JMR Abstracts

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Grain refinement mechanism in undercooled $Cu_{30}Ni_{70}$

J.Z. Xiao, K.K. Leung, H.W. Kui
(The Chinese University of Hong Kong)

When undercooled molten $Cu_{30}Ni_{70}$ crystallizes at an undercooling $\Delta T \cong 145$ K (ΔT is defined as $T_1 - T_k$ where T_1 is the liquidus of $Cu_{30}Ni_{70}$ and T_k is the kinetic crystallization temperature), its grain size undergoes a rapid decrease by as much as two orders of magnitude in a narrow temperature range. This phenomenon is termed grain refinement. It was found that grain refinement is brought about by multiplication of dendrites. Composition analysis of the dendrite indicates that it has the least Ni concentration at its axis. The Ni content then increases radially from the central axis. Therefore, the dendrite is unstable against melting since the melting temperature of Cu-Ni increases with Ni content. The origin of grain refinement is attributed to the remelting of these dendrites.

Order No.: JA704-001

Effects of electroless nickel plating on resistivity-temperature characteristics of $(Ba_{1-x}Pb_x)TiO_3$ thermistor

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Effects of electroless nickel plating on R-T characteristics of $(Ba_{1-x}Pb_x)TiO_3$ thermistor were studied. Comparison experiments showed that not only the permeation of plating solution but also the reaction of electroless nickel plating influences the PTC effect, and that the two effects are different in nature. It is first proposed in this paper that hydrogen atoms generated in electroless nickel plating may reduce components of PTC ceramics.

Order No.: JA704-002

ARTICLES

Seeded crystal growth of $YBa_2Cu_3O_{6.5}$ in semisolid melts

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Melt-textured single crystals of $YBa_2Cu_3O_{6.5}$ (123) superconductors were produced by isothermal solidification from a semisolid melt using single crystal $NdBa_2Cu_3O_{6.5}$ or $SmBa_2Cu_3O_{6.5}$ seeds. The microstructure within the single crystals shows an inhomogeneous segregation of Y_2BaCuO_5 (211) particles trapped in the 123 crystals during solidification. The concentration of 211 particles varies with the crystal axes in 123 crystals produced from precursors with compositions of 80 wt.% 123 powder and 20 wt.% excess 211. The 211 particle concentration along the c-axis in the crystal is much lower than that along the a- or b-axes during initial crystallization. This concentration increases in both directions as the crystal grows larger. The 211 concentration along the c-axis increases more quickly than the concentration along the other axes during solidification, which allows the 211 concentration to approach that on the other axes as the solidification continues. 211 particle segregation in stoichiometric 123 samples formed "X"-shaped tracks instead of the variations in 211 concentration described above. A single crystal growth model of 123 is proposed and employed to interpret these experimental observations. Quenched samples were prepared to investigate the volume fraction of 211 particles in the liquid phase. A constant distribution of 211 particles was observed in the liquid, except very near the crystal interface, where the 211 concentration decreased rapidly. Copper oxide content in the liquid was also measured. It is found that the copper content is lower at the (001) interface compared with (100) or (010) interfaces.

Order No.: JA704-003

In-situ measurements of texture and phase development in $(Bi,Pb)_2Sr_2Ca_2Cu_3O_{10}$-Ag tapes

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Hard x-rays from a synchrotron source were utilized in diffraction experiments performed at elevated temperatures (up to ~870°C) on $(Bi,Pb)_2Sr_2Ca_2Cu_3O_{10}$ (Bi-2223) tapes *completely* encased in silver. The general behavior of the phase and texture development under typical processing conditions was determined, and the effects that several variations in processing conditions had on the phase and texture development were examined. These results and their implications for improving processing conditions are discussed.

Order No.: JA704-004

Transmission electron microscopy observation of the decomposition of $YBa_2Cu_4O_8$ into $YBa_2Cu_3O_{7-\delta}$ and CuO

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The decomposition of $YBa_2Cu_4O_8$ (Y-124) into $YBa_2Cu_3O_{7-\delta}$ (Y-123) and CuO at high temperatures has been expected to create Y-123 with finely dispersed CuO precipitates suitable for flux pinning. In fact, samples of thermally decomposed Y-124 exhibit a critical current density, j_c, which is enhanced with respect to the starting material as well as to pure Y-123.

Transmission electron microscopy (TEM) studies of furnace annealed Y-124 were not suitable to clarify the reason for this j_c enhancement. Nevertheless, the formation and growth of CuO precipitates have been observed by *in-situ* decomposition of the Y-124 starting material due to electron beam heating within the TEM.

Order No.: JA704-005

The fracture toughness of polycrystalline silicon microdevices: A first report

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(Case Western Reserve University)

Polysilicon microfracture specimens were fabricated using surface micromachining techniques identical to those used to fabricate micro-

electromechanical systems (MEMS) devices. The nominal critical *J*-integral (the critical energy release rate) for crack initiation, J_c, was determined in specimens whose characteristic dimensions were of the same order of magnitude as the grain size of the polysilicon. J_c values ranged from 16 to 62 N/m, approximately a factor of four larger than J_c values reported for single crystal silicon.
Order No.: JA704-006

Grain size dependence of mechanical properties in nanocrystalline selenium
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Porosity-free nanocrystalline element selenium (nc-Se) samples with the mean grain sizes ranging from 8 to 70 nm were synthesized by complete crystallization of the melt-quenched amorphous Se solid. Mechanical properties including microhardness (H_v) and elastic modulus (E) of the nc-Se samples were measured by means of nanoindentation tests and microhardness tests, respectively. With a reduction of grain size, the nc-Se samples were found to be substantially hardened. But the grain size dependence of H_v does not follow a simple Hall-Petch relation over the whole grain size range, exhibiting three distinct stages corresponding to three different Hall-Petch slopes. The maximum Hall-Petch slope was found to be in the grain size range of 15~20 nm, corresponding to large values of the elastic modulus. This behavior can be explained in terms of the lattice distortion in the nc-Se samples that were experimentally determined by using quantitative x-ray diffraction measurements. A conclusion is drawn that the lattice structure of the nm-sized crystallites may play an important role in mechanical properties of nanocrystalline materials.
Order No.: JA704-007

Conductive $LaNiO_3$ electrode grown by pulsed laser ablation on Si substrate
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(Nanjing University)

Using the pulsed laser ablation (PLA) technique, conductive $LaNiO_3$ thin films have been successfully grown on the (001) Si substrates. The XRD θ-2θ scan patterns indicate a preferential (110) orientation and the electron probe microanalyzer (EPMA) investigations show that the three elements La, Ni and O distribute uniformly in the films. The resistivity of the as-deposited $LaNiO_3$ films displays a metallic character. Polycrystalline $PbTiO_3$ films are deposited by metalorganic chemical vapor deposition (MOCVD) on these $LaNiO_3$ electrodes. Ferroelectric measurements of the $PbTiO_3/LaNiO_3$ heterostructure prove $LaNiO_3$ to be a promising electrode material in the integration of ferroelectrics and Si wafer.
Order No.: JA704-008

Microstructure and homogeneity of nanocrystalline Co-Cu supersaturated solid solutions prepared by mechanical alloying
J.Y. Huang, Y.D. Yu, Y.K. Wu, H.Q. Ye, D.X. Li
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Mechanical alloying (MA) has been performed in $Co_xCu_{(100-x)}$ (x=10, 25, 50, 60, 75, 90) system. High-resolution electron microscopy (HREM) and field emission gun transmission electron microscopy (FEG TEM) were used to characterize the microstructure and homogeneity of the nanocrystalline $Co_{25}Cu_{75}$ solid solution. After 20 h of MA, all the mixtures show an entirely face-centered-cubic (fcc) phase. HREM shows that the ultrafine-grained (UFG) materials prepared by MA contain high density of defects. Two kinds of typical defects in UFG $Co_{25}Cu_{75}$ are deformation twins and dislocations. The dislocations are mostly 60° type, and in many cases they dissociate into a 30° and a 90° partials. The grain boundaries are ordered in structure, curved and slightly strained, which is similar to that observed in NC-Pd. Nanoscale energy dispersive x-ray spectroscopy (EDXS) shows that the Co concentration in both the interior of grains and the GBs are close to the global composition, which proves that supersaturated solid solutions are indeed formed. In the meantime EDXS revealed that the mixing of Co and Cu in the solid solutions is homogeneous at nanometer scale. MA in Co-Cu system is suggested to be a diffusion controlled process and stress-stimulated diffusion is proposed to be the reason for the formation of supersaturated solid solutions in this immiscible system.
Order No.: JA704-009

Similarities and differences in the microstructure of attritor milled Fe-Al-N compositions
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Although numerous studies of high-energy ball-milled metal powders have been conducted, to date few studies have characterized the mechanical processing of identical elemental compositions of prealloyed powders and of powder blends. This study reports on the mechanical processing (attritor ball milling) in argon and nitrogen gas environments of (a) iron powder and prealloyed iron-2 wt.% aluminum powder, and (b) iron-aluminum, iron-aluminum nitride, and iron-iron nitride powder blends. When nitrogen was milled into iron particles either from nitride powder or by gas infusion, the nitrogen dissolved interstitially in bcc-Fe (principally at the grain boundaries) or was present as bct-Fe nanoparticles at the bcc-Fe nanograin boundaries. The resulting nitrogen distribution was independent of how the nitrogen was added.

Milled blends of iron and aluminum powder and prealloyed iron-aluminum powder resulted in similar microstructures: micrometer size particles with similar nanograin size. The aluminum in the blended powder mixture developed an ultra fine distribution on the grain boundaries, but it did not become uniformly distributed within the bcc-Fe grains. In contrast the aluminum in prealloyed Fe-Al powder remained in solid solution during mechanical milling.
Order No.: JA704-010

The spreading kinetics of Ag-28$Cu_{(L)}$ on $nickel_{(S)}$: Part II. Area of spread on surfaces plated with electrolytic Ni
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Furnace brazing is commonly used in the electronic industry to attach I/O pins, lid-seal rings, and heat spreaders to cofired multilayer ceramic packages. Despite the widespread industry usage of electrolytic and electroless Ni coatings to render base metal surfaces wettable by braze fillers, there is no fundamental treatment of "brazeability" in the published literature that can be used by the materials technologist to design coatings for a given application. In this study, dynamic hot stage microscopy is used to establish the parameters that control the spreading of eutectic Ag-Cu braze on surfaces plated with electrolytic Ni. The effects of plating thickness, substrate type, annealing, and the braze thermal cycle are considered. A braze spreading mechanism developed for polycrystalline Ni in Part I of this study is linked to Ni-plated surfaces through consideration of differences in microstructure. Eventual extension of this improved understanding to surfaces plated with electroless Ni-B and Ni-P deposits will result in shortened product design time and improved manufacturing process control.
Order No.: JA704-011

Analysis of ball-indentation load-depth data: Part I. Determining elastic modulus
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Analysis of ball-indentation process was made by the finite element (FE) method. A series of indentation FE analyses were made on materials with different elastic modulus (E), and a simple relationship between E and the load-depth (F-h) unloading data is presented. In order to check for the influence of other material properties, a thorough research has been performed introducing a combination of response surface (RS) and FE analysis. As a result, a relationship between the indentation unloading slope, E, and the strain hardening exponent was derived. Also, the indenter compliance effect has been investigated. The indenter compliance correction was calculated and applied to the experimentally measured F-h results. Experimental testing was made on three materials with essentially different elastic moduli. Comparison of the results obtained by newly developed equations with the results from other well-known equations is also presented.
Order No.: JA704-012

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The thermal stability of thin copper films deposited on TiO_2 (110) studied by scanning tunneling microscopy

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The morphology of Cu thin films is strongly dependent on the temperature of the substrate during and after deposition. Films grown at temperatures between 300°C and 400°C form clusters distributed in close packed domains and isolated clusters across the surface. Increased substrate temperature results in cluster shape evolution indicative of mass flow and sintering. Deposition of Cu at substrate temperatures higher than 500°C results in a completely different morphology of the film and the suppression of cluster formation. Annealing these Cu films to temperatures of 700°C allows the system to relax into an equilibrium state characterized by large facets in the film and large areas of exposed surface. These observations are discussed in terms of basic thermodynamic data for bulk Cu oxidation and surface tensions for this system.

Order No.: JA704-013

Microstructure of ruthenium dioxide films grown on α-Al_2O_3 (0001), α-Al_2O_3 ($1\bar{1}02$), and $SrTiO_3$ (100) using reactive sputtering

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A quantitative study was made of the composition and microstructure of RuO_2 films deposited on three different substrates using reactive sputtering. Most of the films had a composition within 2.5 at.% of the correct stoichiometry; the only exceptions were films grown on Al_2O_3(0001) at 150°C, which had an oxygen to ruthenium ratio of 1 : 2.24. The excess oxygen was attributed to a thin oxygen-rich layer that encapsulated the grains. Hydrogen concentrations for the films deposited on Al_2O_3(0001) were 14, 6, 6, and <0.5 atomic percent for room, 150, 300 and 450°C growth temperatures, respectively. The films deposited at room temperature were amorphous on Al_2O_3(0001) and $SrTiO_3$(100), but weakly crystalline on Al_2O_3 ($1\bar{1}02$). Highly oriented RuO_2(100) films were produced on Al_2O_3(0001) at deposition temperatures ≥ 150°C. The in-plane alignment was [010]RuO_2 // <$\bar{2}$110> Al_2O_3 and a three-fold mosaic microstructure was observed. The grain boundaries in these films were discontinuous until the substrate temperature was raised to 450°C, where coherent grain boundaries were formed. The films grown on Al_2O_3 ($1\bar{1}02$) at 450°C exhibited the epitaxial relationship: RuO_2(101) // Al_2O_3($1\bar{1}02$). The in-plane alignment was RuO_2 <$\bar{2}$101> // Al_2O_3 <$\bar{1}$101>; and the lattice parameters were the same as found in bulk RuO_2. Transmission electron microscopy indicated a large degree of imperfection in the region between coalescing grains. The RuO_2 films grown on $SrTiO_3$ (100) at room temperature were amorphous. The film grown at 450°C showed preferential orientation with RuO_2 (100) // $SrTiO_3$(100), but without in-plane orientation.

Order No.: JA704-014

***In-situ* sputter deposition of $PbTiO_3$ thin films on different substrates: Influence of the growth temperature and the sputtered lead flux on the perovskite phase formation**

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Thin films of lead titanate were prepared *in-situ* using radio-frequency magnetron sputter deposition. The *in-situ* perovskite phase formation has been studied as a function of the substrate temperature, the sputtered lead flux and the substrate nature. The incident lead flux is controlled by the lead content in the target. An equilibrium zone, i.e., a saturation effect of the lead incorporation, exist where the films are stoichiometric. The temperature where this zone appears depends on the sputtered lead flux and the substrate type. The growth mechanism is governed by a competition between the arrival rate of Pb and their re-evaporation from the film during the growth. The *in-situ* formation temperature of the perovskite phase increased when the incident Pb flux increased. As a result, $PbTiO_3$ films have been prepared at low temperature with appropriate combination of the substrate temperature and the lead content in the target, i.e., the sputtered lead flux. Since the lead sticking coefficient is very sensitive to the substrate material, the perovskite phase appears at different temperatures depending on the substrate nature. $PbTiO_3$ films are obtained at 550°C on $Al2O_3$ and $SrTiO_3$ substrates; on $Si/SiO_2/Ti/Pt$ substrates, stoichiometric films are obtained at 440°C. The structure and the microstructure of the films were examined at various deposition conditions. The substrate temperature strongly influenced the film orientation and the film crystallinity depended on the incident lead flux. High-quality thin films (FWHM = 0.2°) are obtained at 550°C on $SrTiO_3$ substrates. The films deposited at 440°C on $Si/SiO_2/Ti/Pt$ show ferroelectric properties. This self controlling mechanism of the stoichiometric composition allow the growth of ferroelectric films at low temperature compatible with semiconductor technologies for the realization of integrated circuits.

Order No.: JA704-015

Deposition process and property of silica films containing organic groups from aqueous solution of alkoxides

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Silica thin films containing organic groups were directly deposited from aqueous solutions of silicon alkoxides. Effects of functional groups of the alkoxides and the deposition conditions on the preparation of the films were investigated in order to clarify the deposition process. Silica films containing methyl and phenyl groups deposited from aqueous solutions of methyl- and phenyl-trialkoxysilanes, respectively, in the pH region lower than 3 or higher than 6. The composition and the property of the deposited films were influenced by pH and temperature of the solutions and the starting materials. The adhesion of the deposited films on hydrophobic substrates was lower than that on hydrophilic ones although the films were formed on both surfaces. The refractive index of the methyl containing films, ca.1.44, decreased with removal of methyl groups by heating up to 500°C.

Order No.: JA704-016

Sol-gel synthesis of $LaAlO_3$; epitaxial growth of $LaAlO_3$ thin films on $SrTiO_3$ (100)

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A $LaAlO_3$ precursor solution was prepared via an all alkoxide sol-gel route. The solution of lanthanum methoxyethoxide and aluminum methoxyethoxide in 2-methoxyethanol was prepared via ligand exchange starting from lanthanum isopropoxide and aluminum sec-butoxide, and was used to make both $LaAlO_3$ powders and films. Complete hydrolysis of the solution formed a gel that yielded well-crystallized $LaAlO_3$ powders when fired in air at 800°C. A partially hydrolyzed solution was spun-cast on $SrTiO_3$ (100) single crystal substrates. Epitaxial films of $LaAlO_3$ were subsequently formed during pyrolysis in O_2 at 800°C in a rapid thermal annealing furnace for a total of 8 minutes. The films were strongly c-axis oriented, verified by x-ray rocking curve results from the (003) plane with full-width at half-maximum (FWHM) = 0.87°, and had good in-plane texture shown by a ϕ scan of the (202) plane with FWHM = 1.07°.

Order No.: JA704-017

Aging characteristics of a hybrid sol-gel $Pb(Zr,Ti)O_3$ precursor solution

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The "aging" characteristics of an acetic acid/methanol solvent based lead zirconate titanate precursor solution, prepared by the inverted mixing order (IMO) process have been studied for an extended period of time. The changes in film properties were characterized using optical microscopy, optical scattering, and ferroelectric testing. Films generated from the IMO process exhibit an increase in thickness as a function of solution age due to chemical "aging" (esterification) of the precursor solution. This increased thickness results in a decrease in the microstructural uniformity, which affects the electrical and optical properties. In order to understand and eventually control this phenomenon, we have quantified the "aging" of this solution using a variety of analytical methods, including: ^1H NMR spectroscopy, pH measurements, and FT-IR spectroscopy. It is of note that we have discovered a method which circumvents this "aging" problem by removal of the volatile material, forming an IMO powder which can be redissolved to produce high quality PZT thin films whenever desired.

Order No.: JA704-018

Electrically-controlled flame synthesis of nanophase TiO_2, SiO_2, and SnO_2 powders

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Nanophase particles with precisely controlled characteristics are made by oxidation of their halide vapors in electrically-assisted hydrocarbon flames using needle-shaped or plate electrodes. The particle size and crystallinity decrease with increasing field strength across the flame. The field generated by the electrodes across the flame decreases the particle residence time in the high temperature region of the flame. Furthermore, it charges the newly formed particles resulting in electrostatic repulsion and dispersion that decreases particle growth by coagulation. Electric fields reduced the primary particle size of TiO_2, the agglomerate size of SnO_2 and both the agglomerate and primary size of SiO_2.

Order No.: JA704-019

A study on the microstructure of preferred orientation of lead zirconate titanate thin films

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The lead zirconate titanate (PZT) thin films were fabricated using sol-gel spin coating onto Pt/Ti/glass substrates. Effects of the holding time for pyrolysis and the coating cycle on the preferred orientation of the PZT thin films were studied. The films were fabricated with different coating cycles (3, 5, 7, 9, 11), dried at 330°C for different holding times (5, 30, 60 min) and then annealed at the same temperature of 650°C using rapid thermal annealing (RTA). The preferred orientations of the films were investigated using x-ray diffraction and glancing angle x-ray diffraction. The microstructure and the selected area diffraction pattern of the PZT thin films were also investigated using scanning electron microscopy (SEM) and transmission electron microscopy (TEM), respectively.

Order No.: JA704-020

Joining of AlN to Cu using In-base active brazing fillers

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Brazing of AlN (which is good for a ceramic substrate in high power electronic applications) to copper was investigated using In-base active fillers. Compositions of brazing fillers were chosen as In-1wt.%Ti(IT1), In-19wt.% Ag-2wt.%Ti(IAT2), In-15wt.%Ti(IT15) and In-52wt.%Ag-20wt.%Cu-3wt.%Ti(ACIT3). Brazing operation was performed in vacuum at temperatures of 650°–900°C. The brazing fillers showed good wetting on AlN and led to a strong bond between AlN and braze alloy. From the microstructural analysis, no evidence of reaction layer was clearly found at the interface under the experimental brazing conditions. The composition of brazing alloy layer changed into Cu_9In_4 phase due to the extensive dissolving of Cu from base metal. Bond strength, measured by 4-point bend test, was obtained as high as 23–30 kgf for the Cu/AlN/Cu joint brazed with IT15 and ACIT3 fillers, and shown to be nearly constant even when the temperature was varied within 700–800°C. Most of the fracture appeared to proceed through the interior of the AlN ceramic. Based on the experimental results, it was believed that a strong bonding between AlN and braze alloy can be achieved without the apparent forming of Ti-rich reaction layer at the interface.

Order No.: JA704-021

High strength, electrically conductive pore-free TiO_2 ceramics made by hot isostatic pressing

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A high-purity single phase TiO_2 ceramic with high density, strength and electrical conduction was developed as a key structural material for the production equipment of semiconductors. Green bodies were made of high purity rutile TiO_2 of very fine powder. They were sintered in air at 1200°C for 2 hr and then were hot isostatically pressed (HIPed) in argon at 1000°C, 150 MPa for 2 hr. HIPed TiO_2 ceramics were found to be electrically conductive and pore-free. Their relative density, specific resistance and bending strength were 100%, 1Ω · cm and 300 MPa, respectively. No strength degradation was found to temperatures up to 1000°C. This material has high potential for the electrically conductive structure materials in the semiconductor industry.

Order No.: JA704-022

Adsorption of poly(vinyl butyral) in nonaqueous ferrite suspensions

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The adsorption of poly(vinyl butyral) (PVB) on NiCuZn ferrite powder in binary solvent systems of 1-butanol and toluene has been investigated. The adsorption isotherms of different PVBs on ferrite powder from various solvent mixtures follow closely the Langmuir monolayer types and can be explained by adsorption competition between solvents and PVB. A relatively poor solvent for PVB increases its adsorption on ferrite powder and thus improves the dispersion of the powder in the nonaqueous suspension. The adsorbance of PVB increases with increasing hydroxyl content in PVB, suggesting that PVB is bonding strongly to the protruding surface hydroxyl groups on ferrite powder.

Order No.: JA704-023

Crystallization mechanisms of some $Se_{100-x}Te_x$ glassy alloys

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The coupling of calorimetric and microscopic techniques shows that the whole crystallization process for some $Se_{100-x}Te_x$ (x= 10, 15) glassy alloys proceeds by two different mechanisms, which we call surface and bulk. These mechanisms are activated differently depending on the particular heating rate used and on the temperature of the isothermal heat treatment chosen. The nucleation frequencies and growth rates were determined from reflection polarized optical microscopy analysis and a good agreement is found between these experimental results and predictions done by the classical nucleation and the normal growth theories. The apparent activation energy from the whole crystallization process which is obtained via differential scanning calorimetry is higher for $Se_{85}Te_{15}$ than for $Se_{90}Te_{10}$, and the relation with these values and those obtained from activation energies of nucleation and growth is established. A detailed discussion about the meaning of the different Avrami indexes found is presented.

Order No.: JA704-024

Magnetic properties of graphitically encapsulated nickel nanocrystals

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Graphitically encapsulated ferromagnetic Ni nanocrystals have been synthesized via a modified tungsten arc-discharge method. By virtue of the protective graphitic coating, these nanocrystals are stable against environmental degradation, including extended exposure to strong acids. The magnetic properties of the encapsulated particles are characterized with regard to the nanoscale nature of the particles, and the influence of the graphitic coating which is believed to be benign insofar as the intrinsic magnetic properties of the encapsulated nanocrystals are concerned. The Curie temperature of graphitically encapsulated Ni nanocrystal is the same as that of microcrystalline Ni. However, saturation magnetization, remanent magnetization, and coercivity of these particles are reduced, for a range of temperatures. The unique features are compared with those of unencapsulated nanocrystalline and coarse microcrystalline nickel particles.

Order No.: JA704-025

Investigation of NiAl-TiB_2 *in-situ* composites

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A hot-pressing aided exothermic synthesis (HPES) technique to fabricate NiAl matrix composites containing 0 and 20 vol.%TiB_2 particles was developed. The conversion of mixtures of elements to the product was complete after processing, and TiB_2 particles in the matrix were uniformly dispersed. The microstructure and interfaces were very thermally stable. The interfaces between NiAl and TiB_2 were atomically flat, sharp and generally free from interfacial phases. In some cases, however, thin amorphous layers existed at NiAl/TiB_2 interfaces. At least three kinds of orientation relationships between TiB_2 and NiAl were observed. The compressive yield

strengths at room temperature and at 1000°C of the composite were approximately three times as strong as that of the unreinforced NiAl. The tensile yield strength at 980°C of the composite was about three times stronger than that of NiAl. The ambient fracture toughness of the composite was slightly greater than that of the monolithic NiAl.
Order No.: JA704-026

Optically transparent polymethyl methacrylate composites made with glass fibers of varying refractive index
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The dependence of the optical and mechanical properties of optically transparent polymethyl methacrylate (PMMA) composites on the annealing temperature of BK10 glass fibers was investigated. Annealing was used to modify the refractive index (R.I.) of the glass fiber so that it would more closely match that of PMMA. Annealing increased the refractive index of the fibers and narrowed the distribution of refractive index of the fibers, but lowered their mechanical strength so the mechanical properties of composites reinforced with annealed fibers were not as good as for composites containing as-pulled (chilled) glass fibers. The refractive index of as-pulled 17.1 μm diameter fibers (R.I. = 1.4907) increased to 1.4918 and 1.4948 after annealing at 350°C to 500°C for 1 hr or 0.5 hr respectively. The refractive index of glass fibers annealed at 400°C/1 hr best matched that of PMMA at 589.3 nm and 25°C, so, the composite reinforced with those fibers had the highest optical transmission. Because annealed glass fibers had a more uniform refractive index than unannealed fibers, the composites made with annealed fibers had a higher optical transmission. The mechanical strength of annealed fiber/PMMA composites decreased as the fiber annealing temperature increased. A composite containing fibers annealed at 450°C/1 hr had a tensile strength 26% lower than that of a composite made with as-pulled fibers, but 73% higher than that for unreinforced PMMA. This decrease was avoided by treating annealed fibers with HF. Composites made with annealed and HF(10 vol.%)-treated (for 30 sec) glass fibers had a tensile strength (~200 MPa) equivalent to that of the composites made with as-pulled fibers. However, as the treatment time in HF increased, the tensile strength of the composites decreased because of a significant reduction in diameter of the glass fiber which reduced the volume percent fiber in the composite.
Order No.: JA704-027

Fatigue of *in-situ* reinforced Ti-8.5Al-1B-1Si
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The effect of temperature on the fatigue and fracture properties of an *in-situ* reinforced super α alloy Ti-8.5Al-1B-1Si (wt.%) was investigated. At room temperature the as-extruded composite has a strength of 631 MPa with limited ductility. On increasing the temperature to 700°C only a marginal drop in strength to 610 MPa was observed, along with a significant improvement in ductility to 5.9%. Low cycle fatigue results indicate a marginal decrease in fatigue life as temperature is increased from room temperature to 700°C. Fatigue crack growth studies in the as-extruded microstructure indicate a strong influence of R-ratio on both the threshold for fatigue crack growth and crack growth rates in the Paris regimes. At elevated temperatures, the resistance to fatigue crack growth increases with temperatures below approximately 500°C. At 600°C, however, there s an increase in the near threshold crack growth rate due to embrittlement effects. At higher ΔK values ($\Delta K > 9$ MPa$\sqrt{m}$), the resistance to fatigue crack growth at elevated temperatures is always better than that at room temperature. This improvement is attributed to the increase in the inherent resistance of the matrix to fatigue crack growth.
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Momentum and thermal boundary-layer thickness in a stagnation flow chemical vapor deposition reactor
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Explicit expressions have been derived for momentum and thermal boundary-layer thickness of the laminar, uniform stagnation flows characteristic of highly convective chemical vapor deposition pedestal reactors. Expressions for the velocity and temperature profiles within the boundary-layers have also been obtained. The results indicate that, to leading order, the momentum boundary-layer thickness is inversely proportional to the square root of the Reynolds number, while the thermal boundary-layer thickness is inversely proportional to the square root of the Peclet number. Values computed using the approximate expressions are compared directly with numerical solutions of the equations of motion and thermal energy equation, for a specific set of conditions typical of diamond chemical vapor deposition. Because values of the Lewis number do not vary significantly from unity for many different chemical vapor deposition systems, the expression derived here for thermal boundary-layer thickness may be used directly as an approximate concentration boundary-layer thickness.
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Synthesis and characterization of the inorganic ion exchanger based on titanium 2-carboxyethylphosphonate
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An inorganic ion exchanger based on titanium 2-carboxyethylphosphonate (TiPC) has been synthesized by reaction between solutions of $TiCl_3$ and 2-carboxyethylphosphonic acid at elevated temperature. The solid was characterized by chemical analysis. ^{31}P MAS NMR, x-ray powder diffraction, IR spectroscopy and TG analysis. It was found that TiPC is a highly crystalline layered solid with the interlayer distance 13.1 Å, and exhibits a high thermal stability. The intercalation of *n*-alkylamines and the ion exchange properties of TiPC towards alkali, alkaline earth and some transition metal cations have been studied. The exchanger shows high affinity to alkaline earth metal cations and some di- and trivalent cations.
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Effects of glass elements on the structural evolution of *in-situ* grown ferroelectric perovskite crystals in sol-gel derived glass-ceramics
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Several ABO_3 perovskite ferroelectric crystals, $PbTiO_3$, $Pb(Zr,Ti)O_3$, and $BaTiO_3$ have been *in-situ* grown from amorphous gels with glass elements, and the structural evolution has been systematically investigated using x-ray diffraction (XRD), infrared spectra (IR), differential thermal analysis (DTA), thermogravimetric analysis (TGA), and dielectric measurements. It is found that in the Si contained glass-ceramic systems, Si and B glass elements are incorporated into the crystalline structures, resulting in the variation of the crystallization process, change of lattice constant and dielectric properties. Some metastable phases expressed by a general formula $A_xB_yG_zO_w$ (A = Pb and Ba; B = Zr and Ti; G for glass elements, especially for Si) have been observed and discussed.
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Preparation of epitaxial $BaTiO_3$ thin films by dipping-pyrolysis process
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Epitaxial $BaTiO_3$ thin films were prepared on $SrTiO_3(100)$ substrates by dipping-pyrolysis process using metal naphthenates as starting materials. Highly oriented $BaTiO_3$ thin films were crystallized by heat treatment at 800°C and higher, from amorphous precursor films pyrolyzed at 470°C. XRD pole-figure and reciprocal-space mapping analyses showed that the films were epitaxially grown on $SrTiO_3$ substrates and were pseudo-cubic phase with $a_{//}/a_{\perp}$ ratio of 1.00$_3$, smaller than c_0/a_0 ratio (= 1.011) of bulk tetragonal $BaTiO_3$.
Order No.: JA704-032

***In-situ* growth of fatigue-free $SrBi_2Ta_2O_9$ films by pulsed laser ablation**
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In-situ growth of $SrBi_2Ta_2O_9$ (SBT) films as a function of Bi concentration in the target, substrate temperature, oxygen pressure, and the thickness of bottom Pt electrode by pulsed laser deposition was studied. The SBT phase was initially formed at a temperature of 500–520°C. The SBT films grown from the stoichiometric target generally showed Bi deficiency. A well-crystallized and stoichiometric SBT film could be grown at a temper-

ature of 550–580°C in 300 mTorr of O_2 from the surplus Bi targets, which showed c-axis preferred orientation. The formation temperature of $SrTa_4O_{11}$ (ST) phase was above 600°C, depending on the Bi concentration in the target. Higher oxygen pressure raised the formation temperatures of the SBT and ST phases and concomitantly enriched the Bi concentration of the SBT films. For the bottom Pt electrode 1200 Å thick the voids were not observed in the SBT overlayer until the deposition temperatures were above 590°C. Annealing at temperatures above 700°C in an atmosphere of O_2 was required to improve the contact between Pt electrode and the SBT film and hence the ferroelectric properties of the SBT film. In the present study, a smooth, stoichiometric and c-axis oriented SBT film, about 350 nm thick, could be grown on Pt(1200 Å)/Ti/SiO_2/Si at a temperature of 550–580°C in 300 mTorr of O_2 from the Bi surplus targets, which showed remanent polarization (Pr) of 3.0–3.5 μC/cm^2 and coercive field (E_c) of 30–40 kV/cm at 4 V. No fatigue was observed up to 10^9 switching cycles.

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Preparation and characterization of $BaTiO_3$ thin films on MgO-buffered Si(100) substrates by rf sputtering

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We report the results of a study on the deposition and characterization of partially oriented $BaTiO_3$ thin films on MgO-buffered Si(100) by radio-frequency magnetron sputtering. The structural and morphological characteristics of the MgO buffer layer were investigated as a function of substrate temperature. The x-ray θ–2θ, φ scans and observation of surface morphology revealed that MgO grew with a tendency of (001) orientation. Partially (*001*) or (*h00*) textured $BaTiO_3$ thin films were obtained on Si(100) with the MgO buffer layer. While randomly oriented $BaTiO_3$ thin films with large-scale cracks on the surface were made without the MgO layer. Pt/$BaTiO_3$/Pt multistructures were formed on Si(100), MgO/Si(100), and MgO(100) single crystal substrates to conduct preliminary electrical measurements for metal-insulator-metal type capacitor. The comparison of the crystallographic orientation, morphology, and electrical properties between the $BaTiO_3$ films on Si(100) with and without the MgO buffer layer supported the favorable role of the MgO layer as a buffer for the growth of $BaTiO_3$ films on Si(100).

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Electrical and structural properties of $SrTiO_3$ thin films deposited by plasma-enhanced metalorganic chemical vapor deposition

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The microstructure and electrical properties were investigated for $SrTiO_3$(STO) thin films deposited on Pt/Ti/SiO_2/Si substrates by PEMOCVD. The SrF_2 phase existing in the STO films deposited at 450°C influences the dielectric constant, dissipation factor, and leakage current density of STO films. The dielectric constant and dissipation factor of STO films deposited at 500°C were 210 and 0.018 at 100 kHz, respectively. STO films were found to have paraelectric properties from the capacitance-voltage characteristics. Leakage current density of STO films at 500°C was about 1.0 x 10^{-8} A/cm^2 at electric field of 70 kV/cm. The leakage current behaviors of STO films deposited at 500 and 550°C were controlled by Schottky emission with applied electric field.

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