were reduced. In order to reduce the cycle time for vacuum deposition, a robust system for continuous air to vacuum to air (AVA) transportation of discrete substrates has been developed and constructed in this study. This technology allows the insertion of discrete components into vacuum at high rates, without the need for venting the deposition chamber. Substrates have been repeatedly transported from atmosphere to 10<sup>-5</sup> torr in under a second. The capability of the AVA technology was studied through the deposition and characterization of CdS and CdTe films and photovoltaic devices. With the AVA technology, the need for venting the vacuum chamber to insert the substrates and subsequent pumping of the system for deposition is eliminated. The AVA technology could be applied to the processing of silicon wafers, compact disks, optical components, solar cells, cutting tools and fasteners.

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**Morphology of Instability of the Wetting Tips of Eutectic SnBi, Eutectic SnPb, and Pure Sn on Cu**

H.K. Kim, H.K. Liou, K.N. Tu

(University of California-Los Angeles)

The Pb-based solder used in the microelectronics industry is becoming an environmental issue. To understand the wetting behavior of solders with and without Pb, we have studied the surface morphology and wetting reaction of eutectic SnBi, eutectic SnPb, and pure Sn on Cu through the measurements of wetting angle change and wetting tip stability by SEM and EDX. The wetting angle remains constant after the initial spread, but the eutectic SnPb/Cu continues to react and forms a reaction band in front of the solder edge as well as intermetallic compounds at the interface. For eutectic SnBi/Cu, there is no reaction band at the wetting tip and the wetting angle does not change much, however, the interfacial reaction between eutectic SnBi and Cu forms intermetallic compounds at the solder joint; the wetting tip is not in a static equilibrium. A rough surface and edge was observed on the eutectic SnBi/Cu joint, but the eutectic SnPb/Cu has a smoother surface and edge.

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**A Silver-Tin Alternative to Dental Amalgams**

M.P. Dariel, U. Admon, D.S. Lashmore, M. Ratzker, A. Giuseppetti, F.C. Eichmiller

(National Institute of Standards and Technology)

This paper describes a novel technology for a mercury-free metallic direct filling material, substitute to dental amalgams. The consolidation relies both on cold-welding that takes place under moderate pressure between suitably surface-treated silver particles, and on silver-tin intermetallic compound formation at ambient temperature. A dilute acid is used for removing the silver surface oxide layers, thereby promoting the cold-welding process. The condensability, namely the ability of a loose powder to undergo consolidation within a short time duration, at body temperature and under moderate pressure has been investigated for a variety of mixtures of silver, tin, and pre-alloyed silver-coated intermetallic powders. The resulting metallic composite material displays transverse rupture strength values higher than those of amalgams, and somewhat lower values of compressive strength and Knoop hardness.

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**Aerosol Synthesis of AlN by Nitridation of Aluminum Vapor and Clusters**

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(\*University of Cincinnati, \*The Dow Chemical Co.)

Aluminum nitride (AlN) powders were produced in an aerosol flow reactor by direct nitridation of aluminum vapor with ammonia and nitrogen in flowing argon. In the presence of excess NH<sub>3</sub>, pure AlN powders were obtained from 1400 to 1873 K. These powders had higher specific surface areas than commercially available AlN powders. The effects of reactor temperature and gas flow rate on AlN purity, yield, and grain and crystallite size were investigated. The BET grain diameter of AlN increased as the process temperature increased, indicating sintering controlled particle formation and growth. Both the crystallite size and the BET grain size of pure AlN powders slightly decreased as ammonia flow rate was increased. Increasing temperature and flow rate increased the AlN yield.

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**Biocompatible Whiskers with Controlled Morphology and Stoichiometry**

W. Suchanek, H. Suda, M. Yashima, M. Kakhana, M. Yoshimura (Tokyo Institute of Technology)

Hydroxyapatite whiskers have been prepared by the hydrothermal method. The crystals had diameter, length, and aspect ratio in the range of 1–10 μm, 30–50 μm, and 5–20 μm, respectively. Their Ca/P molar ratio varied from 1.59 to 1.62. The morphology of the crystals

can be easily controlled by the concentrations of species in the starting solution, while the Ca/P ratio is almost independent of them. Through the reaction with calcite powder at 600°C, the Ca/P ratio of the whiskers has been improved even to the stoichiometric value of 1.67. Taking into account morphology and chemical composition of the HAP whiskers, they should not be health hazardous and may find applications as substitutes for asbestos and other fibrous materials which presently have restricted use because of their carcinogenic natures.

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#### Design of Highly CO<sub>2</sub>-Soluble Chelating Agents for Carbon Dioxide Extraction of Heavy Metals

A.V. Yazdi, E.J. Beckman  
(University of Pittsburgh)

Carbon dioxide is an attractive organic solvent in today's chemical process environment in that it is non-flammable, inexpensive, and exhibits low toxicity. Further, materials solubilized in carbon dioxide are easily and completely recovered/concentrated from solution via a simple pressure quench. Despite these favorable properties, CO<sub>2</sub> is non-polar, and therefore is a very poor solvent for materials such as conventional metal chelating agents, thus blocking application of carbon dioxide in metal extraction/recovery. Consequently, we are exploring the molecular design of materials which are highly CO<sub>2</sub>-phillic, that is, they exhibit solubilities in carbon dioxide which are significantly greater than alkanes with the same number of main-chain atoms. By functionalizing chelating moieties with CO<sub>2</sub>-phillic oligomers, we have generated materials which both effectively extract metals from solid matrices and which dissolve in carbon dioxide in significant quantities. The application of such chelating agents is not limited to soil cleaning operations. In fact, these chelates make the use of CO<sub>2</sub> possible in many applications where precision clean-up/recovery of metal ions are required. For example, CO<sub>2</sub> has been promoted as a replacement for CFC's in cleaning processes in the electronics industry. Use of these chelates would allow removal of metals along with other impurities in a CO<sub>2</sub> clean-up procedure.

Order No.: JA503-008

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#### A Process Engineering Approach to Remedy an Environmental Problem of Fugitive Lead Emissions during Lead Refining

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(University of Missouri-Rolla)

The refining of lead blast furnace bullion involves the transfer and handling of hot impure lead bullion. Fugitive emissions of lead-containing fumes create a plant hygiene problem. The cause of the emissions is the high vapor pressure of lead and its compounds when lead blast furnace bullion is transferred in an open ladle at ≈1000°C from the blast furnace and poured into the drossing kettle, and later during the manual skimming of powdery dross. A laboratory study was conducted on a new concept for lead refining which eliminates contact between hot lead and the environment, and thus abates fugitive lead emissions. The new process takes place in two steps: controlled solidification of bullion as it flows from the blast furnace, followed by remelting in a closed centrifuge to separate lead and dross. Refined lead was produced with <0.05% copper and <0.01% of all other impurities. Suggestions are outlined for implementing the process.

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#### Monoclinic ZrO<sub>2</sub> and Its Supported Materials Co/Ni/ZrO<sub>2</sub> for N<sub>2</sub>O Decomposition

H.C. Zeng, J. Lin, W.K. Teo, J.C. Wu, K.L. Tan  
(National University of Singapore)

Monoclinic ZrO<sub>2</sub> and its supported materials Co/Ni/ZrO<sub>2</sub> (Co:Ni=1:1) for catalytic decomposition of N<sub>2</sub>O have been studied with GC, FTIR, EDAX, XPS, and the evaluation of catalytic activity of the materials. It is found that monoclinic ZrO<sub>2</sub> alone has the catalytic effect for N<sub>2</sub>O decomposition although higher activities are found for Co/Ni/ZrO<sub>2</sub> systems. XPS study shows that only Co exists in the surface region of ZrO<sub>2</sub>, which is attributed to the formation of NiO-ZrO<sub>2</sub> solid solution resulting from an inter-diffusion between Ni<sup>2+</sup> and ZrO<sub>2</sub>

matrix. The gas decomposition on Co/Ni/ZrO<sub>2</sub> can be described as first order with respect to partial pressure of N<sub>2</sub>O. Surface reactions on ZrO<sub>2</sub> and Co/Ni/ZrO<sub>2</sub> will also be addressed.

Order No.: JA503-010

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#### Development of Copper-on-Alumina Catalytic Materials for the Cleanup of Flue Gas and the Disposal of Diluted Ammonium Sulphate Solutions

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Some aspects of the industrial development of copper-on-alumina catalytic materials for the combined removal of SO<sub>2</sub>(DeSO<sub>x</sub>) and NO<sub>x</sub>(DeNO<sub>x</sub>) from flue gas of power plants are discussed. The application of these catalytic materials for the recovery of sulphuric acid from diluted aqueous solutions of ammonium sulphate are also outlined. In particular, the following specific topics are analyzed: i) the relationship between textural and reactivity properties; ii) the problem of the design of samples with improved DeSO<sub>x</sub> properties in relation with the stability of the samples over extended operations; and iii) the optimization of the regeneration characteristics of the samples. Details on the flow sheet of the technology are also given.

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#### Activated Carbon for Control of Nitrogen Oxide Emissions

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Activated carbons were used to selectively remove NO<sub>x</sub> from simulated flue gas at temperatures between 25–125°C. Processing conditions and physical/chemical characteristics of the carbons which affected NO<sub>x</sub> adsorption, storage and release were investigated. Oxygen as a coreactant was necessary to maximize the conversion of NO to NO<sub>2</sub> and condensation of NO<sub>2</sub> within the pores of the carbons. A NO-to-NO<sub>2</sub> conversion mechanism is presented and discussed relative to previous research. A process for selectively removing NO<sub>x</sub> and concentrating it as NO<sub>2</sub> in an alternate process stream is outlined. The purified NO<sub>2</sub> stream could be used for chemicals manufacturing.

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#### ARTICLES

##### Indentation Induced Deformation and Microcracking of Highly Textured Superconducting (Bi,Pb)<sub>2</sub>Sr<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> Ceramic

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A high T<sub>c</sub> ceramic superconductor has been prepared having a high degree of preferred orientation, this having been generated by means of a large magnetic field during early stages of processing. The texture of the material has been characterized using XRD textural analysis, and the microstructure by high resolution electron microscopy. Pyramidal indentation (Vickers indent), deformation and cracking have been investigated using high resolution SEM. Semi-spherical deformation zones were formed under indents, a result of slipping of adjacent ab/ab (basal) plane grain boundaries and some microcrack development, together with lattice deformation on the basal plane. Densification of the green compact was also observed in the deformation zones, where lateral cracking has been seen to take place along the ab/ab plane grain boundaries. Radial cracking has been seen to take place along the low angle grain boundaries of the lattice ab/ab plane when indentations were made on the surface perpendicular to the preferred texture surface of the materials, and also at the highly deformed corners of indent diagonals. The stresses generated resulted in the fracture of the flake shaped grains and initiated small radial cracks. The Vickers microhardness of the textured ceramics was found to decrease with increasing load.

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### Cluster/Dislocation Interactions in Dilute Aluminum Based Solid Solutions

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The influence of single solute atoms and solute clusters on an extended edge dislocation dipole in Al was studied by atomistic simulation. Single Cu/ and Ag/dislocation interaction energy calculations showed that Cu interacts strongly with an Al extended dislocation and prefers sites in the compressive region, in agreement with elasticity theory predictions. Single Ag atoms, however, are strongly repelled by an Al extended dislocation, in contrast with elasticity theory predictions. Monte Carlo simulations of Al:1%Cu, Al:2%Cu, Al:1%Ag, Al:0.5%Cu,0.5%Ag, and Al:0.75%Cu,0.25%Ag were carried out in the presence of an extended dislocation dipole at 600 K allowing for solute segregation. Cu atoms in the binary alloys were observed to segregate to the compressive regions of the extended dislocation dipole, forming widespread "atmospheres" over the width of both extended dislocations which did not affect the partial dislocation spacing. Ag in the binary alloy formed small Ag zones which also had little influence on the spacing between the partials. The ternary systems, however, exhibited highly localized solute clusters which had a large impact on the extended dislocation dipole structure, increasing the separation between the partial dislocations. The resulting cluster structures are discussed along with their influence on the apparent stacking fault energy of the alloy systems.

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### Monte Carlo Simulations of Long Range Order Kinetics in B2 Phases

K. Yaldram, V. Pierron-Bohnes, M.C. Cadeville, M.A. Khan

*(IPCMS-GEMME)*

The thermodynamic parameters that drive the atomic migration in B2 alloys are studied using Monte-Carlo simulations. The model is based on a vacancy jump mechanism between nearest neighbor sites, with a constant vacancy concentration. The ordering energy is described through an Ising Hamiltonian with interaction potentials between first and second nearest neighbors. Different migration barriers are introduced for A and B atoms. The results of the simulations compare very well with those of experiments. The ordering kinetics are well described by exponential like behaviors with two relaxation times whose temperature dependences are Arrhenius laws yielding effective migration energies. The ordering energy contributes significantly to the total migration energy.

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### A Study of the Ultrasonic Technique Applied in Fabrication of SiC Fiber Reinforced Aluminum Composites

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By comparing the ultrasonic cavitation in several kinds of transparent liquid medium, we have investigated the cavitation effect in liquid. It is considered that the shock wave created by the cavitation in aluminum melt induces a high pressure and an elevated temperature field around the fibers, which can promote the wetting between fiber and aluminum, and have aluminum melt infiltrate into the fibers. Moreover, the experiment result shows that the fiber resonance catching with the cavitation is also an important factor for SiC/Al composites preparation. There exists a damage of the ultrasonic vibration on SiC fiber, if the fiber is acted long enough.

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### Fabrication, Microstructure, and Mechanical Properties of TaC Particulate and SiC Fiber-Reinforced Lithia-Alumina-Silica Composites

H-H. Shin, R. Kirchain, R.F. Speyer

*(Georgia Institute of Technology)*

Additions of 0 to 9 mol% Ta<sub>2</sub>O<sub>5</sub> to a lithia-alumina-silica glass-ceramic matrix Nicalon SiC reinforced composite increased the elastic modulus and ultimate strength of the composite. The additive fostered spherulitic growth of  $\beta$ -eucryptite solid solution crystals which concentrated Ta<sub>2</sub>O<sub>5</sub> at spherulite boundaries and adjacent to the fiber-matrix carbon-rich interphases. These regions reacted with the interphases as well as soluble carbon monoxide gas to convert them to TaC. The former reaction was shown to be thermodynamically favorable above 983°C while the latter was favorable above 1249°C. The improvement in mechanical properties was attributed to TaC particulate reinforcement, and suggests a simple glass-ceramic route to the fabrication of particulate-reinforced ceramic matrix composites.

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### Fiber Strength Utilization in Carbon/Carbon Composites: Part II.

#### Extended Studies with Pitch- and Pan-Based Fibers

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Measurements of fiber strength utilization (FSU) in unidirectional carbon/carbon (C/C) composites as a function of heat-treatment temperature (HTT) have been extended beyond the original group of DuPont pitch-based E-series fibers to include additional pitch- and PAN-based fibers. Fibers and composites were characterized by tensile strength, optical microscopy, SEM, fiber preferred orientation, and a single-fiber composite (SFC) fragmentation test to provide a relative measure of fiber-matrix interfacial shear strength (IFSS).

Results show that fracture behavior and FSU are dominated by the degree of fiber-matrix bonding, as inferred from the microscopic observations and measurements of IFSS. In the very high modulus pitch-based fibers, the behavior of the E130 is strikingly different from that of the Amoco and Nippon Oil fibers, in that it retains good bond strength and high FSU even with HT to 2400°C, in contrast to the other very high modulus pitch-based fibers that are already weakly bonded at the lowest HTT of 1100°C. All PAN-based fibers and lower modulus pitch fibers are characterized by strong bonding, brittle fracture, and low FSU for the 1100°C HTT. Subsequent heat treatment of these composites to 2150 and 2400°C, in most cases, results in significant recovery of FSU, suggesting an optimum IFSS for each composite. It is suggested that the difference in bonding between the pitch-based E-series and P-series fibers may be related to the similarity in fine structure between the E-fibers and high-modulus PAN-based fibers.

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### Modification of the Surface Properties of Carbon Fibers via the Catalytic Growth of Carbon Nanofibers

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The surface of commercial pitch and PAN-based carbon fibers has been modified by coating the structures with catalytically formed carbon nanofibers. Reaction conditions have been established that enable one to achieve optimum coverage by the secondary nanostructures without inducing any degradation in the mechanical properties of the parent fibers. Using this approach it is possible to produce a dramatic increase in the surface area of the fibrous structure from a nominal value of about 1.0 m<sup>2</sup>/g (untreated condition) up to between 250 to 300 m<sup>2</sup>/g (complete nanofiber coverage). This process results in a significant enhancement in the adhesion properties at the interface between the fiber and matrix components in a composite material. Mechanical tests performed on single uncoated and coated T300 carbon fibers demonstrated that it was possible to obtain an improvement of over 4.75 times in the interfacial shear strength of the fibers following deposition of a critical amount of nanofibers.

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**Change of the Critical Thickness in the Preferred Orientation of TiN Films**

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Recently it was observed through cross-sectional TEM that the preferred orientation of the TiN thin film was changed from (200) to (111) with thickness. In this study, the process of the change in the preferred orientation was studied near the critical thickness by the x-ray diffraction, and the value of the critical thickness could be estimated. The change of the critical thickness was also investigated with the strain energy per unit volume. The strain energy could be changed by controlling the energy of the bombarding particle, i.e., by adjusting the rf power, the working pressure and the substrate bias in sputtering. The critical thickness was decreased monotonically in all cases as the energy of the bombarding particle or the strain energy per unit volume was increased. These results surely show the dependence of the change of the preferred orientation on the strain energy in the TiN thin films.

Order No.: JA503-020

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**Kinetics of the Reactive Spreading of Molten Aluminum on Ceramic Surfaces**

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(Alcoa Technical Center)

The spreading kinetics of molten aluminum on ceramic surfaces bearing reactive coatings has been studied through the direct observation of sessile drops, either formed *in situ* or emplaced at temperature. Analysis of videotapes permitted the assessment of the rate of advance of rapidly spreading droplets. Experimental conditions in this study were chosen to avoid the severe retarding effect of the aluminum oxide film which is typically encountered in aluminum wetting experiments. A variety of reactive coating systems were examined (B, Cu, Ni, Ti, and Ti+B), and the effect of coating amount was assessed. Based upon the experiments of this study, the main effect of the coatings is to drive spreading due to strong exothermic interfacial reactions. The intensity of the interfacial reaction causes the change in free energy per unit area of interface to dominate the rate of movement of the triple line.

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**Investigation of SiC-AlN System: Part I. Microstructure and Solid Solution**

J-L. Huang, J-M. Jih

(National Cheng Kung University)

The primary aim of this present work lied in investigating the solubility, microstructure, thermal stability, AlN polytypes, and interfacial reactions in the SiC-AlN system. Alpha SiC particles of different sizes were incorporated into AlN and hot pressed at 2050°C to 2250°C for 1 to 3 hr. XRD, OM, STEM, WDS, and SAD patterns were utilized in analyzing phases, morphology, and distribution of elements.

Surface area of SiC particles was found as having substantial effects on the formation of solid solution. Multilayered polytypes, which are usually associated with stacking faults, grew and impeded one another. Additionally, the number of planes between subsequent stacking increased with the increase of either hot pressing temperature or time. Affinity of oxygen to AlN probably played an essential role in the formation of polytypes and stacking faults.

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**Mechanical Solid State Reaction for Synthesis of  $\beta$ -SiC Powders**

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Stoichiometric  $\beta$ -SiC powders have been successfully prepared by solid state reaction of elemental silicon and carbon powders via the mechanical alloying process. The mechanical alloying process was

performed in a high energy ball mill under argon gas flow at room temperature. The solid state reacted alloy powders have been characterized as a function of the milling time by means of x-ray diffraction, infrared absorption, scanning and transmission electron microscopy, and chemical analysis. Complete fcc-SiC ( $\beta$ -phase) alloy powders were obtained after 1080 ks of continuous milling. The lattice parameter ( $a_0$ ) of the formed  $\beta$ -SiC was calculated to be 0.4357 nm. No free silicon and/or carbon crystals were observed. The existence of transverse optical (TO) and longitudinal optical (LO)-like phonon modes is observed for the end-product alloy powders. Mechanically alloyed  $\beta$ -SiC powders are stable at elevated temperatures (1773 K) and did not transform to any other phases. The end-product  $\beta$ -SiC alloy powders possess excellent morphological properties such as homogeneous shape (spherical morphology) with fine and smooth surface relief, and uniform size (less than 0.5  $\mu$ m in diameter). The fabricated  $\beta$ -SiC alloy powders have fine cell-like structure with nano-scale dimensions of about 7 nm.

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**Chemistry, Microstructure, and Electrical Properties at Interfaces between Thin Films of Titanium and Alpha (6H) Silicon Carbide (0001)**

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Epitaxial thin films (4–1000 Å) of Ti contacts have been deposited via UHV electron beam evaporation at room temperature on monocrystalline, n-type, alpha (6H)-SiC (0001). The interfacial chemistry and microstructure, and the electrical properties, were investigated at room temperature and after annealing at 700°C up to 60 min. High resolution TEM analyses revealed the formation during annealing of reaction zones consisting of  $Ti_5Si_3$  and TiC. The corresponding electrical properties exhibited considerable stability except after an initial 20 min. anneal. Current-voltage (I-V) measurements showed that the Ti contacts were rectifying with low ideality factors ( $n < 1.09$ ) and typical leakage currents of  $5 \times 10^{-7}$  A/cm<sup>2</sup> at -10 V. The Schottky barrier heights calculated from x-ray photoelectron spectroscopy and I-V and C-V measurements were between 0.79 and 0.88 eV.

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**Epitaxial Growth of PbTiO<sub>3</sub> Thin Films on (001) SrTiO<sub>3</sub> from Solution Precursors**

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A mixed alkoxide liquid precursor was used to form epitaxial PbTiO<sub>3</sub> thin films by spin-coating on cubic (001) SrTiO<sub>3</sub> substrates. The films were heat-treated at temperatures between 380°C/1 h and 800°C/1 h. X-ray diffraction, atomic force microscopy, scanning and transmission electron microscopy were used to characterize the microstructure of the films and to evaluate the epitaxial phenomena. At ~400°C/1 h, a polycrystalline, metastable Pb-Ti-fluorite crystallizes from the pyrolyzed amorphous precursor. At slightly higher temperatures (~420°C/1 h), the thermodynamically stable phase with the perovskite structure epitaxially nucleates at the film/substrate interface. A small number of epitaxial grains grow through the film toward the surface and consume the nanocrystalline fluorite grains. Coarsening of the perovskite grains leads to a reduction in mosaic spread during further heating. Pores, that concurrently coarsen with grain growth, produce a pitted surface as they disappear from within the film. At 800°C/1 h a dense epitaxial PbTiO<sub>3</sub> film with a smooth surface is observed. Parameters governing the formation of *a*- and *c*-domains are discussed as well as the small tilts of the domain axes away from the substrate normal.

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### Synthesis and Characterization of TiO<sub>2</sub> Thin Films on Organic Self-Assembled Monolayers: Part I. Film Formation from Aqueous Solutions

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(Case Western Reserve University)

Self-assembled monolayers (SAMs) bearing sulfonate (-SO<sub>3</sub>H) surface functional groups, on single crystal Si wafers, were used as substrates for the deposition of TiO<sub>2</sub> thin films from aqueous solutions. Polycrystalline TiO<sub>2</sub> thin films over 50 nm thick formed in 2 h by hydrolysis of TiCl<sub>4</sub> in aqueous HCl solutions at 80°C. The films were pore-free, showed excellent adherence and uniformity, and consisted of anatase crystallites 2–4 nm in diameter. Annealing at temperatures up to 600°C caused coarsening of the anatase grains but no loss of adherence or structural integrity.

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### Synthesis and Characterization of TiO<sub>2</sub> Thin Films on Organic Self-Assembled Monolayers: Part II. Film Formation via an Organometallic Route

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(Case Western Reserve University)

Crystalline, uniform, adherent, ultra-thin films of TiO<sub>2</sub> were deposited onto OH-functionalized organic self-assembled monolayers (SAMs) on single-crystalline Si at low temperature (<100°C) from anhydrous ethanolic solutions of titanium isopropoxide. The films were identified as TiO<sub>2</sub> by x-ray photoelectron spectroscopy, electron diffraction, and energy-dispersive x-ray microanalysis. Transmission electron microscopy showed the films to be uniform in thickness (2 ± 0.5 nm) and continuous. On bare Si, in contrast, there was no evidence of TiO<sub>2</sub> deposition under identical conditions. Unlike the anatase films deposited on SAMs from aqueous solutions (described in the preceding paper), the electron diffraction patterns of the films deposited from alkoxide solutions suggest that they were the rutile phase. It is suggested that the functionalized SAMs enable the anchoring of the Ti alkoxide and initiate the formation of an adherent oxide film, and that they are sufficiently uniform that the resulting film is continuous and uniform in thickness.

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### Fabrication of Sr<sub>2</sub>Nb<sub>2</sub>O<sub>7</sub> Thin Films by Sol-Gel Processing

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Sol-gel Sr<sub>2</sub>Nb<sub>2</sub>O<sub>7</sub> thin films were deposited on Si (100) and Pt-coated Si substrates for the first time by spin-coating. The Sr<sub>2</sub>Nb<sub>2</sub>O<sub>7</sub> precursor solution was prepared from strontium metal dissolved in 2-methoxyethanol, acetylacetone and niobium ethoxide. The formation of phase pure Sr<sub>2</sub>Nb<sub>2</sub>O<sub>7</sub> occurred via an intermediate perovskite phase of composition close to Sr<sub>0.82</sub>NbO<sub>3</sub>. Crack-free Sr<sub>2</sub>Nb<sub>2</sub>O<sub>7</sub> films of ~0.4 μm thickness were deposited on these substrates using a single-coating followed by heat treatment at 850°C for 12 h. SEM microstructure and thin film XRD results indicated the deposition of a grain oriented film on the Pt-coated Si substrate. The room temperature dielectric constant and the loss values of the film measured at 10 kHz are 45 and 0.045, respectively.

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### Structures and Electrical Properties of Barium Strontium Titanate Thin Films Grown by Multi-Ion-Beam Reactive Sputtering Technique

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(The Pennsylvania State University)

The structure and electrical properties of multi-ion-beam reactive sputter (MIBERS) deposited barium strontium titanate (BST) films were characterized in terms of Ba/Sr ratio, substrate temperature, annealing temperature and time, film thickness, doping concentration, and secondary low-energy oxygen ion bombardment. Films deposited onto unheated substrates, followed by annealing at 700 C showed

lower dielectric constant (<200), compared to a dielectric constant of about 560, for those deposited at elevated temperatures, probably due to reduced voids. Two types of microstructures (Type I and Type II) were observed depending on the incipient phase of the as-grown films, which also led to two types of time domain dielectric response, Curie-von Schweidler and Debye type, respectively. The current-voltage (I-V) characteristics of Type II films doped with high donor concentration showed a bulk space-charge-limited conduction (SCLC) with discrete shallow traps embedded in trap-distributed background at high electric fields. The I-V characteristics of bombarded films deposited at higher substrate temperatures showed a promising result of lower leakage currents and trap densities.

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### Synthesis of β-Sialon from Coals or Natural Graphite

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The synthesis of β-sialon has been carried out by heat treatment in nitrogen flow of Spanish coals or mineral graphite, both with a high content of mineral matter. The results were compared with those obtained with conventional clay/carbon mixtures. The coals and, especially, the mineral graphite produced a very high yield of β-sialon, with faster reaction rate than the clay/carbon mixtures due to the more intimate contact among the reactants, with the additional advantage of forming much lower proportion of vitreous phases. On the other hand, the results show that in the particular case of graphite, the use of high temperatures (even above 1450°C) does not lead to changes in the crystalline phases of the product, allowing the synthesis to be carried out over a wider temperature range than that used for clay/carbon mixtures. The mechanical properties of the sintered artifacts obtained with the sialon synthesized from natural graphite are superior to those prepared from clay/carbon mixtures and comparable (or even superior) to commercial artifacts manufactured from much more expensive precursors.

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### Effects of Radiation on SiC-Based Nicalon Fibers

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This paper presents neutron and ion radiation effects in the Nicalon SiC polymer precursor fiber. It is shown that the serious structural degradation of this fiber and its composites (e.g., CVD SiC/Nicalon) previously reported for the standard grade of Nicalon is primarily due to the presence of the silicon oxycarbide phase. Results supporting this interpretation include microstructural analysis as well as post irradiation mechanical property measurements. Preliminary results of the effects of irradiation on low-oxygen Nicalon fibers are presented. The reduced oxygen content fibers exhibit radiation induced density, strength, Weibull's and Young's moduli changes typical of monolithic ceramic materials. This contrasts sharply with the poor irradiation behavior of the standard Nicalon fiber and suggests that improved radiation resistance can be expected in SiC/SiC composites fabricated with low oxygen Nicalon fibers.

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### A Combustion Synthesis Process for Synthesizing Nanocrystalline Zirconia Powders

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Materials with nanocrystalline features are expected to have improved or unique properties when compared to those of conventional materials. Methods for the practical and economical production of nanoparticles in large quantities are not presently available. A method based on combustion synthesis for preparing nanocrystalline powders was investigated in this work. Ytria-doped zirconia powders with an

average crystallite size of 10 nm were synthesized. The characteristics of the powder (e.g., surface area and phase content) were found to depend strongly on the fuel content in the starting mixture and on the ignition temperature used in the process. The method is expected to be suitable for commercial fabrication of nanocrystalline multicomponent oxide ceramic powders.

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#### Preparation of Nanocrystalline Yttria-Stabilized Zirconia

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Nanocrystalline powder with an average crystallite size of 8–12 nm that was produced by a combustion synthesis process, was used to prepare dense, nanocrystalline articles. Green compacts of high green density were prepared by dry pressing, and densified by a fast-firing process. During fast-firing, the dwell temperature significantly affected the final grain size and final density. On the other hand, the ranges of heating rates and dwell times that were used had a much less significant effect on the final density and final grain size. It was determined, however, that a high final density (>99% pth) and a very fine final average grain size (<200 nm) can be simultaneously achieved under three different firing conditions. The high densification rates are, in part, a result of the minimal coarsening that the particles undergo when the sample is taken rapidly through the temperature regime in which surface diffusion predominates to the temperature regime in which the densification mechanisms of grain boundary and lattice diffusion predominate.

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#### Influence of Yttria Content on the Preparation of Nanocrystalline Yttria-Doped Zirconia

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Nanocrystalline zirconia doped with 0–10 mol%  $Y_2O_3$  has been prepared by a combustion synthesis process, followed by a rapid densification process. The concentration of  $Y_2O_3$  in the as-reacted zirconia appeared to have a significant influence on the reduction of the crystallite size, in the combustion temperature range studied (450°C–550°C), as well as on the stabilization of the tetragonal and/or cubic phases. The green compacts were densified by a fast-firing process. During fast-firing, the dwell temperature significantly affected the final average grain size and the final density of the article. On the other hand, the ranges of heating rates and dwell times that were used in this study were shown to have a much less significant effect on the article's final density and final average grain size. The yttria content had the largest influence on the final density and final average grain size. The densification took place much more rapidly in the 4 mol%  $Y_2O_3$ - $ZrO_2$  samples than in the 10 mol%  $Y_2O_3$ - $ZrO_2$  samples. In particular, the difference in densification rates between the samples with different  $Y_2O_3$  content was attributed to the influence and magnitude of the associated grain-growth process. It was determined, however, that a high final density (>99% pth) and a very fine final average grain size (<200 nm) could be simultaneously achieved with each of three different heating rates for the 4 mol%  $Y_2O_3$ - $ZrO_2$  articles.

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#### A Novel Process for Combustion Synthesis of AlN Powder

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(National Cheng Kung University)

A SHS process has been established for synthesis of AlN powder under low nitrogen pressures. Al and  $NaN_3$  powders were used as the metal and nitrogen sources, respectively. The compact of the mixture of the reactants was wrapped up with aluminum foil and then wrapped up with an igniting agent (i.e., Ti-C). The synthesis reaction was triggered by the combustion of the igniting agent. The wrappings were found necessary in achieving high product conversions under low nitrogen pressures (<1 MPa). The product conversion was also affected by the reactant composition and the nitrogen pressure. High conversions were obtained when the mass ratio of Al to  $NaN_3$  was 1/2 or lower and the nitrogen pressure was 0.5 MPa or higher. The AlN powders as synthesized were observed to have two major types of morphology, i.e., granular particles with 0.5–3  $\mu$ m in diameter and fibers with aspect ratios of 10–800.

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#### Kinetics of Hydrogen Desorption from Palladium and Ruthenium-Palladium Foils

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The adsorption of hydrogen and carbon monoxide at room temperature by palladium and 5% ruthenium-palladium foils was studied using thermal desorption spectroscopy. It was found that hydrogen readily diffused in the palladium and desorbed as one broad peak at about 650 K. Plots of the  $\ln(\text{rate})$  versus inverse absolute temperature indicate that the desorption order is  $n=1.25$  and the activation energy is about 8.5 Kcal/mol. Carbon monoxide is adsorbed, as two different states, on the surface of the foil and complete coverage is quickly reached below 100 L. Hydrogen also diffuses in 5% ruthenium-palladium foil but to a lesser degree. Two hydrogen desorption peaks are observed in the Ru-Pd alloy. The desorption traces can be fitted with two peaks and the desorption orders are  $n=2$  for the first peak and  $n=1.25$  for the second peak. Activation energies of 10.7 and 5.6 Kcal/mol are obtained for the first and second hydrogen peaks, respectively. The first hydrogen desorption peak is regarded as hydrogen desorbing from the surface sites while the second peak is regarded as hydrogen diffusing from below the surface. Activation energies for bulk diffusion were obtained from hydrogen uptake measurements using a sensitive microbalance. These energies corresponded to 4.4 Kcal/mol for Pd foil and 4.9 Kcal/mol for the Ru-Pd alloy. Discussion about the relation between these results with prior studies of hydrogen adsorption on Pd single crystal is included. The appearance of a fractional order for hydrogen desorption is also discussed.

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