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Simultaneous combustion synthesis and consolidation of intermetallics—$MoSi_2$
J. Subrahmanyam, R. Mohan Rao, S. Subba Rao, K. Somaraju
(Combustion Synthesis Group-Defence Metallurgical Research Laboratory)

A novel technique has been developed for simultaneous combustion synthesis and consolidation of intermetallics in a single step, from elemental powders. The method has been applied for the synthesis and consolidation of $MoSi_2$. Temperature profile of the combusted compact provides the temperature-time regime for consolidation. The products were characterized for density, phase formation and microstructure.
Order No.: JA608-001

Synthesis of oxide perovskite solid solutions using the molten salt method
S. Gopalan, K. Mehta, A.V. Virkar
(University of Utah)

The molten salt method has in the past been employed to synthesize a large number of compounds at low temperatures. In this work we report the formation of solid solutions of $BaTiO_3$-$SrTiO_3$ and $BaZrO_3$-$SrZrO_3$ using a molten salt eutectic of NaOH-KOH as a solvent. Alkaline earth carbonates and titanium oxide were used as precursors for the titanate system and alkaline earth carbonates and zirconium oxide were used as precursors for the zirconate system. It was found that both systems form solid solutions throughout the composition range. The implications of these results with regard to the applicability of the molten salt method as a tool to investigate low temperature phase equilibria are discussed.
Order No.: JA608-002

Microwave-hydrothermal processing of layered anion exchangers
S. Komarneni, Q.H. Li, R. Roy
(The Pennsylvania State University)

We have compared the microwave-hydrothermal (M-H) processing with conventional hydrothermal (C-H) processing in the preparation of two layered anion exchangers, i.e., $Mg_3Al(OH)_8NO_3{\cdot}nH_2O$ and $Ni_{1-x}Zn_{2x}(OH)_2(CH_3COO)_{2x}{\cdot}nH_2O$. Both these phases can be crystallized more rapidly (an order of magnitude) under M-H processing compared to C-H processing. The above layered mixed basic salt of Ni and Zn was found to exhibit very high selectivity for $PO_4^{\equiv}$ (K_d=15,000). Its order of selectivity for various anions in the presence of 0.1N NaCl (ratio of Cl^- to anion in question is 100) increases as follows: $PO_4^{\equiv} >> SO_4^{=} > NO_3^-$.
Order No.: JA608-003

Boron loss in furnace- and laser-fired, sol-gel derived borosilicate glass films
D.J. Taylor*, D.Z. Dent*, D.N. Braski+, B.D. Fabes*
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Borosilicate glass films were made by the sol-gel method from tetraethoxysilane and trimethylborate precursors. The precursor or glass composition at each stage of processing was analyzed to determine the sources of boron loss. The films were heated in a furnace and with a laser to compare boron volatilization by the two heating methods. The films were characterized by infrared spectroscopy, ellipsometry, induction-charged plasma spectroscopy and Auger microscopy. The highest losses of boron occurred during coating and low temperature (<500°C) furnace firing. Films with the highest boron concentrations were made by dip coating and rapid firing, either with a laser or by placing them into a hot furnace. Infrared spectroscopy revealed Si-O-B bonds, indicating incorporation of boron into the borosilicate glass structure for laser- and furnace-fired films.
Order No.: JA608-004

ARTICLES

The formation and stability of 80 K phase in the BiPbSrCaCuO system
W. Zhu, C.K. Kuo, P.S. Nicholson
(McMaster University)

The formation of Pb-doped 80 K phase from nitrate precursors was studied in the $Bi_{1.84}Pb_{0.34}Sr_{1.91}Ca_{2.00}Cu_{3.04}O_{10.05}$ system. $Sr(Pb,Bi)O_3$, $Ca_5Bi_{14}O_{26}$, CuO and CaO were found to be the intermediate compounds reacting to produce 80 K phase between 600°–820°C. Synthesis was complete at 800°C for 24 h. 110 K phase formed at the expense of 80 K phase at temperatures above 820°C. Partial melting was detected and 80 K and 110 K phases were unstable in the presence of liquid phase. They decomposed to 2201, Cu_2O, and (Ca,Sr,Cu) complex oxides. The melting and decomposition were accompanied by oxygen loss.
Order No.: JA608-005

An investigation of grain boundaries in submicrometer-grained Al-Mg solid solution alloys using high-resolution electron microscopy
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High-resolution electron microscopy was used to examine the structural features of grain boundaries in Al-1.5%Mg and Al-3%Mg

solid solution alloys produced with submicrometer grain sizes using an intense plastic straining technique. The grain boundaries were mostly curved or wavy along their length, and some portions were corrugated with regular or irregular arrangements of facets and steps. During exposure to high-energy electrons, grain boundary migration occurred to reduce the number of facets and thus to reduce the total boundary energy. The observed features demonstrate conclusively that the grain boundaries in these submicrometer-grained materials are in a high-energy non-equilibrium configuration.

Order No.: JA608-006 **© 1996 MRS**

Structural relation between a 2D five-fold quasicrystal and crystalline approximants in Al-Co-Ni-Tb alloy

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A two-dimensional quasicrystal with five-fold symmetry and two large-unit-cell crystalline approximants in Al-Co-Ni-Tb alloy, which were observed in previous studies, are suggested to be composed of the same kind of atom cluster. Some characteristics of the atom cluster can be deduced from a high-resolution electron microscopy image of the Al-Co-Ni-Tb quasicrystal when the image is associated to a five-fold aperiodic tiling. By using the cut-and-projection method, a quasiperiodic tiling generated by an irrational projection is proposed as an ideal quasilattice of the Al-Co-Ni-Tb quasicrystal; in the meantime, periodic tilings generated by a rational projection present the lattices of the crystalline approximants.

Order No.: JA608-007 **© 1996 MRS**

The spreading kinetics of Ag-28Cu$_{(L)}$ on Nickel$_{(S)}$: Part I. Area of spread tests on nickel foil

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Dynamic hot-stage microscopy and sessile drop experiments have identified three stages in the spreading of Ag-28wt.%Cu liquid on the surface of high-purity Ni foil: (I) Non-reactive flow, (II) Secondary spreading, and (III) Breakout flow. The first stage is deGennes-type spreading driven by capillary forces and resisted by viscous drag. A (Cu, Ni) reaction layer forms quickly at temperature along the liquid-solid interface. Stage I ends when the liquid braze attains a quasistatic contact angle on the reacted surface. Stage II spreading involves a complex advance of a thin liquid sheet outward from the triple line as a result of differences in wetting between Ni grain surfaces and grain boundaries. The advancing liquid meniscus is distorted as the liquid moves ahead along the better wetted grain boundary regions and is held back (pinned) on those surfaces that are poorly wet resulting in a stick-slip motion of the triple line. The change in contact area with time is linear during this stage and the rate of spreading is independent of temperature in the range of 780–870°C. Although the diffusion of Cu into Ni grain boundaries likely drives the capillary flow, it is not the controlling process since an activation energy is not observed. The final stage of spreading, breakout flow, involves the flooding of the liquid braze over previously-wetted surfaces due to a change in the balance of interfacial energies. Spreading ends during Stage II or III either by isothermal solidification which stems from interdiffusion between the braze filler and the substrate or by curtailment of the liquid supply when it pulls back on the (Cu, Ni) reaction layer. Hold time, peak temperature, and heating rate all have an affect on both the terminal area of spread and the spreading kinetics of braze flow on polycrystalline Ni. The heating rate effect has not been emphasized in previously-published literature for soldering and brazing and, if overlooked, could easily impair ones ability to apply test results to other studies or practical situations. Roughness-enhanced spreading was not observed with the Ni foil surfaces used in this study. There was, however, a localized effect on the shape of the triple line which did not affect spreading kinetics or terminal area of spread in a systematic fashion.

Order No.: JA608-008 **© 1996 MRS**

The effect of Hf and Ti additions on microstructure and properties of Cr_2Nb-Nb *in-situ* composites

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The present paper describes the effect of Hf and Ti additions on the microstructures and mechanical properties of two-phase composites based on the Cr_2Nb-Nb eutectic. The microstructures of directionally solidified *in-situ* composites containing 50–70% by volume of the Laves phase Cr_2Nb which was modified with Hf (7.5–9.2%) and Ti (16.5–26%) are described. Partitioning of Hf and Ti between the two phases is discussed using microprobe and EDS results. The tensile properties at 1100 and 1200°C are described and compared with those of an analogous niobium silicide-based composite. The $Cr_2(Nb)$-(Nb) composite tensile yield strengths at 1200°C were increased over that of monolithic Cr_2Nb to ~130 MPa. However, at 1200°C the yield strengths of the silicide-based composites were approximately twice those of the $Cr_2(Nb)$-(Nb) composites.

Order No.: JA608-009 **© 1996 MRS**

In-depth and ion image analysis of minor and trace constituents in V-Cr-Ti alloy welds

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This paper describes application of dynamic secondary ion mass spectrometry (SIMS) to the study of the chemistry of welds in V-Cr-Ti alloys and presents preliminary data on the distribution of minor and trace elements (H, C, N, O, P, S and Cl) in welds produced by gas tungsten arc (GTA) and electron beam techniques. The motivation for this research is to develop techniques which determine correlations between the concentration and distribution of trace elements in alloy metal welds and the physical properties of the weld. To this end, quantitative SIMS techniques were developed for N, O and S analysis in vanadium alloy welds using an ion implantation/relative sensitivity factor methodology. The data presented in this paper demonstrates that trace compositions and distributions of selected welds correlate, at least qualitatively, with such properties as microhardness and tensile elongation. This data supports continuing these investigations to develop microanalysis methods which quantitatively correlate weld composition with mechanical properties.

Order No.: JA608-010 **© 1996 MRS**

Mechanical properties and microstructural analysis of a diamond-like carbon coating on an alumina/glass composite

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We investigate the mechanical and microstructural properties of a diamond-like carbon coating (DLC) which is deposited by plasma enhanced chemical vapor deposition onto an alumina/alumino-silicate glass composite used for biomedical applications. Ball-on-ring tests yield the fracture strength which is essentially influenced by the surface topology/roughness. The surface topology of the coating is investigated by atomic force microscopy (AFM). Tribology tests and nanoindentation represent the wear resistance and hardness—these are properties that are mainly influenced by the microstructural properties of the DLC coating. This microstructure is investigated by transmission electron microscopy (TEM) and analyzed by parallel electron energy loss spectroscopy (PEELS). For the general applicability of the coated composite, the interfacial adhesion of the DLC coating on the comparably rough substrate (roughness amplitudes and wavelengths are in the micrometer range) is important. Therefore, we focus on TEM investigations that show the interface to be free of gaps and pores that we, together with a characteristic microstructure adjacent to the interface, relate to the excellent adhesion. The interlayer consists of a high density of SiC grains, part of them directly bound to the substrate, and part of them

bound to other SiC grains. This interlayer is followed by an essentially different region of the coating as concerns the microstructure: this region consists of nanocrystalline diamond particles embedded in an amorphous carbon matrix. It is this heterogeneous microstructure to which we attribute: (i) the good adhesion based upon the interface stabilizing SiC grains, and (ii) the high hardness and wear resistance based upon the diamond nanocrystals in the coating.
Order No.: JA608-011

Mathematical modelling of cement paste microstructure by mosaic pattern: Part I. Formulation
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This paper develops a mathematical model using mosaic patterns to characterize structural features of complex, multiphase and multi-dimensional microstructures, such as those for cement paste. A multiphase microstructure can be characterized by m independent parameters: the first m-1 parameters are equivalent to the volume fractions of the phases, while the final parameter describes the grain size, and thus, the spatial arrangement of the microstructure. An evaluation procedure for the parameters is given; they can be evaluated based on a 2D image and then the 3D microstructure can be simulated by the present model. The relationships among the model parameters and material parameters, such as water-to-cement ratio and particle size distribution, are also established.
Order No.: JA608-012

Room temperature perovskite production from bimetallic alkoxides by ketone assisted oxo supplementation (KAOS)
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Barium titanate has been prepared at room temperature from a well-characterized crystalline barium titanium oxo alkoxide by reaction with acetone. An aldol condensation apparently supplies oxygen to condensing oxo alkoxide clusters. Transmission electron microscopy confirms that the crystallites so formed are dense and perfect with an average size of approximately 85 Å. Characterization of reactants and products provides a tentative understanding of structural evolution and the intermediates of the transformation. Crystalline $SrTiO_3$ and $BaZrO_3$ were also formed at room temperature by this same method.
Order No.: JA608-013

Kinetic and structural studies of oxygen availability of the mixed oxides $Pr_{1-x}M_xO_y$ (M = Ce, Zr)
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One composition of Pr-Ce mixed oxide and a range of compositions of Pr-Zr mixed oxide were prepared by co-precipitation methods and characterized by x-ray powder diffraction, thermogravimetric analysis, and x-ray photoelectron spectroscopy. Based on phases formed, the PrO_y-ZrO_2 system in an oxygen-containing atmosphere at moderate temperatures (up to 800–1000°C) is analogous to that of CeO_2-ZrO_2. Addition of either Ce or Zr to pure Pr oxide affects both the total amount of oxygen which can be reversibly exchanged between oxide and gas phase and the kinetics of the redox processes: Ce dramatically increases the amount (per Pr atom) and lowers the temperature of exchange, Zr slightly decreases the amount and also lowers the temperature of exchange, and both modifiers speed up the rate. These observations are rationalized in terms of bulk and surface structural features of the mixed oxides.
Order No.: JA608-014

Ferroelasticity of the displacive tetragonal phase in Y_2O_3 partially-stabilized ZrO_2 (Y-PSZ) single crystals
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Ferroelasticity of the tetragonal displacive (t′) phase was studied on 4.7 mol% Y_2O_3 partially-stabilized zirconia single crystals. Samples were deformed at 1400°C at constant strain rate to induce the ferroelastic behavior. Domain reorientation due to the applied stress has been studied as a function of the compression axis and aging time at 1600°C. Domain switching was found in the as-received and two-hours aged crystals deformed along the <100> direction, in which an exceptional high flow stress was reached (>700 MPa). Transmission electron microscopy observations were performed on deformed and undeformed crystals to study the microstructural changes associated with the domain switching. Incremental strain steps on the stress-strain curves and surface texture on the lateral faces of the deformed samples were correlated with the microstructural evidence.
Order No.: JA608-015

The effect of nitrogen on pulsed laser deposition of amorphous silicon carbide films: Properties and structure
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The influence of nitrogen on amorphous silicon carbide films deposited at room temperature using pulsed laser ablation has been investigated. Depositions were carried out either in ultra-high vacuum or in a nitrogen ambient ranging from 10 to 100 mT. The mechanical and optical properties as well as composition and structure of the resulting films were evaluated using a variety of analytical techniques. Vacuum deposited films exhibited high hardness but suffered from high compressive stresses (> 1 GPa). At low nitrogen background pressures (< 30 mT), films with an optimum balance between hardness (~16 GPa), adhesion, and intrinsic stress (< 220 MPa) were found making them ideal candidates for protective coating applications. As nitrogen pressure was increased, mechanical performance degraded due to the increasing amount of SiO_2 found in the films as evidenced by spectroscopic ellipsometry, infrared spectroscopy and Auger electron spectroscopy measurements. The source of oxygen is attributed to residual water vapor present in our vacuum system. Optical emission spectroscopy was used to confirm the presence of Si-O species in the laser induced plasma plume.
Order No.: JA608-016

Analysis of nanoindentation load-displacement loading curves
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Nanoindentation load-displacement curves provide a "mechanical fingerprint" of a materials response to contact deformation. Over the last few years, much attention has been focused on understanding the factors controlling the detailed shape of unloading curves so that parameters such as true contact area, Young's modulus and an indentation hardness number can be derived. When the unloading curve is well behaved (by which we mean approximating to linear behavior, or alternatively, fitting a power-law relationship) then this approach can be very successful. However, when the test volume displays considerable elastic recovery as the load is removed [e.g., for many stiff hard materials and many inhomogeneous systems (e.g., those employing thin hard coatings)], then the unloading curve fits no existing model particularly well. This results in considerable difficulty in obtaining valid mechanical property data for these types of materials. An alternative approach, described here, is to attempt to understand the shapes of nanoindentation loading curve and thus quantitatively model the

relationship between Young's modulus, indentation hardness, indenter geometry and the resultant maximum displacement for a given load. This paper describes the development and refinement of a previous approach by Loubet et al. (1986)[1] originally suggested for a Vickers indenter but applied here to understanding the factors which control the shape of the loading curve during nanoindentation experiments with a pointed, trigonal (Berkovich) indenter. For a range of materials, the relationship $P = K_m\delta^2$ was found to describe the indenter displacement, δ, in terms of the applied load P. For each material, K_m can be predicted from the Young's modulus *(E)* and the hardness *(H)*. The result is that if either of E or H is known, then the other may be calculated from the experimental loading curve. This approach provides an attractive alternative to finite element modelling and is a tractable approach for those cases where analysis of unloading curves is unfeasible.

Order No.: JA608-017

Effect of $BaSnO_3$ on the microwave dielectric properties of $Ba_2Ti_9O_{20}$

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The effect of $BaSnO_3$ on the phase formation and the dielectric properties of $Ba_2Ti_9O_{20}$ was investigated as a function of the amount of $BaSnO_3$ in the temperature range of 20°C to 80°C at 7 GHz. In the reaction of $2BaCO_3+9TiO_2 \rightarrow Ba_2Ti_9O_{20}+2CO_2\uparrow$, the batch with the addition of $BaSnO_3$ enhanced the reactivity compared to the batch with the addition of SnO_2. The enhancement of reactivity caused single phase $Ba_2Ti_9O_{20}$ to form effectively with less amounts of $BaSnO_3$. As the amount of $BaSnO_3$ increased up to 0.03 mol, the unloaded Q increased due to an increase of the $Ba_2Ti_9O_{20}$ phase; for further addition of $BaSnO_3$ over 0.3 mol, the unloaded Q decreased due to the increase of rutile and $BaTi_4O_9$ phases. The dielectric constant increased with increasing $BaSnO_3$. As single phase $Ba_2Ti_9O_{20}$ was present in the specimen, the $Q \cdot f_0$ value, the dielectric constant, and the TCF were approximately 37900, 38.7, and 1.7 ppm/°C, respectively.

Order No.: JA608-018

Electrical breakdown of the positive temperature coefficient of resistivity barium titanate ceramics

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Positive temperature coefficient of resistivity (PTCR) barium titanate ceramic is a semiconductor at room temperature, so it is self-heated under certain applied voltage, and then changed into an insulator.

The electrical breakdown has been investigated with the resistance-temperature characteristics of the three samples which have different compositions. The grain size effect on the breakdown voltage also has been discussed.

As the applied voltage increased, the electrical breakdown was initiated when the specimen interior was heated above the temperature corresponding to the maximum resistance on the resistance-temperature curves by joule heat.

Order No.: JA608-019

Inversion domain boundaries in ZnO ceramics

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Inversion domain boundaries (IDB's) in ZnO ceramics, associated with Sb_2O_3 doping, have been characterized using a range of electron microscopy techniques. The IDB's lie primarily on basal planes, but frequently are stepped along prismatic {1210} planes. The basal IDB can be characterized as (i) an inversion which causes an antisite exchange of cations and anions across the boundary; (ii) an effective displacement of the six-fold screw axis in the wurtzite structure vectors by a translation of 1/3 $<10\bar{1}0>$; and (iii) a displacement normal to the boundary. Significant Sb segregation is detected in the basal IDB segments in agreement with previous work, and in ceramics doped with Sb_2O_3 and Bi_2O_3. These IDB's contained both Sb and Bi, suggesting that while Bi does not participate in IDB nucleation, it resides in the boundary. Comparison of experimental and calculated HREM images suggests that the IDB is composed of a monolayer of Type 1 (111) zinc antimonate spinel, consisting of a single layer of octahedrally-coordinated zinc and antimony cations.

Order No.: JA608-020

Preparation of Al_2O_3/Mo nanocomposite powder via chemical route and spray drying

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A route to prepare nanometer-sized Mo particulates in Al_2O_3 was attempted by a combination of solution reactions in molecular scale and forcing precipitation by a spray-drying technique. MoO_3 was firstly dissolved in ammonia water and then added in the slurry with high purity, submicrometer Al_2O_3 powder. Mixed suspension was spray-dried, then the dried granules were reduced by hydrogen gas and further hot-pressing to a bulky composite at various temperatures. Dissolution of Mo oxide, adsorption reactions on alumina surface and surface potential of alumina particles in homogeneous ammonia suspension were studied. Characterization of the granules, including compactability, flowing properties, surface morphology, grain growth of Mo and Al_2O_3 and mixing homogeneity were examined. Homogeneity of the spray-dried granules was determined by the calculation of mixing index and the observation of the microstructure of sintered body. The existence of intergranular, intragranular and nano-sized Mo particulates within Al_2O_3 grains was observed by transmission electron microscopy (TEM). All the evidences revealed that homogeneous composites with nanometer-sized Mo had been successfully prepared by this attempt with the proposed chemical route and following spray-drying process.

Order No.: JA608-021

Hybrid materials based on the reaction of poly-organophosphazenes and SiO_2 precursors

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New molecular composite materials can be prepared based on an inorganic oxide network and an organic polymer. The polymeric component generally requires low process temperatures, due to the presence of the organic backbone or side groups. A sol-gel process therefore is suitable for synthesizing the inorganic component by dissolving soluble polymers into sol-gel precursor solutions, in order to obtain ceramic and polymeric solid phases. In this work poly-organophosphazenes were used because they have many technologically interesting properties (chemical, optical, electrical, mechanical). The methods to obtain covalent bonds between polymer and inorganic network and to obtain homogeneous, transparent hybrid materials without phase separation were studied. It was possible to avoid phase separation by preparing phosphazenes containing free hydroxyl functions and by adequately choosing the experimental conditions.

Order No.: JA608-022

Effect of interface design on high-temperature failure of laminated composites

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The fracture strength and toughness of alumina can be increased by lamination with strategically placed nickel layers and with a modified Ni/Al_2O_3 interface through tape casting. In order to examine the potential of this type of laminated composite in high-temperature applications, the laminates were tested at elevated temperatures. This paper describes how a modified tortuous interface, instead of a smooth interface, increases the creep resistance of the laminates. Interface modifi-

cation can control high temperature laminate behavior and is critical to successful composite design.
Order No.: JA608-023

Protective coatings of nanophase diamond deposited directly on stainless steel substrates
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Composed of sp^3 bonded nodules of carbon, nanophase diamond films are deposited in vacuum onto almost any substrate by condensing carbon ions carrying keV energies. These multiply charged ions are obtained from the laser ablation of graphite at intensities in excess of 10^{11} W cm^{-2}. The high energy of condensation provides both for the chemical bonding of such films to a wide variety of substrates and for low values of residual compressive stress. Coatings of 2–5 μm thicknesses have extended lifetimes of materials such as Si, Ti, ZnS, ZnSe and Ge against the erosive wear from high-speed particles by factors of tens to thousands. In this research, emphasis has been placed on studies of the bonding and properties realized by the direct deposition of nanophase diamond films on stainless steel substrates. Examinations of interfacial layers showed deep penetrations of carbon atoms into steel substrates. Resistances to low and high impact wear were estimated by a tumbler device and a modified sand blaster, respectively, and results indicated significant increases in lifetime of stainless steel samples. The characterization studies performed in this work demonstrated nanophase diamond as an attractive material for use as a protective coating in current industrial applications.
Order No.: JA608-024

Fabrication and structural analysis of ZnO coated fiber optic phase modulators
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Fiber optic modulators were fabricated by coating optical fibers with electrode and piezoelectric ZnO layers. The techniques of piezoelectric fiber optic modulator (PFOM) fabrication are presented, and the microstructure and crystallographic texture of the coatings are analyzed. In order to produce thick (approximately 5 μm) ZnO coatings it was necessary to study the reactive dc magnetron sputtering process in O_2/Ar gas mixtures under conditions close to the transition between an oxidized and non-oxidized Zn target surface. *In-situ* quartz crystal microbalance measurements of the deposition rate revealed three distinct regions in the deposition rate (R) versus oxygen partial pressure (P_{02}) behavior, at constant total pressure, for sputtering under conditions that provided an oxidized Zn target surface. Additionally, a transition between oxygen and argon dominated sputtering was observed by varying the sputtering pressure while maintaining a constant P_{02}. The transition between oxygen and argon dominated sputtering influences R to varying extents within the three R versus P_{02} regions for an oxidized target surface. Correlations between the cathode current and voltage, deposition rate, and gas flow rate are presented to give a better understanding of the reactive sputtering processes occurring at the oxidized Zn target surface. Sputtering conditions optimized for a high ZnO deposition rate were used to produce <001> radially oriented ZnO fiber coatings for PFOM devices that can produce optical phase shifts as large as 0.38 rad/V.
Order No.: JA608-025

Composition dependence of morphology, structure and thermoelectric properties of $FeSi_2$ films prepared by sputtering deposition
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Direct β-$FeSi_2$ film preparation from gaseous phase was examined using a radio frequency (rf) sputtering deposition apparatus equipped with a composite target of iron and silicon. Films composed of only β-$FeSi_2$ phase were formed at substrate temperatures above 573 K when the chemical composition of the film was very close to stoichiometric $FeSi_2$. The β-$FeSi_2$ films thus formed showed rather large positive Seebeck coefficient. When the chemical composition of the films were deviated to Fe-rich side, ε-FeSi phase was formed along with β-$FeSi_2$. On the other hand, α-$FeSi_2$ phase, which is stable above 1210 K in the equilibrium phase diagram, was formed at the substrate temperature as low as 723 K when the chemical composition was deviated to Si-rich side. The formation of α-$FeSi_2$ phase induced drastic changes in the morphology and thermoelectric properties of the films. The α-$FeSi_2$ phase formed in the films was easily transformed to β-$FeSi_2$ phase by a thermal treatment.
Order No.: JA608-026

Structural transitions and electrical conductivity of C_{60} films at high temperature
J. Gong, G. Ma, G. Chen
(Lanzhou University)

X-ray diffraction analysis on C_{60} films shows that beside fcc phase, there also exists hcp phase as well as a new crystalline phase with interplanar spacing (d-spacing) of planes parallel to the substrate 0.95 nm. The new phase may relate to the intercrystalline packed C_{60} molecules between fcc crystallites. The room temperature electrical conductivity of C_{60} films is found to be in the range of 10^{-5}–10^{-8} $(\Omega \cdot cm)^{-1}$. The room temperature conductivities of C_{60} films annealed at temperatures above 473 K are lower by one order of magnitude than those at temperatures below 463 K. This is because the interconnection between the fcc crystallites is weakened due to the disappearing of the new intercrystalline phase and the subsequent heightening of the intercrystalline potential barrier. From the measurement on the conductivity versus time when the film is maintained at a constant temperature, we identified the increase of conductivity is the result of the decrease of hcp phase, while the decrease of conductivity is due to the decreasing of the new intercrystalline phase. Because the structures of the films become highly ordered, and defect states in the energy band gap decrease on annealing at high temperature, the conductivity activation energy increases.
Order No.: JA608-027

Microstructural development in sol-gel derived PZT thin films: The role of precursor stoichiometry and processing environment
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The role of precursor stoichiometry and local firing environment on the microstructural development of sol-gel derived PZT thin films were investigated. Typically, excess Pb is added to films to compensate for PbO volatilization during heat treatment. Here, it is shown that the use of stoichiometric precursors with either a PbO atmosphere powder or a PbO overcoat during the crystallization heat treatment are attractive and viable alternative methods for control of film stoichiometry. Using these approaches, we have fabricated single phase perovskite thin films with microstructures and electrical properties (P_r ~36 μC/cm^2 and E_c ~45 kV/cm) comparable to those of films using optimized solution chemistries and excess Pb additions. The potential advantage of increasing PbO partial pressure, or activity, during firing versus excess Pb additions is discussed from the standpoint of a proposed crystallization scenario based on the kinetic competition between Pb loss and the nucleation and growth rates of the perovskite phase.
Order No.: JA608-028

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Reduced thermal decomposition of OH-free $LiNbO_3$ substrates even in a dry gas atmosphere

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A thermal diffusion process of Ti into a $LiNbO_3$ substrate for optical waveguides has generally been carried out under a wet gas atmosphere in order to prevent undesirable Li out-diffusion. In this work, such thermal decomposition was confirmed to be significantly suppressed for an OH-free $LiNbO_3$ substrate, even after a dry atmosphere annealing. No extra x-ray diffraction peak for $LiNb_3O_8$ was detected from the OH-free substrate after 10 hours of annealing at 1000°C in a dry O_2. Furthermore, the surface morphology of this sample, and as well an unannealed one, were smooth. In a conventional $LiNbO_3$ substrate containing many OH ions, subjected to a similar dry annealing, the presence of the $LiNb_3O_8$ phase and a surface coarsening were observed.

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Effect of nickel addition on the combustion reaction of Ti-C system during mechanical alloying

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Explosive reactions, or self-propagating high-temperature synthesis (SHS), take place during milling of $Ni_{20}Ti_{50}C_{30}$ and $Ni_{50}Ti_{30}C_{20}$ elemental powder mixtures. The coexistence of agglomerates and powders in products indicates the occurrence of melting and solidification. TiC phase and NiTi compound were obtained during milling of $Ni_{20}Ti_{50}C_{30}$, while no compound of nickel and titanium was observed when milling $Ni_{50}Ti_{30}C_{20}$. The final product is TiC and Ni. It is suggested that the explosive reaction is ignited by the heat releasing from initial formation of TiC through hearty collisions of milling balls. The reaction between Ni and Ti, as well as the existence of Ni-Ti liquid, makes the following reaction self-sustained. The variation of the addition of nickel did not affect the reaction time in both compositions, but made the reaction temperature different due to the difference of composition of Ni and Ti. It is estimated that the temperature during the reaction in $Ni_{20}Ti_{50}C_{30}$ rises above 1112°C, while in $Ni_{50}Ti_{30}C_{20}$ it might rise above 1349°C. However, no phenomenon suggests the melting of pure elemental Ti. The formation of TiC is mainly controlled by diffusion mechanism in SHS.

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High-temperature creep of low-dielectric-constant glass composites

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The constant-stress compressive creep behavior of a low-dielectric-constant (low-k) glass composite, containing a low-softening-point borosilicate glass (BSG) and a high-softening-point high silica glass (HSG), has been investigated at 800–950°C. For all stages of creep, the deformation behavior exhibits linear viscoelasticity, and is controlled by viscous flow of the low-softening-point borosilicate glass. An analytical expression is proposed to describe mathematically the creep behavior of the glass composite, and the results show a fairly good agreement with experimental observations.

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Luminescence and decay times of Eu(III) and Nd(III) in polymer electrolytes

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Time resolved spectroscopy of poly(ethylene) oxide (PEO) and poly(propylene) oxide (PPO) electrolytes containing different concentrations of Eu^{3+} and Nd^{3+} ions is reported. A description of the main luminescence features of the Nd^{3+}-electrolytes is also presented. Lifetimes regarding the main transitions of the luminescence spectra ($^5D_0 \rightarrow {}^7F_{1,2}$ and $^4D_{3/2} \rightarrow {}^4I_{11/2}$ for Eu^{3+} and Nd^{3+}, respectively) are determined and are presented as a function of temperature in the range of 13 to 310 K. The order of magnitude of the values obtained at room temperature (0.2–0.6 ms and ≈0.7 ms for Eu^{3+} and Nd^{3+}, respectively), is a further indication of the technological potential of these new polymeric materials. For the Eu^{3+} ion the thermally activated quenching of the $^5D_0 \rightarrow {}^7F_2$ luminescence is discussed in terms of the observed energy superposition between the $^5D_{0,1}$ levels and the ligands-to-metal charge-transfer states.

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COMMENTS AND REPLY

Comments on "A new procedure for measuring the decohesion energy for thin ductile films on substrates" [J. Mater. Res. 9, 1734 (1994)]

O. Jørgensen, A. Horsewell, B.F. Sørensen
(Risø National Laboratory)

A recently proposed method for measuring decohesion energy of ductile films on substrates is discussed. The loading mechanism which causes the decohesion of the ductile film is that of gradually depositing an additional layer, with large residual tensile stresses, on top of the film. Hence the method involves the decohesion of a bilayer film on a substrate. The suggested method assumes that the unloading of the film is controlled entirely by elasticity. This assumption is a prerequisite for the suggested linear elastic analysis, from which the interfacial debond energy is derived in closed form. However, as is shown in the present communication, large scale yielding can occur in the wake of the crack tip and is prohibitive to the suggested linear elastic analysis. A sufficient condition for the occurrence of said large scale yielding is outlined in the present communication. Indeed it is shown that large scale plasticity must have occurred in the experiments described by Bagchi et al.[1]

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Reply to the comments of O. Jørgensen et al.

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Large scale yielding (LSY), in general, has a profound influence on the fracture toughness of metal/dielectric interfaces. For thin metal film/dielectric systems exhibiting "weak" bonding, small-scale yielding (SSY) prevails due to local plastic dissipation intrinsic to crack growth and the high yield strength of metal thin films. For systems involving low yield strength materials and strong interfaces, a more detailed LSY methodology needs to be developed.

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