JMR Abstracts

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Volume 10, Number 8 *Abstracts for August 1995 Journal of Materials Research*

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ABSTRACTS

COMMUNICATIONS

Tribology and Mechanical Properties of Excimer Laser Processed Ti-Si_3N_4 Surfaces

T.R. Jervis*, J-P. Hirvonen+, M. Nastasi*, H. Kung*
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Titanium films were mixed, using excimer laser radiation, into the surface of bulk Si_3N_4 materials. The tribological and mechanical properties of these surfaces were then evaluated using pin-on-disc and nanoindenter techniques, respectively. Reduced friction and a change in the wear mechanism that resulted in a more benign failure mode were observed. These results are interpreted as resulting from the establishment of a transfer film, changes in the compliance of the surface which reduces instantaneous stresses in the surface, and toughening of the surface, all results of the laser process.

Order No.: JA508-001

Proton Induced Fluorescence Properties of Terbium Gallium Garnet

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(Alabama A&M University)

The authors completed a 3 MeV proton irradiation test on a terbium gallium garnet crystal sample. The main goal was to determine the proton dose required to reduce the fluorescence intensity to half its original value (half brightness dose) at ambient temperature. The 3 MeV proton half brightness dose was found to be $1.25x10^{15}$ p/cm^2 using the Birks and Black relation. This decay is comparable to other fluors irradiated by the authors. The sample exhibited a yellow glow when irradiated in a 3 MeV beam. The fluorescence spectrum was composed of 4 peaks at wavelengths of 487.2 nm, 542.4 nm, 589.92 nm, and 624.1 nm.

Order No.: JA508-002

ARTICLES

Annealing of Tweed Microstructure in High T_c Superconductors in the Presence of Impurities

K. Parlinski, Y. Watanabe, K. Ohno, Y. Kawazoe
(Tohoku University)

A two-dimensional model of oxygen deficit layer of superconducting material $YBa_2Cu_3O_7$ has been simulated by molecular-dynamics technique in order to study the influence of the impurities in the site of copper on the low-temperature microstructure. The microstructure pattern arises as a result of quenching the system from a high-temperature tetragonal phase to the low-temperature orthorhombic one and subsequent annealing. The potential of the impurity is modified in such a way that it promotes occupation of opposite nearest neighbor sites around the impurity by an oxygen and vacancy simultaneously. The simulations of the annealing processes showed that the domain pattern becomes very tiny with increased concentration of randomly distributed impurities. Domains of larger sizes would appear if the impurities were able to diffuse to the domain walls. This is confirmed by annealing the sample containing linear chains of impurities. The tweed microstructure depends on the magnitude of the force constants of the elastic subsystem and at too large coupling the randomly distributed impurities are not able to pin the stiff domain walls. The results resemble the electron-microscope photographs made for cobalt in $YBa_2(Cu_{1-x}Co_x)_3O_{7-\delta}$.

Order No.: JA508-003

Post-Annealing Induced Defects and Their Influences on $Bi_2Sr_2CaCu_2O_y$ Superconducting Thin Films

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Defects in $Bi_2Sr_2Ca_{n-1}Cu_nO_y$ superconducting thin films annealed in an oxygen atmosphere are examined by high-resolution electron microscopy (HREM). In addition to the majority 2212 (n=2) phase, subsequent slabs of other homologous phases with n values up to n=10 are found intergrown in the films. Large angle tilt grain boundaries and various secondary phases such as CuO, Sr-Cu-O oxides are formed in the films. The occurrence of these defects are attributed to an inhomogeneous Sr, Ca and Cu distribution induced by the post-annealing. Superconducting transition temperature (T_C) is increased by the annealing under suitable conditions.

Order No.: JA508-004

Magnetic Alignment in 2212 Bi-Based Superconducting System: Part II. $Bi_2Sr_2Ca_{1-x}Dy_xCu_2O_{8-y}$ x=0.2 Glass Recrystallized in 0.6 T Magnetic Field

S. Stassen, R. Cloots, A. Rulmont, M. Ausloos
(University of Liège)

Starting from a glassy precursor, $Bi_2Sr_2Ca_{1-x}Dy_xCu_2O_{8-y}$ (for x=0.2) was recrystallized under a 0.6 T magnetic field. After splat quenching, the samples were heated and sintered at different temperatures T_1, then slowly cooled. X-ray diffraction data sometimes showing 001 peak splitting and electron scanning microscopy pictures were

collected. The results showed that the magnetic field could orient the grains and led to a magnetically textured growth process. Secondary phases formed in the system during this process were identified by EDX analysis. The optimum T_1 for texturing was found to be between 930°C and 950°C.
Order No.: JA508-005

Doping and Crystallization of Amorphous SiGe Films with an Excimer (KrF) Laser
S. Krishnan, M.I. Chaudhry, S.V. Babu
(Clarkson University)

Amorphous silicon germanium (a-SiGe) films, deposited on silicon substrates at room temperature in a molecular beam epitaxy system, were transformed into a single crystal film and doped with phosphorous by exposure to KrF laser pulses. Electron channeling patterns showed that laser exposure resulted in crystallization of the undoped a-SiGe films. The SiGe films were doped by laser irradiation, using a phosphorus spin-on-dopant. The sheet resistance of the doped films decreased with increasing numbers of pulses, reaching a value of about ~$5x10^4$ ohms/□ after 15 pulses. I-V data from mesa-type n-SiGe/p-Si diodes devices were used to determine the effect of laser processing on the quality of the SiGe films.
Order No.: JA508-006

Heat Conduction in Silicon Thin Films: Effect of Microstructure
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A study was made of the thermal properties of low pressure chemical vapor deposition silicon thin films with amorphous and polycrystalline microstructures, produced by varying the substrate temperature. Thermal diffusivity measurements were conducted using a thermal wave technique. The thermal diffusivity of the polycrystalline films was found to be about three times that of the amorphous films but about one-eighth that of bulk silicon single crystals. There was also an indication that the diffusivity increased with deposition temperature above the transition temperature from the amorphous to the polycrystalline state. The relationships between the thermal properties and microstructural features, such as grain size and grain boundary impurities, are discussed.
Order No.: JA508-007

Formation of Metastable π Phase in Mechanically Alloyed Tellurium Rich Ag-Te Alloys
J. Chitralekha, K. Raviprasad, E.S.R. Gopal, K. Chattopadhyay
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This paper reports the formation of metastable π phase on mechanical alloying of elemental Ag and Te powders in the composition range of 50 to 75 at.%Te. Contrary to the reported results in vapor deposited thin films, no amorphous phase could be detected during mechanical alloying. The extent to which the π phase forms on milling is restricted, compared to rapid solidification. Formation of the metastable π phase coincides with the achievement of nanometric grain size and is preceded by the formation of intermetallic compound Ag_2Te. An approximate estimation of the free energies of the competing phases has been attempted to provide an insight to the phase selection process. It is suggested that tellurium diffusion through the nanoscale grain boundaries plays an important role in the formation of the metastable π phase.
Order No.: JA508-008

On The New Structural Phases in $Al_{65}Cu_{20}Cr_{15}$ Quasicrystalline Alloy
V. Khare, N.P. Lalla, R.S. Tiwari, O.N. Srivastava
(Banaras Hindu University)

The quasicrystalline (qc) alloy $Al_{65}Cu_{20}Cr_{15}$, unlike its Ru and Fe bearing counterparts like $Al_{65}Cu_{20}Ru_{15}$ and $Al_{65}Cu_{20}Fe_{15}$, is a metastable phase. This qc-alloy has been shown to possess several structural variants and curious structural characteristics. We have investigated the qc-alloy $Al_{65}Cu_{20}Cr_{15}$ with special reference to the possible occurrence of new structural variants. TEM exploration of the as-quenched qc-alloy has indeed revealed the existence of several new phases. These are (a) b.c.c. (a=12.60Å, disordered) and s.c. (a=12.60Å, ordered), which are the 1/1 approximants of the primitive icosahedral phase (i-phase), (b) a 2-times order induced modulated cubic phase (b.c.c., a=25.20Å) which has been shown to correspond to 1/1 approximant of the ordered i-phase (i.e., FCI), and (c) real crystalline b.c.c. (a=8.90Å) and f.c.c. (a=17.98Å) phases possessing specific orientation relationship with icosahedral matrix phase. Tentative structural models bringing out the interrelationships between the b.c.c./f.c.c. phases have been outlined.
Order No.: JA508-009

The Study on Charge-Density Distribution in TiAl by Quantitative Electron Crystallography Method
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Structure factors of γ-TiAl equiaxed grain in TiAl duplex intermetallic compound before and after V-alloying were measured by quantitative electron crystallography method. Then the structure factors were transferred into charge-density distributions of real space. Comparing the charge-density distributions in γ-TiAl with that in V-alloyed γ-TiAl, it was found that V-alloying with the optimum amounts decreases the electronic charge density in Ti-Ti interatomic bond, and increases the electronic charge density in Al-Al interatomic bond and Ti-Al interatomic bond. Thus, the anisotropic of charge-density distribution in γ-TiAl equiaxed grain is reduced.
Order No.: JA508-010

On the Microstructure and Thermal Stability of Rapidly Quenched Fe-B Alloys in the Intermediate Composition Range Between the Crystalline and Amorphous States
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The structure and the thermal stability of the $Fe_{0.89}B_{0.11}$ rapidly quenched alloy have been investigated. Transmission Mössbauer measurements were carried out as a function of temperature in the range from 148 K to 513 K. Room temperature x-ray diffraction, and transmission and conversion-electron Mössbauer experiments, as well as 4.2 K spin-echo nuclear magnetic resonance measurements were also performed after some selected thermal treatments for one hour between 523 K and 1273 K. Based on these experiments it is suggested that the alloy is inhomogeneous at nanoscopic scale and consists of a fine dispersion of a defective boride phase with an o-Fe_3B-like short range order, embedded in an α-Fe matrix. This result gives support to the models which indicate phase separation in the amorphous phase with o-Fe_3B short range order prevailing in the hipereutectic iron concentration range. This phase was found to be less stable than the undefective one present in the less boron concentrated alloys. The transformation into the equilibrium phases, analyzed with an Arrhenius-type temperature dependence for the increase of the relative fraction of Fe_2B, led to an activation energy E_α=1.38±0.68 eV/atom.
Order No.: JA508-011

Microstructures of Thermomechanically Treated Eutectoid Zn-Al Alloy (II)
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The evolution of microstructure in a cast, extruded and aged eutectoid Zn-Al-Cu alloy is described based on x-ray diffraction and micrographic observations. Whereas the three phases α'_s, β'_s and η'_s were found in the as-cast state, the three phases α, T' and η'_E were observed in this alloy after extrusion at 250°C. The Al-rich FCC α

https://doi.org/10.1557/S0883769400037039 Published online by Cambridge University Press

phase appeared as isolated particles with clear boundaries. The zinc-rich η'_E phase decomposed upon aging into α, T' and η phases. It was found possible to control the phase makeup of the alloy by controlling extrusion temperature. At extrusion temperatures greater than 268°C, α, ε and η'_E were detected, whereas at temperatures below this, the phases α, T' and η'_E were found. After prolonged aging, the phase makeup of the alloy was found to be the same regardless of prior treatment routes. Early shrinkage of the extruded alloy occurred after aging at 91 and 150°C and was related to precipitation of aluminum from the η'_E phase during its decomposition to α, T' and η products.

Order No.: JA508-012

Solute-Atom Segregation at High-Angle (002) Twist Boundaries in Dilute Au-Pt Alloys

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Solute-atom segregation is studied by Monte Carlo simulations for three high-angle symmetrical (002) twist boundaries in Au-1 at.% Pt and Pt-1 at.% Au alloys at T=850 K. It complements our previous study that focused mainly on low-angle boundaries in the same alloys. Solute enhancement occurs on the Pt-rich side of the phase diagram, while on the Au-rich side net depletion in solute is observed. Following the trend observed for low-angle boundaries, Au as a solute prefers the structural units of the perfect crystal type, while Pt as a solute is depleted at those sites. The solute concentration at structural units depends on the planar fraction of those units in the boundary.

Order No.: JA508-013

Growth by Molecular Beam Epitaxy of (Rare Earth-Group V Element)/III-V Semiconductor Heterostructures

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This paper is dealing with the growth by molecular beam epitaxy of semimetallic (Rare Earth-group V element) compounds on III-V semiconductors. Results are presented, first on the *Er-Ga-As* and *Er-Ga-Sb* ternary phase diagrams, second on the lattice mismatched ErAs/GaAs ($\delta a/a \approx +1.6\%$), YbAs/GaAs ($\delta a/a \approx +0.8\%$) and ErSb/GaSb ($\delta a/a \approx +0.2\%$) heterostructures, and third on the lattice matched $Sc_{0.3}Er_{0.7}As/GaAs$ and $Sc_{0.2}Yb_{0.8}As/GaAs$ systems ($\delta a/a<0.05\%$). At last the growth of $YbSb_2$ on GaSb(001) is reported.

The studies made in-situ by reflection high-energy electron diffraction and x-ray photoelectron diffraction, and ex-situ by x-ray diffraction, transmission electron microscopy, He^+ Rutherford backscattering and photospectrometry are presented. We discuss the atomic registry of the epitaxial layers with respect to the substrates, the appearance of a mosaic effect in lattice mismatched structures and the optical and electrical properties of the semimetallic films. The problems encountered for III-V overgrowth on these compounds (lack of wetting and symmetry related defects) are commented on, and we underline the interest of compounds as $YbSb_2$ which avoid the appearance of inversion defects in the GaSb overlayers.

Order No.: JA508-014

Activation Energy for Pt_2Si and PtSi Formation Measured Over a Wide Range of Ramp Rates

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The activation energies, E_a's, for Pt_2Si and PtSi formation were determined using *in-situ* resistance measurements with ramp rates ranging from 0.4°C/m to 100°C/s. Measurements were performed using both conventional furnace and rapid thermal annealing (RTA). Pt films were evaporated on undoped polycrystalline Si and single crystal Si on sapphire substrates. The E_a's determined from Kissinger plots ranged from 1.41±0.08 to 1.63±0.03 eV for Pt_2Si formation and from 1.50±0.07 to 1.91±0.12 eV for PtSi formation. These are the first reported measurements of E_a's for Pt_2Si and PtSi formation over such a wide range of heating rates (greater than four orders of magnitude), and at such high heating rates. The phase formation sequence remained the same for the range of heating rates examined.

Order No.: JA508-015

Crack Progression and Interface Debonding in Brittle/Ductile Nanoscale Multilayers

D.K. Leung, N.T. Zhang, R.M. McMeeking, A.G. Evans
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Crack initiation and progression have been studied in nanoscale brittle/ductile multilayers of Cu and Si. Variations in the interface debond energy on the cracking behavior have been examined by using thin interlayers comprising either Cr (strong interface) or Au (weak interface). For strongly bonded Cr interfaces, it has been found that cracks forming in the Si invariably extend through the Cu layers, despite the ductile rupture characteristics of the Cu. This behavior occurs even when the Cu layers comprise more than 70% of the multilayer volume. It also contrasts with the crack arrest capabilities exhibited by relatively thick ductile layers (~10–100 μm). The disparity in behavior is attributed to the relatively large cracking strain required for the thin brittle layers.

Weak Au interfaces result in debonding which, in turn, can suppress the propagation of cracks into adjacent layers. However, when the interface has strongly bonded sections, the debond arrests, and often kinks into the attached Si. In this case, cracking still progresses sequentially through the Si layers. Careful control of the interface debond energy is needed to fully suppress crack progression in nanoscale multilayers.

Order No.: JA508-016

Regeneration of PAN-Based Activated Carbon Fibers by Thermal Treatments in Air and Carbon Dioxide

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(Feng Chia University)

PAN-based activated carbon fibers were saturated by dye adsorption and then were regenerated by thermal treatment in carbon dioxide and in air. The dye adsorption and the regeneration were carried out in several cycles. The changes in fiber physical properties and the capacity of dye adsorption will be discussed. Activated carbon fibers regenerated in air had greater dye adsorption and weaker mechanical properties than those regenerated in carbon dioxide. The preferred orientation changed slightly during air reactivation, but it decreased gradually after carbon dioxide regeneration. The regeneration processes led to a decrease in the weight and degradation of mechanical properties, but the processes increased the capacity of dye adsorption. After the second regeneration, the dye adsorption capacity of activated carbon fibers which were recycled by air regeneration was 15% higher than those which were recycled by carbon dioxide regeneration. But, after the third regeneration, the fibers recycled by air regeneration lost their mechanical properties. For carbon dioxide regeneration, fibers retained satisfactory mechanical properties even after the fourth regeneration. This study indicates that multiple effective applications can be accomplished with carbon dioxide treatment in place of air regeneration. The structural changes of activated carbon fiber during different regenerations are proposed.

Order No.: JA508-017

The Effect of Hydrogen on the Formation of Carbon Nanotubes and Fullerenes

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A novel method to synthesize "clean" carbon nanotubes with relatively high yield in a hydrogen arc discharge has been developed. The quality and yield of the tubes depend sensitively on the gas pressure in the arc discharge. Sharp, open-ended nanotubes with clear lattice

fringes at the edges and empty interiors have been observed. The existence of these frozen-open-ended tubes as part of nanotube-bundles provides evidence for an open-ended growth model for nanotubes. Using time of flight mass spectrometry, it was found that fullerenes, such as C_{60} and C_{70}, are almost absent from the soot collected in the hydrogen arc discharge. The effect of hydrogen on the formation of fullerenes, both in the laboratory and in space, will be discussed.
Order No.: JA508-018

Influence of Surface Roughness on the Wetting Angle
X.B. Zhou, J.Th.M. De Hosson
(University of Groningen)

In this paper the influence of surface roughness on contact angles in the system of liquid Al wetting solid surfaces of Al_2O_3 has been studied. It was observed that contact angles of liquid Al vary significantly on different rough surfaces of Al_2O_3. A model is proposed to correlate contact angles with conventional roughness measurements and wavelengths by assuming a cosine profile of rough grooves with a Gaussian distribution of amplitudes. In comparison with the experimental results, the model provides a good estimate for describing the influence of surface roughness on contact angles of liquid Al on Al_2O_3.
Order No.: JA508-019

A Simplified Analytical Model of Diamond Growth in Direct Current Arcjet Reactors
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A simplified model of a direct current arcjet-assisted diamond chemical vapor deposition reactor is presented. The model is based upon detailed theoretical analysis of the transport and chemical processes occurring during diamond deposition, and is formulated to yield closed-form solutions for diamond growth rate, defect density, and heat flux to the substrate. In a direct current arcjet reactor there is a natural division of the physical system into four characteristic domains—plasma torch, free stream, boundary-layer, and surface—leading to the development of simplified thermodynamic, transport, and chemical kinetic models for each of the four regions. The models for these four regions are linked to form a single unified model. For a relatively wide range of reactor operating conditions, this simplified model yields results that are in good quantitative agreement with stagnation flow models containing detailed multicomponent transport and chemical kinetics. However, in contrast to the detailed reactor models, the model presented here executes in near real-time on a computer of modest size, and can therefore be readily incorporated into process control models or global dynamic loop simulations.
Order No.: JA508-020

Smooth Diamond Films Grown by Hot Filament Chemical Vapor Deposition on Positively Biased Silicon Substrates
G. Popovici, C.H. Chao, M.A. Prelas, E.J. Charlson, J.M. Meese
(University of Missouri)

Diamond films have been grown by hot filament chemical vapor deposition on mirror-polished positively biased Si substrates. Very smooth films, a few micrometers thick, were obtained in only 30 minutes. SEM, x-ray diffraction patterns, and Raman were used to characterize the films. Not only diamond but other carbon phase was also detected. The initial structure showed a high density of defects and large stresses. Structural changes in time were found to occur with films apparently undergoing a phase transformation.
Order No.: JA508-021

Phase Relations in the System $Na_2ZnP_2O_7$-$Zn_2P_2O_7$
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Data on phase relations in the system $Na_2ZnP_2O_7$-$Zn_2P_2O_7$ reported in the literature are scarce and contradictory.[1,2] The system was first studied by S.I. Berul, et al.,[1] who established the existence of a congruently melting intermediate compound, $Na_8Zn_6(P_2O_7)_5$. In the paper[2] the system $Na_2ZnP_2O_7$-$Zn_2P_2O_7$ is considered to be eutectic. The subsolidus phase relations are represented by a mixture of two phases—terminal members of the system. The existence of the above mentioned compound was not confirmed for this system.

In the present work we studied the phase relations in the system $Na_2ZnP_2O_7$-$Zn_2P_2O_7$ on samples obtained by solid-state synthesis and glass crystallization. The sequence of crystallization of phases was investigated, and the equilibrium and metastable phase diagrams were constructed for the system.
Order No.: JA508-022

The Relationship Between Indentation and Uniaxial Creep in Amorphous Selenium
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Ultra-low load indentation techniques can be used to obtain time-dependent mechanical properties, termed indentation creep, of materials. However, the comparison of indentation creep data to that obtained during conventional creep testing is difficult, mainly due to the determination of the strain rate experienced by the material during indentation. Using the power-law creep equation and the equation for Newtonian viscosity as a function of stress and strain rate, a relationship between indentation strain rate, $\dot{\varepsilon}_i = \dot{h}/h$, and the effective strain rate occurring during the indentation creep process is obtained. Indentation creep measurements on amorphous selenium in the Newtonian viscous flow regime above the glass transition temperature were obtained. The data was then used to determine that the coefficient relating indentation strain rate to the effective strain rate is equal to 0.09, or $\dot{\varepsilon} = 0.09\dot{\varepsilon}_i$.
Order No.: JA508-023

Chemisorptive Electron Emission and Atomic Force Microscopy as Probes of Plastic Deformation During Fracture at a Metal/Glass Interface
S. Nakahara, S.C. Langford, J.T. Dickinson
(Washington State University)

We examine the use of chemisorptive electron emission (electron emission accompanying the adsorption of a reactive gas on a metal surface) and atomic force microscopy as measures of plastic deformation during fracture along a metallic Mg/glass interface. Localized ductile deformation in the metallic phase enhances the fracture energy, exposes metallic Mg to the reactive O_2 atmosphere, and produces intense emissions. The number of electrons emitted following fracture in low-pressure oxygen atmospheres is strongly correlated with the total energy expended during failure (peel energy). The presence of localized ductile deformation is verified by atomic force microscopy (AFM): voids are observed on surfaces yielding significant emissions and enhanced fracture energies. These voids are not observed on samples yielding the lowest peel energies and emission intensities, i.e., where the contribution of deformation to the peel energy is negligible. Quantitative use of roughness data derived from the AFM images is, however, problematic. The potential for chemisorptive electron emission as a probe of deformation along interfaces involving Mg, Ti, Zr and Al is promising.
Order No.: JA508-024

On the Evolution of Structure and Composition in Sol-Gel Derived Lead Zirconate Titanate Thin Layers
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(University of Illinois at Urbana-Champaign)

The evolution of structure and chemical distribution in sol-gel derived $Pb(Zr_{0.53}Ti_{0.47})O_3$ thin layers was monitored by x-ray diffraction, analytical electron microscopy and diffuse reflectance Fourier transform infrared spectroscopy. Electron microscopy confirmed the as-deposited coatings were amorphous with short-range order. Medium-range order developed on heat treatment, and chemical heterogeneity was observed at the nano-scale. The extent of compositional heterogeneity decreased with increasing temperature. Above 500°C, the coatings crystallized into an intermediate phase which converted to the perovskite phase above 600°C.
Order No.: JA508-025

https://doi.org/10.1557/S0883769400037039 Published online by Cambridge University Press

Conventional and Microwave Sintering Studies of $SrTiO_3$

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Using the non-conventional sintering technique, such as microwave sintering, it is observed to enhance the densification rate of $SrTiO_3$ materials as effectively as employing the highly active powders prepared by chemical route. Although the chemically derived powders demonstrate better sinterability than the mixed oxide powders, the thermal analysis indicates that the segregation of Ti^{4+}-containing clusters during decomposition of precursors in the direct pyrolysis (DP) process induces the occurrence of TiO_2 particles (anatase phase) prior to the formation of $SrTiO_3$ phase. These particles retard the necking process required to sinter the materials. The spray pyrolysis (SP) process can circumvent the preferential nucleation of TiO_2 phase and, therefore, produce powders exhibiting superior sintering behavior to the DP derived powders.

The microwave sintering technique, on the other hand, substantially enhances the rate of diffusion of the ions in the materials such that even the mixed oxide powders can be sintered at a temperature about 200°C lower than that needed to achieve the same density in a conventional sintering process. Fine grain (~4 μm) microstructure is obtained for the materials microwave sintered at 1220°C for 10 minutes. The migration of grain boundaries requires higher temperature to initiate than the formation of neckings between the grains. The grain growth occurs only when the material was sintered at temperatures higher than 1250°C.

Order No.: JA508-026

The Influence of Monomer and Polymer Properties on the Removal of Organic Vehicle from Ceramic and Metal Moldings

S.A. Matar, J.R.G. Evans, M.J. Edirisinghe, E.H. Twizell
(Brunel University)

This paper describes the effects of monomer and polymer properties on the competition between degradation of organic vehicle and transport of degradation products in ceramic moldings during pyrolysis. An experimentally tested model is studied systematically for ranges of material and process parameters characteristic of known polymers and their degradation products. The work highlights the properties having the greatest influence on the successful removal of organic vehicle from molded ceramics. The polymer properties controlling the diffusion constant are linked to the temperature dependence of viscosity of the molten suspension. Enthalpy of vaporization of the organic vehicle and the activation energy for the diffusion coefficient have a commanding influence on the critical heating rate for avoidance of defects. Preliminary guidelines emerge for the design of polymers for plastic forming of ceramic suspensions.

Order No.: JA508-027

Synthesis of Nanophase Silicon, Carbon, and Silicon Carbide Powders Using a Plasma Expansion Process

N. Rao, B. Micheel, D. Hansen, C. Fandrey, M. Bench, S. Girshick, J. Heberlein, P. McMurry
(University of Minnesota)

Nanophase powders of Si, C, and SiC with narrow size distributions are synthesized by dissociating reactants in a DC arc plasma and quenching the hot gases in a subsonic nozzle expansion. The plasma is characterized by calorimetric energy balances and the powders by on-line aerosol measurement techniques and conventional materials analysis. The measured nozzle quench rate is around $5x10^6$ K/s. The generated particles have number mean diameters of about 10 nm or less, with Si forming relatively dense, coalesced particles, while SiC forms highly aggregated particles. Our data suggest that SiC particle formation is initiated by the nucleation of small silicon particles.

Order No.: JA508-028

Microwave Dielectric Properties of $(Zr_{0.8}Sn_{0.2})TiO_4$ Ceramics with Pentavalent Additives

K.H. Yoon, Y.S. Kim, E.S. Kim
(Yonsei University)

The microwave dielectric properties of $(Zr_{0.8}Sn_{0.2})TiO_4$ were investigated as a function of the amount of additives such as Nb_2O_5, Ta_2O_5, and Sb_2O_5 in the temperature range of 20°C to 80°C at 7 GHz. As the amount of additives increased up to 1.0 mol%, the unloaded Q increased due to the decrease of oxygen vacancies in the $(Zr_{0.8}Sn_{0.2})TiO_4$ lattice and then decreased with further addition of additives because the electron concentration was increased. The temperature coefficient of the resonant frequency turned more negative with increasing additives. Although the Nb^{+5}, Ta^{+5}, and Sb^{+5} ions have a similar ionic size and the same valence electrons, each resulted in different microwave dielectric properties.

Order No.: JA508-029

Metal Incorporation in Sputter-Deposited MoS_2 Films Studied by Extended X-ray Absorption Fine Structure

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Solid lubricant films produced by cosputtering metals with MoS_2 and by forming metal/MoS_2 multilayers are being planned for use in the next generation of solid lubricated devices on spacecraft, including gimbal and sensor bearings, actuators, and sliding electrical contacts. The films exhibit increased densities and wear lives compared to films without additives, but the mechanism of density enhancement is not well understood. The extended x-ray absorption fine structure (EXAFS) technique is ideal for elucidating the structure of these poorly crystalline films. We analyzed MoS_2 films cosputtered with 0, 2, and 10% Ni, as well as Ni/MoS_2 and Au(Pd)/MoS_2 multilayer films. The results obtained at the Mo-K absorption edge showed that the metal-containing films comprised predominantly the same nanocrystalline phases present in similar films without added metals: pure MoS_2 and a $MoS_{2-x}O_x$ phase. $MoS_{2-x}O_x$ is isostructural with MoS_2, with O atoms substituting for S atoms in the MoS_2 crystal lattice. For all Ni-containing films, EXAFS data obtained at the Ni-K absorption edge showed that the Ni had not chemically reacted with the $MoS_{2-x}O_x$ and MoS_2, but formed a disordered NiO_x phase. However, Ni-cosputtered films showed decreasing Mo-Mo bond lengths in the $MoS_{2-x}O_x$ phase with increasing Ni content, probably due to preferential oxidation of Ni compared to MoS_2. EXAFS of these Ni-cosputtered films showed only a small decrease in short-range order with Ni content, while x-ray diffraction showed a concurrent large decrease in long-range order. The results indicate that film densification in Ni-cosputtered films is caused by NiO_x formation at the edges of nucleating $MoS_{2-x}O_x/MoS_2$ crystallites, limiting the crystallite size attainable within the films.

Order No.: JA508-030

X-ray Studies on the Morphology of Zwitterionic Polymers

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WAXS (Wide Angle X-ray Scattering) and SAXS (Small Angle X-ray Scattering) were applied to elucidate the microstructure and morphology of two zwitterionic copolymers. The first system is a sulfobetaine derivative of poly (4-vinyl pyridine) with an ionic content of 10% (10% of degree of quaternization). The copolymer is almost amorphous, with a small degree of crystallinity (10%). The second copolymer is a N-oxide derivative of the poly(N,N dimethyl aminoethyl methacrylate) highly crystalline (90%). The latter forms superstructures of globular shape with crystalline domains of coordinated polymer-salt systems. X-ray data is in accordance with those published by Castaño, Cardoso and Manero[5] who report TEM micrographs of zwitterionic systems; clusters with grainy appearance were observed within the length of scale range found in this work. Models for the morphology of these copolymers are proposed for each case.

Order No.: JA508-031

Interpretation of Mercury Porosimetry Applied to Aerogels
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The observation of aerogels submitted to a pressure of mercury indicates that this porous material is compacted and not intruded by the mercury. Consequently, the classical Washburn's equation cannot be applied. A relation is established between the pressure P of compaction and the size L of the largest pores. The size of pores is estimated by using the nitrogen adsorption-desorption isotherms analysis and SEM measurements. A relation is found in which P is proportional to L^{-4}. The new relation is applied to mercury porosimetry. Finally, a mechanical model is proposed that reproduces successfully the behavior of aerogels under high pressure of mercury.

Order No.: JA508-032

Amine-Reactive Surface Chemistry of Zinc Phosphate Glasses
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Surface chemical studies on zinc phosphate glasses were carried out with an ammonia probe using FTIR and XPS. Low softening point zinc phosphate glasses can be co-extruded with high softening point polymers to form polymer filled blends. NH_3 reacts with P-OH groups (Brønsted acid sites) to form bound NH_4^+ and with the zinc ions (Lewis acid sites) to form coordinately bound NH_3. Bulk nitridation reactions, forming various P-N bonds to >100 nm, occur concurrently. The glass surfaces were depleted in Zn compared to the batch compositions. Exposure to ambient water vapor removed Lewis acid bound ammonia; aqueous washing removed both types. Di- and tri-methyl amines also reacted with surface Brønsted and Lewis acid sites. These amine reactions have the potential for binding polymer chains to the glass surface.

Order No.: JA508-033

Glass Formation from Low Molecular Weight Organic Melts
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Glass formation from the melt of organic monomers was studied for a variety of different organic molecular structures with T_g near ambient temperature. Crystallization is suppressed by one or more of the molecular properties, hydrogen bonding, interlocking, dipolar, and hydrogen bonding combined with hindered rotational isomerism. Examples of materials in each category are presented for illustration. The viscosity of undercooled liquids was characterized by the VTF equation, $\eta=Aexp[DT_0/(T-T_0)]$ where A, D and T_0 are experimentally determined parameters. D provides a measure of the network strength relative to the internal energy. Our experimental D values are discussed in relation to the molecular structure and glass formation mechanism. The insight provided by our interpretation is intended to assist in the design of new molecular structures with controlled viscosity-temperature characteristics as well as glass forming ability by cooling from melts.

Order No.: JA508-034

The Effects of Melting Reactions on Laboratory-Scale Waste Vitrification
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At the U.S. Department of Energy's Hanford Site, processes are being developed to vitrify waste generated during nuclear materials processing. One of the wastes slated for vitrification is known as neutralized current acid waste (NCAW). The batch chemistry of simulated NCAW was varied with oxidants and reductants. Untreated, formated, nitrated, or sugar-added samples were combined with frit to produce melter feed. Offgas measurements of the formated melter feed showed that formates decomposed at temperatures too low for participation in a glass redox reaction. Sugar pyrolyzed and produced CO and H_2 at temperatures exceeding 665°C. For the sugar-added samples, the glass quenched from 1200°C produced an $Fe^{2+}/\Sigma Fe$ of 0.79. The measured iron redox ratios from the glasses made from untreated, formated, and nitrated wastes were essentially indistinguishable (0.0024 at 1000°C and 0.032 at 1200°C). However, the batch chemistry affected volume expansion and the reaction paths.

Order No.: JA508-035

https://doi.org/10.1557/S0883769400037039 Published online by Cambridge University Press