JMR Abstracts

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Abstracts for February 1995 Journal of Materials Research *Volume 10, Number 2*

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ABSTRACTS

COMMUNICATIONS

Nanophase Ni Particles Produced by a Blown Arc Method
M.H. Teng, J.J. Host, J-H. Hwang, B.R. Elliott, J.R. Weertman, T.O. Mason, V.P. Dravid, D.L. Johnson
(Northwestern University)

Nanophase Ni particles (<10 nm in diameter) were produced by a blown arc method. A helium gas stream directed at the arc reduces the Ni vapor concentration and increases the quench rate. The helium gas velocity is the predominant factor influencing the size of the Ni particles. Gas velocities of 20 m/s and 56 m/s (at 26.6 kPa total helium pressure) resulted in Ni particle sizes of 13 nm and 7 nm, respectively.
Order No.: JA502-001

Retention of Nanostructure in Aluminum Oxide by Very Rapid Sintering at 1150°C
S.H. Risbud*, C-H. Shan*, A.K. Mukherjee*, M.J. Kim+, J.S. Bow+, R.A. Holl#
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Aluminum oxide powders doped with MgO (300 to 500 nm) were sintered to almost theoretical density within just 10–15 minutes at 1150°C using a plasma activated sintering process based on charging the loosely filled powders with an electric discharge prior to densification by resistance heating. The microstructure of the consolidated disks was examined by high resolution transmission electron microscopy (HREM) and electron energy loss spectroscopy (EELS) and revealed excellent grain to grain contact with virtually no grain growth and structurally clean grain boundaries.
Order No.: JA502-002

Phase Relationships in the System Si_3N_4-SiO_2-Yb_2O_3
T. Nishimura, M. Mitomo
(National Institute for Research in Inorganic Materials)

Silicon nitride is usually densified with the addition of oxides. The oxides produce liquid phase and retain in intergranular phase after sintering. As intergranular phase dominates strength at high temperature, a number of attempts to produce intergranular phase with high melting temperature have been done. Scandium oxide, yttrium oxide, and some kinds of lanthanide oxides have been used for this purpose.[1–6] Even if just one kind of oxide is added, ternary system Re_2O_3-SiO_2-Si_3N_4 (Re = Sc, Y, Lanthanide) should be considered as intergranular phase because SiO_2 exists on the surface of Si_3N_4 powder.
Order No.: JA502-003

Zircon: A Host-Phase for the Disposal of Weapons Plutonium
R.C. Ewing*, W. Lutze*, W.J. Weber+
*(*University of New Mexico, +Pacific Northwest Laboratory)*

Zircon, $ZrSiO_4$, is a well-characterized, naturally occurring phase that is extremely durable. Zircon has been synthesized with Pu-concentrations up to ten weight percent and radiation-damage effects studied to saturation doses of nearly 0.8 displacements per atom. We propose that zircon be used as a waste form for the disposal of the more than 100 metric tons of plutonium that will result from the dismantling of nuclear weapons. There are already several demonstrated processing technologies, of which hot pressing offers the most potential. This highly durable material, even under hydrothermal conditions, with its high waste loading and smaller volume allows deep, permanent disposal of the weapons plutonium in geologic environments in which the borosilicate waste form glass would not be stable.
Order No.: JA502-004

Vapor Grown Carbon Fiber Reinforced Aluminum Composites with Very High Thermal Conductivity
J-M. Ting, M.L. Lake
(Applied Sciences, Inc.)

The first use of continuous vapor grown carbon fiber (VGCF) as reinforcement in aluminum metal matrix composite (Al MMC) is reported. Al MMC represents a new material for thermal management in high-power, high-density electronic devices. Due to the ultra-high thermal conductivity of VGCF, 1950 W/m-K at room temperature, VGCF reinforced Al MMC exhibits excellent thermal conductivity that cannot be achieved by using any other carbon fiber as reinforcement. An unprecedented high thermal conductivity of 642 W/m-K for Al MMC was obtained by using 36.5% of VGCF.
Order No.: JA502-005

Carbon Nanostructures in Silica Aerogel Composites
X-Y. Song, W. Cao, M.R. Ayers, A.J. Hunt
(University of California-Berkeley/Lawrence Berkeley Laboratory)

A new method of preparing carbon nanotubes and their derivatives using silica aerogels as a matrix for the deposition of carbon is repeated. We present results of observations of graphite tubes and rings including nested structures in nanometer dimensions using high resolution transmission electron microscopy. Furthermore, we propose a model for the growth of carbon nanotubes in three steps including nucleation, growth, and closure of tubes.
Order No.: JA502-006

On the Use of Shape Correction Factors for Elastic Indentation Measurements
B.C. Hendrix
(National Laboratory for Mechanical Behavior of Metallic Materials)

Elastic properties of small volumes of materials can be measured from the unloading of small indentations using the so-called nano-indentors. The analytic elastic solutions for axisymmetric indentors are currently used to calculate modulus from the unloading curve, sometimes using corrections derived for flat rigid punches. It is shown that these corrections represent an upper limit for the correction. More realistic corrections are derived for the Vickers, Berkovich, and Knoop indentor shapes using the assumption of uniformly loaded area. Results show that the axisymmetric solution overestimates the elastic compliance of the Vickers indentor by a factor of 1.0055, of the Berkovich indentor by a factor of 1.0226, and of the Knoop indentor by a factor of 2.682.

Order No.: JA502-007

Investigation of the Electroplastic Effect Using Optical and Conventional Techniques
C.T. Stanton, C.S. Coffey, F. Zerilli
(Naval Surface Warfare Center)

The electroplastic effect in materials is an interesting and potentially useful phenomenon in which an applied electric field affects the plastic flow properties of materials under strain. We have undertaken a study to use optical methods to monitor changes in alkali halide crystals undergoing the electroplastic effect. Some preliminary results from this work are presented along with more conventional quasi static measurements of the electroplastic effect.

Order No.: JA502-008

ARTICLES

Microstructure and Growth Mechanisms of $YBa_2Cu_3O_x$ Films Prepared by rf Thermal Plasma Evaporation
J. Tsujino, N. Tatsumi, Y. Shiohara
(Superconducting Research Laboratory-ISTEC)

We prepared $YBa_2Cu_3O_x$ films on (100)MgO and (100)$SrTiO_3$ substrates by rf thermal plasma evaporation, and investigated microstructure and growth mechanisms of these films by observation of the surfaces using an AFM technique. As a result, 2-D nucleation and further coalescence between vicinal grains were observed in the initial stage of growth. In the films prepared for deposition time of 3 min, the different complex growth modes including spiral growth, "birth and spread" growth, and 2-D growth were observed, which might be due to the high growth rate over 55 nm/min of this process.

Order No.: JA502-009

Simulated Growth and Microstructure of $DyBa_2Cu_3O_{7-x}$ with and without Dy_2BaCuO_5 Addition
N. Vandewalle, R. Cloots, M. Ausloos
(Université de Liège)

We present optical observations of magnetically melt-textured $DyBa_2Cu_3O_{7-x}$ with and without 20 wt.% excess of Dy_2BaCuO_5. From these observations, we propose some kinetic mechanism of the growth of 123 compounds. Kinetic processes can be simulated on computers. Two (very) simple models derived from the well-known Eden model are presented. They simulate the growth of the grain front. The simulated patterns agree with the observations. The microstructure of such materials cannot be explained by thermodynamic and chemical considerations alone, but explanations must include the kinetics of the growth front as well. From our observations, we conclude that the growth probability ratio g_{110}/g_{100} and g_{100}/g_{001} are of the order of 10 and 50, respectively.

Order No.: JA502-010

$(Mn,Zn,Fe)_{1-x}O$ Thin Films Showing Ferrimagnetic Property Deposited by Ion Beam Sputtering
H.S. Cho, S.K. Ha, M.H. Kim, H.J. Kim
(Seoul National University)

We deposited $(Mn,Zn,Fe)_{1-x}O$ thin films of the wüstite structure of SiO_2/Si(100) by ion beam sputtering using a single crystal Mn-Zn ferrite target. The wüstite structure of the as-deposited film, confirmed by XRD, TEM, and XPS analysis, appeared to originate from an oxygen-deficit ambient and also from the preferential resputtering of the oxygen ions in films during deposition. The as-deposited films showed ferrimagnetic characteristics having quite a large M_s in spite of their crystallographic structure—wüstite. Such an unusual phenomenon is presumably due to the different magnetic moments of the constituent cations with disordered distribution. The wüstite phase could be transformed into the spinel ferrite phase with the same preferred orientation during post-annealing under an appropriate oxygen partial pressure. The interplanar distance of the as-deposited films decreased with increasing T_s due to a release of compressive stress. The M_s of the film had a maximum value at about 275°C, while the resistivity, mainly governed by the grain boundaries, was almost of the same, irrespective of Ts.

Order No.: JA502-011

Precursors of Amorphization in Supersaturated Nb-Pd Solid Solutions
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The possibility that crystal-to-amorphous phase transformations can be induced by one or more underlying instabilities of the crystalline phase has been investigated in highly supersaturated solid solutions of Nb-Pd. Several unusual properties were discovered that may be identified as precursor effects of the collapse of the bcc α-Nb terminal solution to the amorphous phase. Elastic neutron diffraction measurements of α-Nb solutions found, with increasing Pd concentration, an anomalously large increase of the average atomic root-mean-square displacement to about half of the value at which the Lindemann criterion predicts the lattice should melt. Low-temperature heat capacity measurements yielded a concomitant decrease in the Debye temperature, suggesting that supersaturation causes an elastic modulus to soften. Single crystals of α-Nb solutions at high supersaturations have a highly anisotropic structure that is visible in transmission electron microscopy images; it is consistent with the development of a soft phonon mode leading to a bcc-to-ω phase transformation. Considered together with the results of other recent experiments, these findings suggest that shear instability of the crystalline phase plays an important role in the crystal-to-amorphous transformation and that the average static mean-square displacement of atoms in the lattice acts as a useful parameter for the stability of the crystal with respect to amorphization.

Order No.: JA502-012

Magnetic Hardening of Melt Spun 2:14:1-Based Materials by High Heating Rate and Short Time Crystallization Treatments
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Systematic studies have been carried out about the effects of the thermal treatment parameters on melt spun materials quenched at different cooling rates and based on the 2:14:1 hard magnetic phase. Samples of nominal compositions $Dy_3Nd_{10.2}Fe_{79.6}B_6Si_{1.2}$ and $Pr_3Nd_{10.2}Fe_{79.6}B_6Si_{1.2}$ were annealed at temperatures above that of crystallization of the amorphous phases present upon quenching, for times ranging from 1 to 30 minutes and by using different heating rates up to the annealing temperature. It is concluded that best hysteretic properties can be achieved in samples quenched at intermediate cooling rates by means of short time thermal treatments performed by

using high heating rates up to the treatment temperature. Low heating rates and long time anneals lead to the deterioration of the hard magnetic behavior, due to the segregation of soft crystalline phases.
Order No.: JA502-013

Preparation of Textured Alumina Films by the Sol-Gel Route
J. Campaniello, P. Berthet, F. d'Yvoire, A. Revcolevschi
(Université Paris Sud)

Alumina films were fabricated by the sol-gel route under various preparation conditions. The peptization rate and the structure of colloidal particles depend on these conditions. In particular, the peptization of a dried boehmite precipitate prepared from aluminum alkoxide was achieved within a few seconds without heating. The resulting sol is made of highly-dispersed crystallites; this allows the formation of well-textured xerogel films as evidenced by the Weissenberg x-ray method.
Order No.: JA502-014

The Oxidation of an Aluminum Nitride Powder Studied by Bremsstrahlung-Excited Auger Electron Spectroscopy and X-ray Photoelectron Spectroscopy
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Bremsstrahlung-excited Auger electron spectroscopy (AES) was used to study the oxidation kinetics of an aluminum nitride powder oxidized in air at 750, 800, 850, and 900°C. An equation was derived to calculate the average surface oxide film thickness from the aluminum AES spectra. The oxidation of this powder was found to follow a parabolic rate law within this temperature range. The measured activation energy was 230 ± 17 kJ/mol (55 ± 4 kcal/mol). Analysis with x-ray photoelectron spectroscopy (XPS) showed that in addition to the nitride N 1s peak, there was a second N 1s peak. This peak has been observed in previous studies and can be attributed to N-O bonding either within the growing oxide film or at the Al_2O_3/AlN interface.
Order No.: JA502-015

Preparation of Barium Titanate Ceramics from Amorphous Fine Particles of Ba-Ti-O System and its Dielectric Properties
S. Wada, T. Suzuki, T. Noma
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Using titanium nitrate solution stabilized by chelation, amorphous fine particles of Ba-Ti-O system were prepared by mist decomposition method in air. After the calcination of these particles, barium titanate ceramics were prepared using hot uniaxial pressing method, and various properties were investigated. As a result, the grain sizes could be controlled over the range from 58 nm to 187 nm by the sintering temperatures and/or the calcination temperatures, keeping the density almost constant. Moreover, the dielectric properties of the samples showed that the relative permittivity decreased with decreasing grain size, and Curie temperature also shifted to lower temperatures in the same way. In this study, we first found that Curie temperature existed in the barium titanate ceramics with grain sizes from 58 to 147 nm.
Order No.: JA502-016

Microwave Characteristics of $BaPr_2Ti_4O_{12}$ and $BaPr_2Ti_5O_{14}$ Ceramics
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Microwave dielectric properties and microstructures of $BaPr_2Ti_4O_{12}$ and $BaPr_2Ti_5O_{14}$ ceramics which have extremely similar crystal structure were investigated, including those of the solid solution represented with the formula of $Ba_{6-x}Pr_{8+2x/3}Ti_{18}O_{54}$ ceramics. It is suggested that $BaPr_2Ti_5O_{14}$ ceramics are composed of mixed phases, approximately 85.0 vol% $Ba_{4.05}Pr_{9.3}Ti_{18}O_{54}$ (x=1.95), 8.1 vol% TiO_2 and 6.9 vol% $BaTi_4O_9$. The microwave dielectric properties of $Ba_{6-x}Pr_{8+2x/3}Ti_{18}O_{54}$ system are strongly dependent on *x* value, which is interesting for studying the relationship between microstructures and dielectric properties. Far infrared reflection spectra were also measured to study the mixed phases formed in these ceramics in more detail.
Order No.: JA502-017

Low Pressure Chemical Vapor Deposition of B-N-C-H Films from Triethylamine Borane Complex
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In this study, films consisting of B-N-C-H have been synthesized by low pressure chemical vapor deposition using the liquid precursor triethylamine borane complex (TEAB) both with and without ammonia. When no NH_3 is present, the growth rate was observed to follow an Arrhenius behavior in the temperature range of 600 to 800°C with an apparent activation energy of 11 kcal/mol. A linear dependence of growth rate is observed as a function of square root of flow rate for the TEAB range of 20 to 60 sccm indicating that the reaction rate is controlled by the adsorption of borane. The addition of NH_3 to TEAB had the effect of lowering the deposition temperature down to 300°C and increasing the apparent activation energy to 22 kcal/mol. Above 650°C, the carbon concentration of the deposits increased significantly reflecting the break-up of the amine molecule. X-ray diffraction measurements indicated the films to be in all cases amorphous. Infrared spectra of the films showed absorption peaks representing the vibrational modes of B-N, B-N-B, B-H, and N-H. The index of refraction varied between 1.76 and 2.47 depending on composition of the films. Films deposited with no NH_3 above 700°C were seen to be compressive while films below that temperature were tensile. In the range of 350 to 475°C, the addition of NH_3 to TEAB resulted in films that were mildly tensile, while below 325°C and above 550°C, the films were found to be compressive. Both the hardness and Young's modulus of the films decreased with higher temperatures reflecting the influence of the carbon presence.
Order No.: JA502-018

Reactive IrO_2 Sputtering in Reducing/Oxidizing Atmospheres
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(EIC Laboratories)

An Ir metal target was reactively rf sputtered in a planar magnetron source to develop iridium oxide deposition conditions. Gas blends of hydrogen, oxygen, and argon were used to provide competitive control over the reduction/oxidation characteristics of the sputter plasma. Optical emission spectroscopy allowed direct observation of hydrogen, oxygen and iridium atomic peaks and OH molecular bands. Each of the twelve gas flow conditions could be clearly defined as either reducing or oxidizing by plasma emission spectroscopy. A given plasma reduction/oxidation state can be maintained over a wide range of gas flow conditions by coordinated adjustment of hydrogen and oxygen flows. The electrochemical properties of the iridium oxide films change dramatically in the vicinity of the reduction/oxidation plasma transition.
Order No.: JA502-019

Accelerated Microwave Synthesis of Magnesium Sulfide with the Pro-Heating Medium of Graphite
Y. Xu, X. Xiao
(Tsinghua University)

Two reaction routes had been tried for the synthesis of magnesium sulfide by applying microwave irradiation. In the first trial, finely grounded Mg and S were mixed intimately and heated in a microwave oven for various lengths of time (5 + 5 + 8 + 10 and 12 + 12 + 35 + 45 minutes) in a sealed quartz tube. In the second trial, the pro-heating medium (PHM) of graphite was introduced into the mixture of Mg and S and microwaved for only one minute. Results of x-ray diffraction analyses of the reaction products indicated that MgS polycrystallites (cubic, a_0 = 5.201 ± 0.001) had formed in the second trial, and that the MgS yield was greater than 98%. Data of EDAX and EPMA gave a formula of MgS with atomic ratio of Mg:S = 1.0:1.0. In contrast, MgS could not be identified in the reaction mixtures in the first trial. Obviously, graphite, as a PHM, played a key role in the dramatic enhancement of the rate of the reaction between Mg and S powders. Furthermore, the effect of different molar ratios of graphite to Mg on the rate of microwave synthesis was investigated.
Order No.: JA502-020

Characterization and Stabilization of Si_3N_4 Suspensions
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Two commercial Si_3N_4 powders were mixed with Al_2O_3 and Y_2O_3 through coprecipitation of the oxides from solutions of nitrates. The samples were characterized by XPS spectroscopy and electrophoretic mobility determinations on the suspensions. Sedimentations tests indicated that an oxylignin based polyelectrolyte proved effective in the dispersion of the powders. The adsorption of the deflocculant followed Langmuir type isotherms characterized by values of the standard free energy of adsorption in the range typical of physisorption processes. The results of the different characterizations are discussed pointedly and different localizations of the dispersant in the interfacial region of the different samples are proposed.
Order No.: JA502-021

Effects of Nb_2O_5 in (Ba, Bi, Nb)-Added TiO_2 Ceramic Varistors
S-L. Yang, J-M. Wu
(National Tsing Hua University)

Novel (Ba, Bi, Nb)-added TiO_2 ceramic was previously proved to be potentially used as varistor materials, and by varying atmosphere compensation the roles of barium and bismuth have been explored. The present work attempted to investigate how the third additive, niobium, operates on varistor characteristics. The content of added niobium is in the range from 0.125 to 1.0 cat%, while that of the other additives is always maintained at a constant value. The results show that adequate addition of niobium, 0.25 cat% Nb, is beneficial to the improvement of varistor characteristics. The variations of varistor behavior are discussed in terms of a point defect model. Two kinds of charge compensation, for the substitutional incorporation of niobium into the titanium rutile lattice, are also used to illustrate the variation. The detailed results and discussions are shown in this chapter.
Order No.: JA502-022

Rapid Synthesis of Transition-Metal Borides By Solid-State Metathesis
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A rapid self-sustaining solid-state precursor route to transition-metal borides, boride solid solutions and boride composites has been developed. Solid-state metathesis (SSM) reactions between transition-metal chlorides and magnesium boride (MgB_2) produce crystalline borides and magnesium chloride. Boride solid solutions are formed using mixed chloride precursors. By using a third precursor, such as NaN_3, boride-nitride composites are synthesized. The reaction products are characterized by powder x-ray diffraction, scanning electron microscopy, energy dispersive spectroscopy and inductively coupled plasma atomic absorption spectroscopy. These boride reactions become self-propagating when the adiabatic temperature is greater than the melting point of the byproduct salt, $MgCl_2$ (mp 987 K).
Order No.: JA502-023

Effects of Heat Treatment on Ag-Particle Growth and Optical Properties in Ag/SiO_2 Glass Composite Thin Films
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Small Ag particles were embedded in SiO_2 glass thin films by a multi-target sputtering method. The mean diameter of Ag particles in the as-deposited film with 28.0 at% of Ag was estimated to be 4.4 nm and it was increased to 24.0 nm when the film was heat-treated at 700°C for 3 h. The diameter was proportional to the cube root of the heat treatment time, suggesting that the Ag particles grew in the supersaturated solid solution. In the optical absorption spectra of the heat-treated films, the absorption peak due to the surface plasmon resonance of Ag particles was observed around 410 nm. The peak intensity became large and the full width at half maximum of the absorption band was decreased with increasing the diameter of Ag particles.
Order No.: JA502-024

Development of Fullerene-Reinforced Aluminum
E.V. Barrera, J. Sims, D.L. Callahan
(Rice University)

Powder metallurgy and casting have been used to produce aluminum with 1.3, 4, and 8 volume percent fullerene additions. Fullerene extract was mixed with Al and heat treated to obtain various levels of dispersion of the fullerenes. Intergranular dispersion of stable fullerenes was accomplished by both powder metallurgy and casting, however, x-ray diffraction indicated the formation of some Al_4C_3. Homogeneous dispersion did not occur because of limited diffusion in the solid state or limited solubility of fullerene in Al in the liquid state. Enhancements in hardness over that for Al were observed yet were not comparable to precipitation hardened Al alloys since a less homogeneous dispersion was achieved. Interest in Al having fullerene additions is for development of fullerene strengthened materials where fullerenes act as nanosize dispersoids for dispersion strengthening of metals or as a lightweight reinforcement in metal-matrix composites.
Order No.: JA502-025

Development of a Scanning Laser Crack Detection Technique for Corrosion Fatigue Testing of Fine Wire
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A scanning laser crack detection technique has been developed for use in corrosion fatigue testing of fine metallic wires. The technique has been integrated into a computerized data acquisition and control system allowing the unattended operation of extended fatigue tests. The system is capable of detecting cracks with surface lengths as small as 100 μm, with crack opening displacements as low as 1 μm. Detection schemes of light loss and light scattering have been successfully used to monitor crack initiation in air and in 0.9% sodium chloride solution. The present scanning laser system has been used for crack initiation detection in over 50 fatigue experiments and has the potential for use in crack growth monitoring. The method can provide information concerning other surface phenomena in addition to the study of cracks. The technique has potential applications beyond metallic wires, including fibers used in optics and ceramic reinforcement fibers used in structural composites.
Order No.: JA502-026

***In-Situ* X-ray CT Under Tensile Loading Using Synchrotron Radiation**
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Internal damage in metal matrix composite (MMC) under static tensile loading was observed by *in-situ* x-ray computed tomography based on synchrotron radiation (SR-CT). A tensile testing sample stage was developed to investigate the fracture process during the tensile test. Aluminum alloy matrix composites reinforced by long or short SiC fibers were used. The projection images obtained under tensile loading showed good performance of the sample stage, and matrix deformation and breaks of the long SiC fibers could be observed. In the CT images taken at the maximum stress just before failure, debondings of the short SiC fibers to the matrix, many pull-outs of the fibers, and matrix cracking could be clearly observed. The *in-situ* SR-CT allowed the observation of generation and growth of such defects under different tensile stress levels. The results from the nondestructive observation revealed that the MMC was broken by propagation of the matrix cracks which might be caused by stress concentration at the ends of the short fibers. A three-dimensional CT image reconstructed from many CT images provided easy understanding of the fiber arrangement, crack shape, and form of the void caused by fiber pull-out. *In-situ* SR-CT is a useful method for understanding failure mechanisms in advanced materials.
Order No.: JA502-027

An Experimental Fracture Mechanics Study of a Strong Interface: The Silicon/Glass Anodic Bond

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(University of Minnesota)

The fracture behavior of the silicon/Pyrex glass anodic bond was investigated using the methods of linear elastic bimaterial fracture mechanics. Due to the high bond strength, interfacial cracks were invariably observed to kink away from the interface into the more compliant glass under approximately Mode I remote tensile loading. Kink angles measured by profilometry increased from 14 to 28° as bonding temperature increased from 300 to 450°C. A regime of stable cracking accompanied penetration of cracks into the glass, with maximum load and corresponding fracture toughness measurement occurring at a location significantly removed from the interface. Approximately Mode I, near-interface, plane-strain fracture toughness values (K_{IC}) measured by rising load testing of chevron-notched and straight-thru-cracked compact-tension specimens increased from 0.63 to 0.68 MPa-$m^{1/2}$ and 0.66 to 0.75 MPa-$m^{1/2}$, respectively, as bonding temperature increased from 300 to 450°C. In addition, XPS measurements revealed a sodium depletion zone of decreasing size and depletion magnitude with increasing bonding temperature over the same range. The near-interface region of the glass also experiences compressive residual stresses which decrease linearly with distance from the interface according to linear elastic computations. These stresses increase in magnitude with increasing bonding temperature due to enhanced differential thermal contraction upon cooling to room temperature. It is proposed that the trends in toughness and in kink angle with bonding temperature can be at least partially accounted for by variation of crack tip shielding with compressive residual stress magnitude, the effects of interfacial crack tip shear stresses induced by the thermal mismatch, and by an increase in Young's modulus of the near-interface glass accompanying sodium depletion.

Order No.: JA502-028

A Model of Diffusion/Viscous Mass Transport in Silicates During Liquid-Phase Sintering

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The model of capillary transport of liquid metals driven by shear stress resulted from the displacement of menisci[1,2] is applicable to liquid-phase sintering of silicate/aluminosilicate glasses. The movement of a liquid phase between adjacent particles is compared with that in capillaries. It appears that the transport property of intergranular melt may be expressed by the viscosity (η) and volume diffusion (D) parameters if mean displacement of menisci is compared with the mean diffusive jump length of atoms/molecules (L). This leads to the following relation: $(\gamma/\eta)L = D_{cap}$, where α and D_{cap} are a specific permeability and volume diffusion coefficient. The use of this model requires the assumption that the diffusing species are also the viscous flow units, and they can be either atoms or structural units. This assumption seems to be applicable for depolymerized silicate melts if the dominant mass transport is initiated by the diffusion of both nonbridging oxygen and silicon atoms.

Order No.: JA502-029

EXAFS and RDF Studies of TeO_2-Li_2O Glasses

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Local arrangements around Te atoms of TeO_2-Li_2O glasses with four different Li_2O contents (15, 20, 25 and 30 mol.%) with Te K EXAFS spectroscopy and x-ray diffraction by making use of synchrotron radiation. EXAFS results based on the two-shell fitting method indicate that inter-atomic distances of Te-O in axial (ax) sites decrease from 0.208 to 0.197 nm with increasing Li_2O contents while distances between tellurium atom and oxygen atoms in equatorial (eq) sites change slightly from 0.190 to 0.188 nm. Total coordination numbers seemed to decrease slightly with increasing Li_2O contents. These results suggest the coordination states of tellurium atoms are changed from TeO_4 trigonal bipyramids to TeO_{3+1} polyhedra and TeO_3 trigonal pyramids. RDF results also suggest the changes of coordination states of tellurium atoms. TeO_{3+1} polyhedra in glasses are considered to be connected at the vertices with $Te\text{-}_{eq}O_{ax}$-Te or $Te\text{-}_{ax}O_{ax}$-Te linkage as seen in crystalline α-$Li_2Te_2O_5$.

Order No.: JA502-030

Exploration of the Deposition of Sub-Micrometer Particles by Spin-Coating

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The deposition of Cu, Zn, Pt and Co precursor particles from solution onto a flat silicon wafer using a spin coater was studied. Homogeneously distributed monodisperse particles can be obtained. The dependence of particle size and number density on solution concentration and rotation frequency was investigated. Different solvents and support modifications were studied. The particles were analyzed using dark field microscopy, scanning electron microscopy and atomic force microscopy.

Order No.: JA502-031

Nucleation and Selected Area Deposition of Diamond by Biased Hot Filament Chemical Vapor Deposition

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(North Carolina State University)

This paper describes a process for uniformly enhancing the nucleation density of diamond films on silicon (Si) substrates via dc-biased hot filament chemical vapor deposition (HFCVD). The Si substrate was negatively biased and the tungsten (W) filaments were positively biased relative to the grounded stainless steel reactor wall. It was found that by directly applying such a negative bias to the Si substrate in a typical HFCVD process, the enhanced diamond nucleation only occurred along the edges of the Si wafer. This resulted in an extremely non-uniform nucleation pattern. Several modifications were introduced to the design of the substrate holder, including a metal wire-mesh inserted between the filaments and the substrate, in the aim of making the impinging ion flux more uniformly distributed across the substrate surface. With such improved growth system designs, uniform enhancement of diamond nucleation across the substrate surface was realized. In addition, the use of certain metallic wire mesh sizes during biasing also enabled patterned or selective diamond deposition.

Order No.: JA502-032

Effect of Hydrogenated Amorphous Carbon Films on Nucleation of Diamond Particles by Hot-Filament Chemical Vapor Deposition

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To enhance a nucleation rate of diamond particles, hydrogenated amorphous carbon (a-C:H) intermediate layers have been formed by radio frequency plasma chemical vapor deposition (CVD) on silicon substrates prior to diamond deposition by hot filament CVD and the effect of a-C:H intermediate layers on the nucleation and growth rate of diamond particles is studied by varying the thickness of a-C:H films. It is found that diamond particles are well synthesized on thin a-C:H intermediate layers, and the nucleation density and growth rate are decreased by increasing the thickness of a-C:H films. Atomic force microscope observations show that a-C:H intermediate layers with rough surface are more effective than the smooth surface for diamond synthesis. Raman spectroscopy shows that the bonding state of carbon atoms in a-C:H films does not change by varying the thickness of a-C:H films. It is proposed that diamond nucleation is affected by the surface morphology rather than the bonding state of carbon atoms in a-C:H films.

Order No.: JA502-033

A Study of Temperature and Pressure Induced Structural and Electronic Changes in $SbCl_5$ Intercalated Graphite: Part III. Analysis of the T and p Dependence of the C-Axis Resistivity

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We present experimental data for the c-axis electrical resistivity of $SbCl_5$ intercalated graphite between 20 and 300 K. The data are analyzed together with our previous results for these and other samples (O.E. Andersson, et al., J. Mater. Res. **7**, 2989 (1992)). Before the analysis, we correct the experimental data to constant volume, as assumed by theorists. We show that the correction factor is much larger for these materials than for normal metals. Although the original data showed significant non-linearities with T, the corrected data are linear in T to within the experimental accuracy for low-stage compounds below the intercalate crystallization temperature. We compare our results with several models and conclude that both the temperature dependence, the pressure dependence, and the relative changes in the in-plane and c-axis resistivities associated with intercalate crystallization can be best described by a band conduction model.

Order No.: JA502-034

Characterization of $PbTiO_3$ Thin Films Deposited on $Pt/Ti/SiO_2/Si$ Substrates by ECR PECVD

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Electron cyclotron resonance plasma enhanced chemical vapor deposition (ECR PECVD) method is used to prepare ferroelectric $PbTiO_3$ films. Single-phase perovskite $PbTiO_3$ films with smooth surfaces and fine grain size were successfully fabricated on $Pt/Ti/SiO_2/Si$ substrates at low temperatures of 400~500°C using metal-organic (MO) sources. The chemical compositions, structural phases, surface morphologies and depth profiles of the $PbTiO_3$ thin films were investigated using EDS, XRD, SEM, RBS and AES. The variations of those properties with process temperature and gas supply ratio were discussed. When the process temperature was above 450°C, the stoichiometric perovskite $PbTiO_3$ films could be obtained even though the MO source supply ratio was varied in a wide range if the oxygen supply was sufficient.

Order No.: JA502-035

An Incommensurate-Commensurate Phase Transformation in Antiferroelectric Tin-Modified Lead Zirconate Titanate

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Antiferroelectric tin-modified lead zirconate titanate ceramics (PZST), with 42 at% Sn and 4 at% Ti, were studied by hot- and cold-stage transmission electron microscopy and selected area electron diffraction techniques. The previously reported tetragonal antiferroelectric state is shown to be an incommensurate orthorhombic state. Observations revealed the existence of incommensurate 1/x<110> superlattice reflections below the temperature of the dielectric maximum. The modulation wavelength for this incommensurate structure was found to be metastably locked-in near and below room temperature. An incommensurate-commensurate orthorhombic antiferroelectric transformation was then observed at lower temperatures. However, an intermediate condition was observed over a relatively wide temperature range which was characterized by an intergrowth of <110> structural modulations, which was strongly diffuse along the <110>. These structural observations were correlated with dispersion in the dielectric properties in the same temperature range. No previous reports of an incommensurate orthorhombic antiferroelectric state or an incommensurate-commensurate orthorhombic antiferroelectric transformation are known to exist.

Order No.: JA502-036

Effect of Process Variables on the Grain Growth and Microstructure of $ZnO\text{-}Bi_2O_3$ Varistors and their Nanosize ZnO Precursors

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The basic building block of the ZnO varistor is the ZnO grain formed as a result of sintering. Nanosized ZnO particles are prepared by carrying out the reaction in the controlled size nanoreactors—the droplets of microemulsions. Chemical doping of the ZnO nanoparticles provides ZnO-based ceramic varistors displaying superior varistor properties. These varistors show higher value of the non-linear coefficient, lower leakage current and higher critical electric field value as compared to those for conventional samples in their logE versus logJ curve. The present work has also been aimed at studying the effect of processing variables such as sintering temperature and duration on the microstructure and grain growth of ZnO nanoparticles and $ZnO\text{-}Bi_2O_3$ ceramics. The activation energy calculated from this data is found to be 175 kJ/mol for pure ZnO. For Bi_2O_3 doped ZnO, the activation energy is found to decrease considerably (~148 kJ/mol). All these advantages are due to greater structural homogeneity, smaller particle size, higher surface area and higher density of the ZnO nanoparticles which are precursors for ZnO varistors, as compared to coarser particles for making varistors.

Order No.: JA502-037

Study of Polycarbonate Degradation Induced by Irradiation with He^+ Ions

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A stack of 5 polycarbonate foils, each 1.4 μm thick, was irradiated with 1.3 MeV ^4He ions to the dose of $1.1 \times 10^{14} cm^{-2}$. Ion beam induced polymer degradation as a function of the particle energy was studied by UV-VIS and IR spectroscopy of individual foils. In the irradiated foils, a significant reduction of characteristic absorption bands is observed indicating polymer degradation. Significant increase of the surface polarity, characterized by polar component of the surface free energy, is also found. Both the degree of the polymer degradation and the surface polarity correlate with the total energy deposited by $^4He^+$ ions in the foils.

Order No.: JA502-038

Characterization of Hydroxyapatite Laser Ablation Plumes by Fast Intensified CCD-Imaging

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ArF excimer laser pulses (193 nm, 20 ns, 150 mJ) have been focused on a hydroxyapatite (HA) target in similar conditions to those normally used for thin film deposition. Fast intensified CCD images of HA laser ablation plumes have been taken in vacuum and under different water vapor pressures ranging from 0.01 mbar to 1 mbar. Images of HA ablation in vacuum have shown a plume freely expanding at a constant velocity of 2.3×10^6 cm/s. HA ablation under a water vapor pressure of 0.01 mbar has revealed an expansion behavior very similar to that of ablation in vacuum. Images taken under a water vapor pressure of 0.1 mbar have shown the formation of a shock structure in the plume. Finally, HA ablation under a water vapor pressure of 1 mbar has revealed the development of some irregularities in the shape of the plume.

Order No.: JA502-039