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TABLE OF CONTENTS

ABSTRACTS

COMMUNICATIONS

Crystallographic structure of S´ precipitates in Al-Li-Cu-Mg alloys
J.I. Pérez-Landazábal, M.L. Nó, G. Madariaga, J. San Juan
(Universidad del País Vasco)

The crystallographic structures of some phases present as precipitates in Al-Li-Cu-Mg alloys are not perfectly resolved. In particular, several structural models have been proposed for the S´ phase and this controversy is not yet resolved. New x-ray powder diffraction measurements have been performed to compare the theoretical powder diffraction patterns associated with each proposed model with the measured spectra obtained from two different kinds of alloys. The structural model of the S´ phase described by Mondolfo agrees with the experimental results and allows us to reject the two other proposed crystallographic models.

Order No.: JA703-001

Characterization of the disproportionated NdFeCoZrB alloy by means of electron microscopy
J-R. Gao, X-P. Song, X-T. Wang
(Xi'an Jiaotong University)

The microstructure of the disproportionated NdFeCoZrB alloy during the solid-HDDR process was investigated by means of SEM and TEM. Except for a similar colony-type structure to ternary alloy, fine particles including spherical $(Fe,Co)_2B$ phase and undecomposed rim-like $Nd_2(Fe,Co)_{14}B$ compound were found dispersed within the α-(Fe,Co) matrix of the microstructure of the disproportionated NdFeCoZrB alloy. An unknown Fe-rich phase with a comparable size to that of the matrix grain was also detected by electron diffraction. These results strongly suggest that the undecomposed rim-like $Nd_2(Fe,Co)_{14}B$ particles are probably the *memory sites for the origin of anisotropy of the received NdFeCoZrB* materials.

Order No.: JA703-002

Very high pressure sintering of cBN fine particles coated with *TiN-TiB_2 layer formed by disproportionation reaction in molten salts*
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Sintering of a fine cubic boron nitride (cBN) particle with a grain size of less than 2 μm was successfully carried out under 5.5 GPa pressure at 1720 K for 30 min. TiN-TiB_2-coated cBN particles were used as the starting powder without adding any other binding materials. The coating was carried out by dipping the cBN particles in molten salts. The obtained cBN sintered compact shows a smooth microstructure with a well-controlled grain boundary; TiN-TiB_2 is distributed over the cBN-grain boundary in the shape of a net mesh similar to tiled floors. The Vickers microhardness of the obtained compact was found to be higher than that of commercially available typical cBN-cutting tools.

Order No.: JA703-003

Coexistence of 1 : 2 and 1 : 1 long-range ordering types in La-modified $Ba(Mg_{0.33}Ta_{0.67})O_3$ ceramics
H-J. Youn, K-S. Hong, H. Kim
(Seoul National University)

Ordering structure of lanthanum substituted $Ba(Mg_{0.33}Ta_{0.67})O_3$ was investigated using x-ray diffraction. It was observed that the ordering type of this solid solution was transformed from 1 : 2 to 1 : 1 type as the substitution with 10 mol% $La(Mg_{0.67}Ta_{0.33})O_3$ and these two types of ordering

coexisted in a wide range of compositions. This coexistence of ordering types was considered as phase coexistence and its physical origin was investigated with the aid of measurements of microwave dielectric properties. Because of change in the intensity of superlattice reflections and the discontinuity in dielectric properties, it was suggested that coexistence of two ordering types may originate from the overlap of the stability region of each ordering type.

Order No.: JA703-004

Biaxially textured yttria stabilized zirconia buffer layers on rotating cylindrical surfaces

J. Hoffmann, J. Dzick, J. Wiesmann, K. Heinemann, F. Garcia-Moreno, H.C. Freyhardt
(Universität Göttingen)

Biaxially textured yttria stabilized zirconia (YSZ) buffer layers are prepared on rotating cylindrical surfaces by an ion-beam-assisted deposition (IBAD) process. A large fraction of the cylinder surface can be coated at the same time, resulting in an effective deposition rate of 40 nm/h for the whole tube circumference (diameter of the tube is 12 mm). The in-plane alignment depends on the total film thickness and the rotation velocity. The best in-plane textures achieved so far with a FWHM value of 27^0 are sufficient for the preparation of YBaCuO films with critical current densities above 10^5 Acm^{-2} at 77 K and self fields.

Order No.: JA703-005

Sol-gel derived $Ba(Mg_{1/3}Ta_{2/3})O_3$ thin films: Preparation and structure

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$Ba(Mg_{1/3}Ta_{2/3})O_3$ thin films were prepared by a sol-gel process involving the reaction of barium isopropoxide, tantalum ethoxide and magnesium acetate in 2-methoxyethenol and subsequently hydrolysis, spin-coating and heat treatment. Transmission electron microscopy, x-ray diffraction, and Raman spectroscopy were used for the characterization of the thin films. It was shown that the thin films tend to crystallize with small grains sized below 100 nm. Crystalline phase with cubic (disordered) perovskite structure was formed in the samples annealed at a very low temperature (below 500°C), and well-crystallized thin films were obtained at 700°C. Although disordered perovskite is dominant in the thin films annealed below 1000°C, a low volume fraction of 1 : 2 ordering domains were found in the samples and grow with increase of annealing temperature.

Order No.: JA703-006

Phase transformation in $Sr_{1-x}Ba_xNb_2O_6$ ceramics

X. Wang
(Xi'an Jiaotong University)

The phase transformation in $Sr_{1-x}Ba_xNb_2O_6$ ($0.25 < x < 0.8$) ceramics was investigated. There is an intermediate transitive phase before forming the tungsten bronze phase at higher temperatures. The phase transformation from the intermediate type into tungsten bronze type is sluggish, affected principally by temperature. In the compositions rich in Ba ($x > 0.672$), Ba ions prefer to occupy the A_2 sites rather than the A_1 sites of the tungsten bronze structure. The percentages of vacancies in the A_1 sites and A_2 sites are no longer the same. With the increase of Ba, the vacancies in the A_1 sites increase, whereas the vacancies in the A_2 sites decrease.

Order No.: JA703-007

Oxide nanotubes prepared using carbon nanotubes as templates

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Hollow nanotubes of SiO_2, Al_2O_3, V_2O_5 and MoO_3 have been prepared using carbon nanotubes as templates. The procedure involves coating the carbon nanotubes with tetraethylorthosilicate, aluminum isopropoxide or vanadium pentoxide gel, followed by calcination and heating at higher temperatures in air to oxidize the carbon. SiO_2 nanotubes containing transition metal ions have been prepared by this procedure since such materials may be of use in catalysis.

Order No.: JA703-008

Preparation of TiO_2-based powders with high photocatalytic activities

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TiO_2-based powders doped with a small amount of SiO_2 were prepared by a sol-gel method and subsequently were heated to precipitate fine anatase crystals. Although the obtained powders have large specific surface areas (~ 200 $m^2 \cdot g^{-1}$), they showed poorer activity in a photocatalytic property than the undoped TiO_2 powders which have the area of 50 $m^2 \cdot g^{-1}$. The SiO_2-doped TiO_2 powders were treated chemically with aqueous NaOH. Infrared reflection spectra showed that the treatment reduced the amount of SiO_2 in the powders. The photocatalytic property of the powders was extremely improved by the treatment, and the powders showed the higher activity than the undoped TiO_2 powders.

Order No.: JA703-009

Evidence of critical scaling behavior during vapor phase synthesis of continuous filament composites

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We present experimental measurements of the accessible pore fraction in ceramic matrix composites during consolidation by vapor phase infiltration. For two topologically distinct filament architectures, the accessible pore fraction decreased during consolidation with a power law decay and a critical scaling exponent of 0.41 ($R^2 = .97$). A three-dimensional analysis of the percolating pores revealed that the structures became topologically equivalent and simply connected near the critical density.

Order No.: JA703-010

Carbon nanotubes grown *in-situ* by a novel catalytic method

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Carbon nanotubes can be produced by the catalytic decomposition of hydrocarbons on small metal particles. However, nanotubes are generally so obtained together with nontubular filaments and tubes coated by pyrolitic carbon. We propose a novel catalysis method for the *in-situ* production, in a composite powder, of a huge amount of single- and multi-walled carbon nanotubes, having a diameter between 1.5 and 15 nm and being arranged in bundles that may be up to 100 μm long. We anticipate that dense materials prepared from such composite powders could have interesting mechanical and physical properties.

Order No.: JA703-011

Surface composites: A new class of engineered materials

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To integrate irreconcilable material properties into a single component, a new class of engineered materials termed "surface composites" has been developed. In this engineered material, the second phase is spatially distributed in the near surface regions, such that the phase composition is linearly graded as a function of distance from the surface. Surface composites are different from existing engineered materials such as "bulk composites" and "functionally graded materials" (FGM). Unlike bulk composites, the surface phase in surface composites is present only at the near surface regions. In contrast to FGM, the graded properties of surface composites are achieved by unique morphological surface modification of the bulk phase. To fabricate surface composites, the initial surface of the bulk material is transformed using a novel multiple pulse irradiation technique into truncated cone-like structures. The laser induced micro-rough structures (LIMS) possess surface areas which are up to an order of magnitude higher than the original surface. The second phase is deposited on the surface using thin or thick film deposition methods. A key characteristic of surface composites is the formation of a three dimensional, compositionally and thermally graded interface, which gives rise to improved adhesion of the surface phase. Examples of various types of surface composites such as W/Mo, silica/SiC and diamond/steel, etc. are presented in this paper. The

unique properties of surface composites make them ideal engineered materials for applications involving adherent thick film coatings of thermally mismatched materials, compositional surface modification for controlled catalytic activity, and creating adherent metal-ceramic and ceramic-polymeric joints.
Order No.: JA703-012

Thermochemistry of combustion reaction in Al-Ti-C system during mechanical alloying
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The combustion reaction during mechanical alloying (MA) of the Al-Ti-C system has been detected by *in-situ* thermal analysis and the results of XRD. Based on the information provided by *in-situ* thermal analysis, the reaction temperature is estimated to be 1677 K, which is in good agreement with the value of the adiabatic temperature of 1700 K. It is considered that the formation reaction of Ti-C which ignited from the heavy collisions of milling balls induced the following reaction between Ti and Al at high-temperature.
Order No.: JA703-013

ARTICLES

Growth of $TlBa_2Ca_2Cu_3O_{9-y}$ superconducting films with local biaxial alignment extending up to 5 mm on Ag substrates using a spray pyrolysis technique
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We report superconducting properties of $TlBa_2Ca_2Cu_3O_{9-y}$ (Tl-1223) thick films grown on smooth and rough Ag substrates. Thallium-free precursor films of the type $Ba_2Ca_2Cu_3Ag_{0.37}O_7$ were deposited on Ag substrates using a spray pyrolysis technique followed by post-thallination in a two-zone furnace. XRD results showed the presence of a c-axis aligned Tl-1223 films and some degree of local in-plane texture (often referred to as a colony microstructure). The microstructure of the Ag surface dictates the growth behavior of Tl-1223 films. The transport critical-current densities (J_c) for Tl-1223 films grown on smooth and rough Ag substrates were ~65,000 A/cm^2 and ~37,000 A/cm^2, respectively, at 77 K and zero field. The films grown on smooth Ag substrates were strongly linked and had good in-field properties with a J_c value of ~10^4 A/cm^2 at 77 K and 0.5 T.
Order No.: JA703-014

Microstructural characterization of quenched melt-textured $YBa_2Cu_3O_{7-\delta}$ materials
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The microstructure of $YBa_2Cu_3O_{7-\delta}$ (YBCO) materials, melt-textured in air and quenched from the temperature range 900–990°C, has been characterized using a combination of x-ray diffractometry, optical microscopy, scanning electron microscopy, transmission electron microscopy and energy dispersive x-ray spectrometry. $BaCu_2O_2$ and $BaCuO_2$ were found to coexist in samples quenched from the temperature range 920–960°C. The formation of $BaCu_2O_2$ preceded the formation of YBCO. Once the YBCO had formed, $BaCu_2O_2$ was present at the solidification front filling the space between nearly parallel platelets of YBCO. Large Y_2BaCuO_5 particles at the solidification front appeared divided into smaller ones as a result of their dissolution in the liquid that quenched as $BaCu_2O_2$.
Order No.: JA703-015

Growth of (11n) oriented BCSCO films by liquid phase epitaxial method
K.K. Raina, R.K. Pandey
(Texas A&M University)

Films of BCSCO superconductor of the $Bi_2CaSr_2Cu_2O_x$ composition have been grown by the liquid phase epitaxy method (LPE) using a partially closed growth chamber. The films were grown on (110) $NdGaO_3$ substrates by slow cooling under optimized conditions below the peritectic melting point (885°C) of $Bi_2CaSr_2Cu_2O_8$. Optimization of parameters, such as seed rotation, soak of initial growth temperature and growth period results in the formation of the 2122 phase of BCSCO. XRD measurements show that the films grown on (110) $NdGaO_3$ have a preferred (11n)-orientation. The best values of zero resistance transition (T_{c0}) and critical current density (J_c) obtained for films grown on (110) $NdGaO_3$ substrates are 87 K and 5.7 x 10^4 A/cm^2 (at 20 K), respectively. The films grown at rotation rates of less than 30 and more than 80 rpm are observed to be associated with a sub-phase in the $Bi_2CaSr_2Cu_2O_8$ system. Electron microprobe analysis indicates the composition of this sub-phase to be $Bi_{0.07}Ca_{0.93}Sr_2Cu_5O_8$. Higher growth temperatures (>860 °C) also encourage the formation of this phase.
Order No.: JA703-016

Metal-nonmetal transition and resistivity of silicon implanted with bismuth
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Bismuth was implanted at room temperature in (100)-Si wafers with controlled energy and doses to result in a plateau-like implantation profile. The Van der Pauw Si:Bi samples were characterized by Hall effect and resistivity measurements from room temperature down to 13 K. The electron concentration of the prepared samples at 290 K varied from 3.0 x 10^{17} to 1.4 x 10^{20} c^{-3}. The resistivity of the Si:Bi samples presents a larger enhancement, compared to other dopants, when decreasing the Bi concentration. The metal-nonmetal transition was determined to be around 2 x 10^{19} cm^{-3}. The calculated values obtained from the Generalized Drude Approach and an equation derived from Kubo formalism agree very well with the experimental data. The results confirm also the behavior $\rho_c(Bi)<\rho_c(As)<\rho_c(P)<\rho_c(Sb)$ at 290 K.
Order No.: JA703-017

Vacancy structures on the GaN(0001) surface
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Scanning tunneling microscopy images are reported for the wurtzite GaN(0001) surface. Terraces are observed, with three kinds of defect structures that are assigned to ordered N-vacancies: (i) striations perpendicular to the step-edges; (ii) row-defects spaced about 16 Å that intersect the steps at an angle of 30°; and (iii) "oval" defects that result from intersections of lines of vacancies (oriented at 60° with respect to step-edges) with the row-defects.
Order No.: JA703-018

Formation of p-type Cu_3BiS_3 absorber thin films by annealing chemically deposited Bi_2S_3-CuS thin films
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Formation of the ternary compound Cu_3BiS_3 during annealing of chemically deposited CuS (~0.3 μm) films on Bi_2S_3 film (~0.1 μm on glass substrate) is reported. The interfacial atomic diffusion leading to the formation of the compound during the annealing is indicated in x-ray photoelectron depth profile spectra of the films. The formation of Cu_3BiS_3 (Wittichenite, JCPDS 9-488) is confirmed by the XRD patterns. The films are optically absorbing in the entire visible region (absorption coefficient 4 x 10^4 cm^{-1} at 2.48 eV or 0.50 μm) and are p-type with electrical conductivity of 10^2–10^3 Ω^{-1} cm^{-1}. Potential applications of these films as optical coatings in the control of solar energy transmittance through glazings and as a p-type absorber film in solar cell structures are indicated.
Order No.: JA703-019

Enhanced nucleation density of chemical vapor deposition diamonds by using interlayers
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Effects of interlayers on diamond nucleation were investigated for the Si substrates. Interlayers were deposited on the diamond abraded Si substrates by rf sputtering prior to diamond growth using microwave plasma

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chemical vapor deposition (CVD). Compared with 1 x 10^8/cm^2 for the just-abraded substrate, the nucleation density was greatly enhanced to 1~2 x 10^9/cm^2 by 50 nm thick interlayer, irrespective of the kind of interlayer material tried in this study (Si, Mo, Ti, Pt, Ag, TiN, or SiO_2). As the thickness of the Si interlayer decreased from 20 to 500 nm, the nucleation density reached a maximum value, 3 x 10^9/cm^2 at 100 nm. However, the growth rate was monotonically reduced from ~300 nm/hr to ~100 nm/hr. For the 700 nm thick Si interlayer, no diamond growth was observed. These results indicate that there is an optimum interlayer thickness around 100 nm for the higher nucleation density. The role of the interlayer in enhancing the nucleation density is believed to protect the nucleation sites generated by the diamond abrasion, otherwise they could be considerably etched away by atomic hydrogen during the initial diamond deposition.
Order No.: JA703-020 **© 1997 MRS**

Influence of elemental B addition on the heat-treated cast structures of Ti-47Al-2Cr-(2-4)Nb alloys
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(Korea Advanced Institute of Science and Technology)

The influence of elemental B addition on the heat-treated cast structure of Ti-47Al-2Cr(2-4)Nb alloys has been investigated using x-ray diffractometry, optical microscopy, scanning and transmission electron micros-copy, and tensile testing. The phase sequence is $\beta \rightarrow \beta+\alpha \rightarrow \alpha \rightarrow \alpha+\gamma \rightarrow \alpha+\beta+\gamma \rightarrow \beta+\gamma$. The addition of (0-2 at.%)B does not change the phase sequence. It however tends to stabilize phase by shifting the $(\alpha+\beta+\gamma)$ three phase region towards a higher (Cr+Nb) content. The B addition does not significantly alter the equilibrium composition within $(\alpha+\gamma)$ two-phase field. The B addition markedly accelerates the lamellar formation kinetics and enhances the thickening rate of γ plates, despite the fact that it increases both the misfit between α and γ plates and the α/γ interfacial energy. The acceleration of lamellar formation kinetics is thus believed to be primarily due to the enhancement of chemical diffusivity as a result of B addition. The B addition induces a significant refinement of heat-treated cast structure. This is primarily due to the role of boride to disperse the interdendritic γ regions to a fine network and to refine the dendrite cell size. Further refinement arises from the boride's role to act as the nucleation site for γ grains and from the intrinsic B effect to enhance the chemical diffusivity and the γ thickening rate. The addition of a small amount of B enhances both the strength and tensile ductility of near gamma structure. The strengthening arises from grain size refinement and from the boride dispersion. The calculation of fracture strain suggests that an enhancement of ductility for small B addition (up to ~0.2 at.%) is mostly due to its effect to refine the γ grains.
Order No.: JA703-021 **© 1997 MRS**

Characterization of mechanical nanocrystallization process of amorphous Fe-Mo-Si-B alloy by transmission Mössbauer spectroscopy
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The nanocrystallization process of the amorphous Fe-Mo-Si-B alloy under ball milling is characterized by means of transmission Mössbauer spectroscopy in the present paper. It was found that a single α-Fe phase with the bcc structure is formed under ball-milling the amorphous Fe-Mo-Si-B alloy. A significant increase in the relative area of the subspectra of 8Fenn and 7Fenn and a remarkable decrease in isomer shift and half linewidth of the subspectra of various Fe configurations, especially in the case of 6Fenn, were observed during the ball milling process. The diffusion of metalloid atoms from the bcc α-Fe phase to the remaining amorphous phase and α-Fe/α-Fe grain boundaries is suggested to occur during the mechanical crystallization of the current amorphous alloy based on the above TMES investigations.
Order No.: JA703-022 **© 1997 MRS**

Amorphization mechanisms of $NiZr_2$ by ball-milling
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The microstructure of $NiZr_2$ in the course of amorphization by ball-milling is studied by transmission electron microscopy and x-ray diffraction. The evolution from the initial fully crystalline alloy to a fully amorphized material is described. It is shown that prior to amorphization, the powder aggregates achieve a 100% nanocrystalline structure, the amorphous phase then appears and develops to the expense of the nanocrystalline phase. No massive chemical disordering is observed but a small amount cannot be ruled out. It is proposed that amorphization occurs by chemical disordering at interfaces, induced by the scattering of shear waves.
Order No.: JA703-023 **© 1997 MRS**

Plastic deformation of oxide scales at elevated temperatures
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(University of Minnesota)

The atomic force microscope (AFM) has been used to observe and characterize for the first time surface steps and grooves on the faces of Cr_2O_3 grains formed as an oxide scale on Ni-30Cr and Ni-30Cr-0.5Y alloys during high temperature oxidation. The very high spatial resolution of the AFM is required to characterize these features. We propose that these surface features, whose dimensions are in the range of nanometers and tens of nanometers, may be interpreted as evidence of highly localized plastic deformation of the oxide scale. The size and spacing of the steps and grooves are consistent with models of plastic deformation based on slip bands derived from dislocation climb or dislocation glide. Mechanical twinning and the models for stress-driven surface instability are also possibly responsible for some surface features. The addition of yttrium to the alloy seemed to enable enhanced plastic deformation of the scale. The strain corresponding to the observed features, estimated by simple models, could relax a significant part of oxide growth and thermal stresses.
Order No.: JA703-024 **© 1997 MRS**

SiC (SCS-6) fiber reinforced-reaction formed SiC matrix composites: Microstructure and interfacial properties
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Microstructural and interfacial characterization of unidirectional SiC (SCS-6) fiber reinforced-reaction formed SiC (RFSC) composites has been carried out. Silicon-1.7 at.% molybdenum alloy was used as the melt infiltrant, instead of pure silicon, to reduce the activity of silicon in the melt as well as to reduce the amount of free silicon in the matrix. Electron microprobe analysis was used to evaluate the microstructure and phase distribution in these composites. The matrix is SiC with a bi-modal grain-size distribution and small amounts of $MoSi_2$, silicon, and carbon. Fiber push-out tests on these composites showed that a desirably low interfacial shear strength was achieved. The average debond shear stress at room temperature varied with specimen thickness from 29 to 64 MPa, with higher values observed for thinner specimens. Initial frictional sliding stresses showed little thickness dependence with values generally close to 30 MPa. Push-out test results showed very little change when the test temperature was increased to 800°C from room temperature, indicating an absence of significant residual stresses in the composite.
Order No.: JA703-025 **© 1997 MRS**

Characterization of iron oxide-silica nanocomposites in flames: Part II. Comparison of a discrete-sectional model predictions to experimental data
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A discrete-sectional model accounting for particle formation by chemical reaction and growth by coagulation and condensation is developed to predict the evolution of the nanocomposite aerosol size distribution in a multicomponent iron-silicon system in a flame. Particle formation by nucleation of the vapor is represented by an Arrhenius type rate expression, with the rate constant being obtained from experiments and simulation results reported in the literature. Precursor vapor concentrations and the second aerosol volume moment predictions are compared to LIF and light scattering intensity measurements from experiments described in Part I of the paper. The results elucidate the important formation and growth mechanisms of nanocomposite ferric oxide-silica particles in flame reactors. The role of operating parameters such as precursor characteris-

tics and temperature profiles on the final product characteristics are established.
Order No.: JA703-026

Model of chemical vapor infiltration using temperature gradients
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An optimized chemical vapor infiltration (CVI) process has conditions which promote complete densification at the fastest allowable reaction rate. In order to help define optimum conditions a model has been developed to simulate the CVI of a fibrous specimen for determining the effects of temperature gradients along with other processing parameters such as pressure, size, chemistry, rate of reaction, and porosity on the resulting deposition profiles. This model simulates the deposition of alumina matrix within fibers wrapped around a tube. This symmetry reduces the model to a simple one-dimensional problem. Parameters for transport properties, calculated using a local microstructure model, are used in this macroscopic model. The model is applied as a guideline for choosing optimum conditions for producing a dense ceramic matrix composite. From this model, process diagrams are constructed which can help an experimentalist to choose the best conditions for the CVI process using temperature gradients.
Order No.: JA703-027

Effect of Mo microstructure on the critical volume fraction for conduction in Mo-alumina cermets
J.F. Kelso, R.R. Higgins, F.J. Krivda
(Alcoa Technical Center)

The microstructure of Mo in an alumina/frit matrix was found to be dependent on the initial particle sizes of the alumina and Mo powders, the glass content in the matrix ceramic, and the amount of moisture in the firing atmosphere. The Mo microstructure had a significant influence on the critical volume fraction for conductivity in these cermets. Coarser alumina powder, finer Mo powder, and higher glass content promoted coalescence of Mo into conductive networks at lower metal contents. Drier firing atmospheres produced a more coarsened Mo microstructure with a slight decrease in the amount of network contiguity, causing an increase in the amount required for electrical percolation.
Order No.: JA703-028

Chemical vapor deposition SiC (SCS-0) fiber-reinforced strontium aluminosilicate glass-ceramic composites
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Unidirectional $SrO.Al_2O_3.2SiO_2$ glass-ceramic matrix composites reinforced with uncoated chemical vapor deposition (CVD) SiC (SCS-0) fibers have been fabricated by hot pressing under appropriate conditions using the glass-ceramic approach. Almost fully dense composites having a fiber volume fraction of 0.24 have been obtained. Monoclinic celsian, $SrAl_2Si_2O_8$, was the only crystalline phase observed in the matrix by x-ray diffraction. No chemical reaction was observed between the fiber and the matrix after high temperature processing. In three-point flexure, the composite exhibited a first matrix cracking stress of ~231 ± 20 MPa and an ultimate strength of 265 ± 17 MPa. Examination of fracture surfaces revealed limited short length fiber pull-out. From fiber push out, the fiber/matrix interfacial debonding and frictional strengths were evaluated to be ~17.5 ± 2.7 MPa and 11.3 ± 1.6 MPa, respectively. Some fibers were strongly bonded to the matrix and could not be pushed out. The micromechanical models were not useful in predicting values of the first matrix cracking stress as well as the ultimate strength of the composites.
Order No.: JA703-029

Role of matrix microstructure in the ultrasonic characterization of fiber reinforced metal matrix composites
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(Wright Laboratory)

This work deals with the application of ultrasonic nondestructive evaluation for characterizing fiber reinforced metal matrix composites. The method involved the use of a recently developed technique in which the fiber reinforcement acts as a reflector to incident ultrasonic shear waves. Single fiber and multi-fiber, single-ply composites consisting of SiC fibers in several titanium alloy matrices were investigated. The ultrasonic images obtained were correlated with the results of metallographic characterization of the composites. The results showed that the ultrasonic response of the metal matrix composites is significantly influenced by the microstructure of the matrix through which the incident wave traverses. The general effects of matrix on ultrasonic wave propagation are reviewed and the ultrasonic signals obtained from various SiC fiber reinforced titanium alloy composites are discussed in terms of the scattering effects of matrix microstructure.
Order No.: JA703-030

High pressure compaction of nanosize ceramic powders
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High-density ceramic materials from nanosize ceramic powders were produced by high pressure under nearly hydrostatic environment up to 5.6 GPa, on a special configuration in a toroidal-type apparatus, at room temperature. Attempts to use a common solid pressure transmitting medium such as NaCl resulted in cracked samples. Lead and indium, which have an extremely low shear strength, proved to be the suitable choices as a pressure-transmitting medium to compact these ceramic materials in order to obtain high-density samples. Transparent amorphous SiO_2-gel and translucent γ-Al_2O_3 samples, in bulk, with volumes about 40 mm^3, hard and crack-free, were obtained. Densities over 90% of full density for the γ-Al_2O_3 samples and over 80% for the compacted SiO_2-gel samples were obtained. In addition, from the density-pressure curve, the yield strength (σ) for γ-Al_2O_3 was estimated, for the first time, as 2.6 GPa. Vickers microhardness values were in the range of 5.7 GPa for the γ-Al_2O_3 samples, and 4.0 GPa for the SiO_2-gel samples, under loads of 50 g. An important and practical application of these results are the possibility of producing bulk γ-Al_2O_3, a new alumina material, which was not possible to be prepared before due to the conversion to α phase during the normal sintering process. Additionally, especially for SiO_2-gel, a very important application of this study is the possibility of incorporation of organic substances in an inorganic matrix, using high pressure at room temperature.
Order No.: JA703-031

Synthesis of aluminum oxide based ceramics by laser photo-induced reactions from gaseous precursors
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Laser-driven synthesis of Al_2O_3-based ceramic powders from gaseous precursors has been accurately investigated. Different concentrations of the reactant gaseous precursors are shown to influence both the process yield and the synthesized powder composition. Depending on the relative concentration of TMA:$Al(CH_3)_3$ and N_2O, the process leads either to the formation of nanocrystalline γ-Al_2O_3 with large free carbon contamination and traces of the Al_3O_3N phase or to the formation of a mixed γ-Al_2O_3, Al_2OC compound. The different reaction paths have been attributed to the intermediate formation of aluminum carbide. Particular attention has been paid to the gaseous reaction products to correctly interpret the source of carbon contamination observed in the formed powders. Calcining at moderate (900°) and high (1400°C) temperatures induces nanosized γ-Al_2O_3 powder and the $\gamma \rightarrow \alpha$ Al_2O_3 transition with particle coalescence and growth.
Order No.: JA703-032

$SrBi_2Ta_2O_9$ thin films made by liquid source metalorganic chemical vapor deposition
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A liquid source metalorganic chemical vapor deposition system was installed to deposit $SrBi_2Ta_2O_9$ (SBT) thin films on sapphire and $Pt/Ti/SiO_2/Si$ substrates. The process parameters such as deposition temperature and pressure, and ratio of Sr:Bi:Ta in the precursor solutions were optimized to achieve stoichiometric films with good reproducible ferroelec-

tric properties. It was found that the nucleation of SBT started at a deposition temperature close to 500°C, and grain growth dominated at 700°C and higher temperatures. With increasing deposition temperatures, the grain size of SBT thin films increased from 0.01 μm to 0.2 μm, however, the surface roughness and porosity of the films also increased. To fabricate specular SBT films, the films had to be deposited at lower temperature and annealed at higher temperature for grain growth. A two-step deposition process was developed which resulted in high quality films in terms of uniformity, surface morphology and ferroelectric properties. The key to the success of this process was the homogeneous nucleation sites at lower deposition temperature during the first step and subsequent dense film growth at higher temperature. The two-step deposition process resulted in dense, homogeneous films with less surface roughness and improved ferroelectric properties. SBT thin films with grain size of about 0.1 μm exhibited the following properties: thickness: 0.16–0.19 μm, $2P_r$: 7.8–11.4 μC/cm^2 at 5V, E_c: 50–65 kV/cm, $I_{leakage}$: 8.0–9.5x10^{-9} Acm^{-2} at 150 kV/cm, dielectric constant: 100–200, fatigue rate: 0.94–0.98 after 10^{10} cycles at 5 V.

Order No.: JA703-033

Microstructural characterization of a titanium-tungsten oxide gas sensor

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Thin films of Ti-W-O were prepared from a W-Ti alloy target by rf magnetron sputtering in reactive atmosphere. Analysis devoted to investigate the microstructural properties of this material was carried out in order to explain the origin for the high sensing performance of a W-Ti-oxide gas sensor. Scanning and transmission electron microscopy techniques showed that after annealing the film consists of a polycrystalline layer, isostructural to tetragonal WO_3, over which crystallites of pure WO_3 are dispersed. The WO_3 crystallites are insulated from each other and do not enter into the process of conduction of the layer. It was shown that Ti is soluted in the tetragonal WO_3 lattice of the underlying layer. This layer exhibits fine-granularity, which is an optimal feature for materials suited to gas sensing.

Order No.: JA703-034

Extended x-ray absorption fine structure study of incorporation of Bi and Pb atoms into the crystal structure of $Ba_{4.5}Nd_9Ti_{18}O_{54}$

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In extended x-ray absorption fine structure (EXAFS) study of the local environment of Bi^{3+} and Pb^{2+} ions incorporated in $Ba_{4.5}Nd_9Ti_{18}O_{54}$ actual sites of Bi- and Pb- incorporation are determined. Evidences are given that dopant ions are not distributed randomly on all theoretically possible sites: Bi^{3+} selectively enters one out of three possible channels, corresponding to the sites x = 0.9484, y = 0.2500, z = 0.2939 and/or x = 0.0455, y = 0.2500, z = 0.6928 previously occupied by Nd^{3+}, while Pb^{2+} selectively enters site x = 0.4940, y = 0.2500, z = 0.4993 previously shared by Ba^{2+} and Nd^{3+}.

Order No.: JA703-035

Combustion synthesis of Si_3N_4 powder

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A SHS process has been developed for the synthesis of Si_3N_4 powder under low nitrogen pressures. Si and NaN_3 powders were used as the reactants and NH_4Cl powder was added as a catalytic agent. These powders were mixed and pressed into a cylindrical compact. The compact was wrapped up with an igniting agent (i.e., Ti+C) and the synthesis reaction was triggered by the combustion of the igniting agent. Addition of NH_4Cl was found necessary for the combustion synthesis reaction under low nitrogen pressures (<1.2 MPa). The product as synthesized is mostly in the form of agglomerated fine particles (0.1~1 μm in diameter) and is composed mainly of α-phase and a minor amount of β-phase. Effects of various experimental parameters (N_2 pressure, NaN_3, NH_4Cl, and Si_3N_4 contents) on the product conversion and the combustion temperature were investigated. A possible reaction mechanism was proposed, which explains the effects of the experimental parameters on the synthesis reaction.

Order No.: JA703-036

Effect of heat treatment on formation of sol-gel (Pb,La)TiO_3 films for optical application

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Lead lanthanum titanate [(Pb,La)TiO_3] sol-gel films have been prepared to investigate the effect of heat treatment on the fabrication of uniform and crack-free thick films by applying different heating schedules. The surface morphology as well as the optical properties such as refractive index, optical transmission, and optical propagation loss of the films was examined depending on the film thickness. Because the slower and longer heating is enough to remove the organic and nitrate residues and diminish the thermal shock during heating the films, the slower and longer heating can produce the uniform and crack-free thick films having higher refractive index as well as lower optical propagation loss. Also, drying and heating the films on a hot plate in every coating resulted in the fabrication of thick films with above 8000 Å without any defects and microcracks. This film presented the highest refractive index as well as the lowest optical propagation loss which grows exponentially with increasing the film thickness due to the scattering of defects in the film.

Order No.: JA703-037

Synthesis and characterization of sol-gel derived hexa-aluminate phosphors

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Two refractory phosphors, $BaMg_2Al_{16}O_{27}$:Eu^{2+} (BAM) and $MgAl_{11}O_{17.5}$: Ce^{3+}, Tb^{3+} (MAO), have been synthesized both by the conventional solid-state processing route (using oxides as the starting materials) and by reacting precursors made by the sol-gel process using organic precursors. The phases formed were reacted at 1000°C in (a) steam and (b) steam + AlF_3. The phosphors were well crystallized with particle sizes in the range of 1–10 μm. The emission spectra showed the characteristic broad band blue emission of Eu^{2+}, for BAM and a narrow band green luminescence of Tb^{3+} for MAO. The melting point of BAM and MAO were measured to be 1920 ± 20°C and 1950 ± 20°C, respectively, using an Ir-strip furnace and optical pyrometer. BAM and MAO phosphor materials are congruently and incongruently melting, respectively. Excellent crystallization via the sol-gel route was found even at 1220°C. Enhancement of the luminescent output by the steam treatment by some 25% was determined.

Order No.: JA703-038

Role of antimony sulfide buffer layers in the growth of ferroelectric antimony sulfo-iodide thin films

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The growth and properties of ferroelectric antimony sulfo-iodide (SbSI) films on platinized silicon (Pt/Ta/SiO_2/Si) for various applications are reported here. Films were grown with and without antimony sulfide (Sb_2S_3) buffer layers using the physical vapor transport technique (PVT). The Sb_2S_3 buffer layers significantly improve the crystalline orientation and microstructure of the SbSI films. It is possible to control the crystalline orientation of the SbSI films to a large degree by annealing the buffer layers under optimized conditions of temperature and time. The films are chemically homogeneous, uniform in thickness and ferroelectric in nature. The PVT method is effective for the growth of device quality ferroelectric SbSI films with preferred orientation along the c-axis either perpendicular or parallel to the substrate surface. The former configuration is particularly suited for the fabrication of uncooled focal plane arrays whereas the films with c-axis orientation parallel to the substrate are useful for the development of infrared imagers based on the pyro-optic effect. The peak dielectric constant of c-axis oriented films (perpendicular to the substrate) is determined to be 590 at the Curie point of 19°C. This is the highest value of the dielectric constant ever reported for SbSI films.

Order No.: JA703-039

Hydrothermal synthesis of $PbTiO_3$ films
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Well-crystallized polycrystalline films of tetragonal $PbTiO_3$ have been synthesized on Ti metal substrates in concentrated alkaline solutions of $Pb(OH)_2$ containing KOH by hydrothermal method under saturated vapor pressure (2.0 MPa) at 200°C. The film microstructure depended strongly on the $Pb(OH)_2$ and KOH concentration. The grain size became larger approximately from 0.6 to 6 μm with an increase of KOH concentration from 1 to 4 M at 0.07 M $Pb(OH)_2$, whereas grains grew to smaller size with an increase of $Pb(OH)_2$ concentration at 1 M KOH concentration. $PbTiO_3$ film prepared in the aqueous solution of 0.07 M $Pb(OH)_2$ containing 2 M KOH showed a relative dielectric constant of about 215 and loss of about 5% at 1 kHz.
Order No.: JA703-040

A four point bending technique for studying subcritical crack growth in thin films and at interfaces
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A technique was developed to obtain the subcritical crack growth velocity in a 4-point bending sample by analyzing the load-displacement curve. This was based on the observation that the compliance of a beam increases as the crack grew. Beam theory was used to analyze the general configuration where two cracks propagated in the opposite directions. A simple equation relating the crack velocity to the load and displacement was established taking advantage of the fact that the compliance was linearly proportional to the crack lengths, thus the absolute crack length was not important. Two methods of obtaining crack velocity as a function of load were demonstrated. First, by analyzing a load-displacement curve, a corresponding velocity curve was obtained. Secondly, by changing the displacement rate and measuring the corresponding plateau load, a velocity value was calculated for each plateau load. While the former was capable of obtaining the dependence of crack velocity vs. load from a single test, the latter was found to be simpler and more consistent. Applications were made to a CVD SiO_2 system. In both cases of crack propagation either inside the SiO_2 layer or along its interface with a TiN layer, the crack growth velocity changed with the stress concentration at the crack tip exponentially. As a result, a small crack will grow larger under essentially any tensile stresses typically existing in devices, provided that chemical agents facilitating stress corrosion mechanisms are also present.
Order No.: JA703-041

Investigation on the interface reactions of Ti thin films with AlN substrate
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Pure bulk AlN substrates were prepared by hot-pressing to eliminate the influence of an aid-sintering substance on the interface reactions. AlN thin films were deposited on Si(111) substrates to decrease the influence of charging on the analysis of metal/AlN interfaces with x-ray photoelectron spectroscopy (XPS). Thin films of titanium were deposited on bulk AlN substrates by e-gun evaporation and ion beam assisted deposition (IBAD) and deposited on AlN films *in-situ* by e-gun evaporation. Solid-state reaction products and reaction mechanism of Ti/AlN system annealed at various temperatures and under IBAD were investigated by XPS, transmission electron microscopy (TEM), x-ray diffraction (XRD) and Ruthford backscattering spectrometry (RBS). Ti reacted with AlN to form a laminated structure in the temperature range of 600°C to 800°C. The $TiAl_3$ phase was formed adjacent to the AlN substrate, TiN, and Ti_4N_{3-x} as well as Ti_2N were formed above the $TiAl_3$ layer at the interface. Argon ion bombardment during Ti evaporation promoted the interface reactions. No reaction products were detected for the sample as-deposited by evaporation. However, XPS depth profile of the Ti/AlN/Si sample showed that Ti-N binding existed at the interface between the AlN thin films and the Ti thin films.
Order No.: JA703-042

Microstructure and strength of Al-sapphire interface by means of the surface activated bonding method
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Sapphire (α-Al_2O_3) and Al were joined by means of the surface activated bonding (SAB) method in an ultra-high vacuum at room temperature. Tensile tests have shown that failure occurred not along the interface but inside the Al bulk near the interface. High resolution transmission electron microscopy has revealed the formation of a direct interface between Al and sapphire, indicating the possibility to artificially fabricate an atomically direct interface of dissimilar materials at room temperature. However, an intermediate layer was partially observed, which might be attributed to the effect of fast atom beam irradiation of the sapphire surface.
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COMMENTARIES AND REVIEWS

Materials reliability issues with coaxial cable systems for the Information Superhighway
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A frequently advocated design for the *Information Superhighway* that will provide voice, video, and two-way digital communication for businesses and residences calls for transmission on optical fibers from the source (head end) to neighborhood nodes and coaxial cable for distribution from the neighborhood nodes to individual subscribers.

Materials reliability challenges abound from the head end to the customer's premise. The maximum allowed service outage per customer is expected to be less than one hour per year. The fiber portion of the network, including lasers, amplifiers, lenses, and the fiber itself, carries two-way transmission to large neighborhoods. With one fiber serving hundreds of customers, cost/reliability tradeoffs emphasize reliability. At neighborhood nodes, where the network branches, coaxial components carry the signal to the street level, where each subscriber is served by at least one drop cable and one network interface unit. The volume of components is much higher. The challenge is to achieve high reliability at low cost. Indeed, one of the impediments to replacing coaxial distribution in the neighborhood with fiber is the difficulty of achieving low-cost, reliable packaging for lasers and other optical components, while maintaining reliability. Since covering all the many materials aspects of system reliability would fill an entire book, the important design considerations, materials issues, and test methods that bear on the reliability of hybrid fiber coaxial systems will be illustrated by reviewing several aspects of coaxial reliability. The intent is to illustrate the methods used to identify and prevent failure mechanisms and the information that must be assembled for making appropriate decisions on reliability/cost tradeoffs.

While coaxial systems have been used for over 20 years to bring cable TV to homes across North America, the requirements for reliability and signal quality with these one-way analog rf systems are less demanding than those for two way digital data transmission. Many of the reliability issues that could potentially degrade performance characteristics of coaxial cable systems are materials and environment related. This paper discusses these issues to the extent that they are currently understood, presents results from some ongoing research to improve our understanding of the potential materials/environment related causes of signal deterioration, describes some prevention strategies, and discusses some of the many materials challenges that remain.
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