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## ABSTRACTS

### COMMUNICATIONS

**Non-destructive magneto-optical imaging analysis of superconducting  $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$  composites**

M. Turchinskaya\*, D.L. Kaiser\*, A.J. Shapiro\*, G.N. Riley Jr.†, C. Christopherson\*

(\*National Institute of Standards and Technology, †American Superconductor Corporation)

The superconducting filaments in  $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x/\text{Ag}$  composite tapes have been imaged directly through the outer silver sheath of an unpolished tape by means of a magneto-optical imaging technique. The images reveal the morphology and alignment of the uppermost layer of filaments located as much as 112  $\mu\text{m}$  below the unpolished tape surface, the depths of these filaments, and the homogeneity of the magnetic flux distribution within these filaments. These results demonstrate that the magneto-optical technique is a valuable nondestructive tool for analyzing  $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$  composite tapes.

Order No.: JA607-001

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**Fabrication of silicon carbide nano-ceramics**

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Ultra-fine silicon carbide powder with the average particle size of 90 nm was densified by hot-pressing with the addition of  $\text{Al}_2\text{O}_3$ ,  $\text{Y}_2\text{O}_3$  and  $\text{CaO}$  at 1750°C. Silicon carbide nano-ceramics with the average grain size of 110 nm were prepared by the liquid phase sintering at low temperature. The materials showed superplastic deformation at a strain rate of  $5.0 \times 10^{-4}/\text{s}$  at 1700°C, which is the lowest temperature published. The microstructure and deformation behavior of materials from a submicrometer powder were also investigated as a reference.

Order No.: JA607-002

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**X-ray photoelectron spectroscopy study of the interaction of methanol with polycrystalline copper oxide surface**

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(National Chemical Laboratory)

Methanol decomposition on clean polycrystalline copper oxide surface was studied by x-ray photoelectron spectroscopy (XPS). Methanol was adsorbed at 133 K and desorbed over a broad temperature range. When  $\text{CuO}$  was exposed to a very low dose of methanol vapor, dissociative

adsorption took place leading to the formation of  $\text{CH}_3\text{O}$  and  $\text{H}_2\text{O}$ . This is attributed to the presence of pre-adsorbed oxygen on the  $\text{CuO}$  surface.

Order No.: JA607-003

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### ARTICLES

**Transmission electron study of heteroepitaxial growth in the  $\text{BiSrCaCuO}$  system**

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Films of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$  and  $\text{Bi}_2\text{Sr}_2\text{CuO}_6$  have been grown using atomic-layer-by-layer molecular beam epitaxy (ALL-MBE) on lattice-matched substrates. These materials have been combined with layers of closely-related metastable compounds like  $\text{Bi}_2\text{Sr}_2\text{Ca}_7\text{Cu}_8\text{O}_2$  (2278) and rare-earth-doped compounds like  $\text{Bi}_2\text{Sr}_2\text{Dy}_x\text{Ca}_{1-x}\text{Cu}_2\text{O}_8$  (Dy:2212) to form heterostructures with unique superconducting properties, including superconductor/insulator multilayers and tunnel junctions. Transmission electron microscopy (TEM) has been used to study the morphology and microstructure of these heterostructures. These TEM studies shed light on the physical properties of the films, and give insight into the growth mode of highly anisotropic solids like  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ .

Order No.: JA607-004

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 **$\text{Y}_2\text{BaCuO}_5$  addition and its effects on critical currents in large-grains of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ : A quantitative microstructural study**

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The addition of  $\text{Y}_2\text{BaCuO}_5$  (211) particles to large grain melt textured  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (Y123) has significantly improved the critical current density ( $J_c$ ) of this material. Here, a systematic quantitative analysis on the effects of the 211 addition was performed on a microscopic and scale with a systematic variation of the initial volume percent of 211. From the correlation between critical current measurements and quantitative microscopy of both (001) and (110) sections, a maximum value of  $J_c$  is observed corresponding to a measured Y123 volume percent of  $20\% \pm 3\%$ . Accounting for the loss of liquid phase for the present processing, the corresponding optimum initial volume of 211 for the highest measured  $J_c$  is 40%. Further comparison between the weighted  $J_c$  and the true flux pinning force ( $F_p$ ) also shows a maximum pinning force for

an initial 211 addition of 40%. Although the weighted Jc starts to decrease with an initial 211 volume of above 40%, the pinning efficiency at higher magnetic fields (2–4T) of the superconducting Y123 matrix was actually improved with an ever-increasing 211 addition to at least 50%. Though an increasing addition of 211 is effective in producing efficient flux pinning sites in the Y123 matrix, percolation paths in the Y123 matrix become limited for supercurrent. Hence, a measured 211 volume corresponding to 80% 211 is proved to give the best possible critical current density.

Furthermore, crack opening and crack spacing of the superficial cracks are found to decrease with an increasing 211 addition and with a decreasing 211 inter-particle spacing. The penetration and surface length of each of these superficial cracks are hence reduced, which leads to a better electrical connectivity in the Y123 matrix.

Order No.: JA607-005

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#### Thermal expansion behavior of bulk Bi-based (2223) superconductors

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Thermal expansion coefficient of Bi-based 2223 and 2212 ceramics has been measured using dilatometric apparatus. Different typologies of bulk superconducting samples have been tested, in particular: (2223) phase fully dense hot-pressed samples in both direction parallel and perpendicular to the direction of applied pressure; pressureless sintered samples; and finally hot pressed (2212) phase specimen, in order to gather information on the contribution of secondary phase to thermal expansion behavior.

From the observed  $\alpha$  (thermal expansion coefficient) values, accounting for the sample orientation degree, it was possible to distinguish the contributions along the basic crystallographic directions and to determine for (2223) phase:  $\alpha_a = 12.2 \cdot 10^{-6} \text{C}^{-1}$ ,  $\alpha_c = 20.8 \cdot 10^{-6} \text{C}^{-1}$  for temperatures 200–600°C. Theoretical  $\alpha$  values were then calculated for the different samples and successfully compared with the measured ones. As regards (2212) phase, thermal expansion coefficient was evaluated for oriented sample, and value for random one extrapolated, resulting very similar to that of (2223) but lower in respect to previously reported data in air atmosphere.

Order No.: JA607-006

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#### Stability of the Tl-1223 phases

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The thermodynamic stability of  $\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{9-y}$  (1223) and substitutionally related phases has been studied by performing extended high-temperature anneals in a two-zone furnace. This approach allows for independent control of each of the thermodynamic variables: the oxygen and thallos oxide partial pressures  $[P(\text{O}_2)$  and  $P(\text{Ti}_2\text{O})]$ , the sample temperature, and the sample composition.  $P(\text{Ti}_2\text{O})$  determines which of several superconducting phases form in the unsubstituted Tl-Ba-Ca-Cu-O system.  $\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{9-y}$  is stable only within a narrow window of  $P(\text{Ti}_2\text{O})$ . Partially replacing Tl with Pb and Ba with Sr substantially increases the stability of the 1223 phase. The composition  $(\text{Tl}_x\text{Pb}_{0.5})(\text{Sr}_{1.6}\text{Ba}_{0.4})\text{Ca}_2\text{Cu}_3\text{O}_{9-y}$  yields only the 1223 phase under two-zone conditions when  $P(\text{Ti}_2\text{O})$  exceeds a lower bound. The stability of Pb- and Sr-substituted 1223 relative to the 1212 phase are related to the substitutional stoichiometry, rather than  $P(\text{Ti}_2\text{O})$ .

Order No.: JA607-007

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#### Mechanical behavior of MgO-whisker reinforced (Bi,Pb)<sub>2</sub>Sr<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>y</sub> high-temperature superconducting composite

Y.S. Yuan, M.S. Wong, S.S. Wang

(University of Houston)

The inherently weak mechanical properties of bulk monolithic high-temperature superconductors (HTS) have been a concern. Properly

selected reinforcements in fiber and whisker forms have been introduced to the HTS ceramics to improve their mechanical properties. In this paper, mechanical behavior of a MgO-whisker reinforced Pb-doped Bi-2223 (BPSCCO) HTS composite fabricated by a solid-state processing method is studied. The  $(\text{MgO})_w/\text{BPSCCO}$  HTS composite has been shown to exhibit excellent superconducting properties. Elastic properties, strengths, and notched fracture toughnesses of both the monolithic BPSCCO and the  $(\text{MgO})_w/\text{BPSCCO}$  HTS composite are investigated. Detailed mechanical properties are reported for the first time for the  $(\text{MgO})_w/\text{BPSCCO}$  HTS composite. Mechanisms of strengthening and toughening in the MgO-whisker-reinforced HTS composite are also discussed.

Order No.: JA607-008

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#### Can carbon implanted silicon be applied as wide-bandgap emitter?

D.J. Oostra, J. Politiek, C.W.T. Bulle-Lieuwma, D.E.W. Vandenhoudt, P.C. Zalm

(Philips Research Laboratories)

We examine the formation of  $\text{Si}_{1-x}\text{C}_x$  ( $x = 0.04-0.2$ ) by means of  $\text{CF}_4$  ( $y = 0, 1, 3$ ) implantation in p-type Si, for application as a wide-bandgap emitter in a Si heterojunction bipolar transistor. Upon implantation with  $2.5 \times 10^{16} \text{ CF}^+/\text{cm}^2$  at 45 keV and subsequently with  $2.5 \times 10^{16} \text{ C}^+/\text{cm}^2$  at 30 keV an amorphous top layer is formed. Annealing at temperatures up to 900°C leads to a layer consisting of nanocrystalline material. High resolution transmission electron microscopy and secondary ion mass spectrometry show that a well-defined nanocrystalline/crystalline interface is created at an anneal temperature of 550°C. At higher temperatures lattice defects start to develop. Preliminary attempts to dope the material via phosphorus or arsenic implantation indicate that temperatures of at least 900°C are required to activate a fraction of the implanted dopants. This, however, adversely affects the adlayer/substrate interface.

Order No.: JA607-009

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#### Highly conducting transparent thin films based on zinc oxide

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Doped zinc oxide thin films were prepared by rf magnetron sputtering using the dopants Al, Ga, In and Ge. The best results were obtained with Al and Ga doping where room temperature conductivities were as high as 1600 and 1800  $\text{ohm}^{-1}\text{cm}^{-1}$ , respectively. Hall measurements were performed at 77 K and 298 K. The Hall mobility was in the range of 9 to 22  $\text{cm}^2/\text{Vs}$ , and there was generally very little temperature dependence of the mobility or conductivity. Cation doping levels were as high as 10 at.%, but the conductivities did not increase beyond 3 at.% doping level. For films with high conductivity, electron carrier concentrations from Hall measurements were significantly lower than the concentrations of dopants. Optical measurements on the films showed that the average transmittance through the visible range is higher than 85%. The measurements also indicated a blue shift of the absorption edge with doping.

Order No.: JA607-010

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#### Ball-milling of Fe-Zn intermetallics

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(University of Cincinnati)

The ball-milling of pure Fe and Zn elemental powders corresponding to the  $\Gamma$ - $(\text{Fe}_3\text{Zn}_{10})$ ,  $\Gamma_1$ - $(\text{Fe}_5\text{Zn}_{21})$ ,  $\delta$ - $(\text{FeZn}_7)$  and  $\zeta$ - $(\text{FeZn}_{13})$  compositions yields metastable crystalline phases. This is demonstrated by the peaks observed in the DSC measurements of the different phases. These crystalline phases evolve differently with distinct or characteristic stages with heat treatments. Cold-welding and powder agglomeration are extensive, while the milled materials are completely homogeneous.

Order No.: JA607-011

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**A comparison of the sintering characteristics of ball-milled and attritor-milled W-Ni-Fe heavy alloy**

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(\*Technical University of Istanbul, \*University of Idaho)

Blended elemental W-7wt%Ni-3wt%Fe powders were mechanically alloyed in a planetary ball mill and a heavy duty attritor. The structural and morphological characteristics of the as-milled powders were characterized by x-ray diffraction and electron microscopy techniques. A ternary solid solution of Fe and Ni in W formed in both the cases; the amount of Ni and Fe dissolved is higher in the attritor-milled powder than in the ball-milled powder. Morphologically, the W-rich particles in the attritor-milled powders were spheroidal, smaller in size and showed a narrower size distribution than in the ball-milled condition. These differences led to increased density in the attritor-milled powder compact and significant differences in chemical composition of the matrix region and W-rich grains. Transmission electron microscopy investigations of the matrix region in the compacts revealed the presence of Fe<sub>2</sub>W precipitates uniformly distributed in an Ni(Fe,W) matrix.

Order No.: JA607-012

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**Thermally induced solute migration in 2011 Al alloy implanted with Ti, Cr or Al ions**

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A systematic experimental study of solute migration during thermal annealing and oxidation of type 2011 aluminium alloy is described. Specimens of this alloy were implanted with Ti, Cr or Al ions to doses in the range  $2 \times 10^{15}$ – $2 \times 10^{17}$  ions cm<sup>-2</sup>. The implanted substrates were annealed at 500°C in vacuum or an oxygen atmosphere and analyzed with Rutherford backscattering or scanning electron microscopy. Changes to the alloy composition resulting from segregation of constituents in the near surface region occurred for both implanted and unimplanted specimens, though the effect was substantially more produced following implantation. In addition, segregation was affected by the type and dose of the implanted ion. For the Ti implants under oxidizing conditions, the Ti ions were found to diffuse towards the surface and form a thick oxide layer. Segregation of Cu and Pb/Bi then occurred below this oxide layer. In contrast, implanted Cr ions under similar conditions were observed to diffuse into the substrate with only a thin oxide layer being formed at the surface. Consequently, Cu and Pb/Bi segregated close to the surface.

Order No.: JA607-013

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**On the inhomogeneity of the crystallographic rolling texture of polycrystalline Fe<sub>3</sub>Al**

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An intermetallic Fe<sub>3</sub>Al alloy was cast, hot rolled, annealed (870 K) and finally quenched. After this treatment, the alloy had an imperfectly ordered B2 structure. The polycrystalline sample was then warm rolled at 800–830 K. The crystallographic texture of the rolled specimen was quantitatively studied within the range  $\epsilon = 20$ –80%. Even at large strains ( $\epsilon = 80\%$ ), recrystallization was not observed in the microstructure. It was found that the rolling texture of Fe<sub>3</sub>Al is very inhomogeneous through the sample thickness. In the center layer, a large volume fraction of grains with a {111} lattice plane parallel to the sheet surface, {111}<uvw>, and a weak {001}<110> component was observed. In contrast, close to the sheet surface layer a weak texture containing the {11 11 8}<4 4 11> and the {012}<110> orientations was formed. The results are interpreted in terms of the activation of {110}<111> and {112}<111> slip systems. The through-thickness texture gradient was attributed to the inhomogeneous strain distribution during rolling.

leading to plane strain in the center layer and to shear strains close to the surface.

Order No.: JA607-014

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**High-resolution electron microscopy of Al-Ni-Fe decagonal quasicrystal**

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(Tohoku University)

The structure of a stable decagonal quasicrystal with 0.4 nm periodicity, formed in a conventionally solidified alloy with composition Al<sub>71.6</sub>Ni<sub>23.7</sub>Fe<sub>4.7</sub>, was investigated by high-resolution electron microscopy. It was found that this decagonal phase is one of the best-ordered quasi-crystals, without any detectable linear phason strain and with only weak random phason strain. The structure is interpreted as an aperiodic tiling of decagonal atom columns with a diameter of about 1.2 nm. The atomic arrangements in special local regions are discussed on the basis of computer simulations.

Order No.: JA607-015

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**Synthesis, morphology, and formation mechanism of mullite particles produced by ultrasonic spray pyrolysis**

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Submicrometer spherical particles of mullite powder were synthesized by ultrasonic spray pyrolysis of emulsion and solutions, using tetra-ethyl-orthosilicate (TEOS) or silicic-acid and Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, as initial compounds. Crystallization of mullite phase was determined by differential thermal (DT), thermogravimetric (TG), infrared (IR), and x-ray analyses. The synthesis of mullite from TEOS emulsion occurs by crystallization of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (or Al,Si-spinel) from the amorphous phase and its subsequent reaction with amorphous SiO<sub>2</sub> as well as by crystallization of pseudotetragonal mullite below 1000°C and its subsequent phase transformation into orthorhombic mullite. In the powders produced from silicic acid solutions, synthesis of mullite occurs only by crystallization of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> between 900 and 1000°C and its further reaction with amorphous SiO<sub>2</sub> between 1100 and 1200°C. Particle formation mechanism depended directly on the initial emulsion or solution preparation, i.e., on the phase separation in the emulsion and on the silicic-acid crosslinking conditions.

Order No.: JA607-016

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**Material removal and damage formation mechanisms in grinding silicon nitride**

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(National Institute of Standards and Technology)

Surface grinding was performed on two silicon nitrides with different microstructures. The ground surfaces of both materials were observed with scanning electron microscopy (SEM) to consist of areas of microfracture, smeared areas, and areas covered with fine debris particles. It was determined that microfracture is the primary mechanism for material removal. Subsurface grinding damage was revealed by a bonded-interface technique to take the form of median-type cracks extending from the plastic zones. Distributed intergranular microcracks and intragrain twin/slip bands were observed within the plastic zones. The strengths of transverse-ground specimens were measured in four-point flexure. For the silicon nitride with a fine grain size and a mildly rising toughness-curve, grinding damage resulted in a drastic strength degradation compared to polished specimens. In contrast, the silicon nitride with large and elongated grains and a steeply rising toughness-curve showed relatively little strength loss. The relationship between the

ceramic microstructure and the damage tolerance in abrasive machining is discussed in light of these results.

Order No.: JA607-017

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#### Origin of dislocation loops in $\alpha$ -silicon nitride

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Dislocation loops and stacking fault formation mechanism in  $\alpha$ - $\text{Si}_3\text{N}_4$  has been studied by annealing  $\alpha$ - $\text{Si}_3\text{N}_4$  powders at 1500°C and 1750°C. Thermally activated vacancies (extrinsic) and the structural vacancies (intrinsic) generated with replacement of nitrogen by oxygen have been tentatively suggested to be two sources of vacancies in  $\alpha$ - $\text{Si}_3\text{N}_4$ . From the point view of mechanism, incorporation of these vacancies is believed to lay at the building up stage of  $\alpha$ - $\text{Si}_3\text{N}_4$  lattice. As a result of the vacancies agglomeration, dislocation loops and stacking faults seem to be a distinctively structural feature of  $\alpha$ - $\text{Si}_3\text{N}_4$  fabricated by a different route (CVD, silicon nitridation, silica carbothermal reduction, and imide decomposition). A general discussion, extended to the historical controversy over the oxygen and vacancy stabilization of  $\alpha$ - $\text{Si}_3\text{N}_4$  lattice, arose from the facts that the observed unit cell dimension of  $\alpha$ - $\text{Si}_3\text{N}_4$  has a wide variation, and also to some related phenomena in processing  $\text{Si}_3\text{N}_4$ .

Order No.: JA607-018

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#### Powder x-ray diffraction of turbostratically-stacked layer systems

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(Simon Fraser University)

A special form of the Debye formula for calculating the powder x-ray diffraction of a turbostratically stacked layer system is derived, and calculated diffraction patterns for turbostratically stacked graphite and  $\text{MoS}_2$  layers are presented. Single-molecular-layer  $\text{MoS}_2$ , prepared by exfoliation of lithium-intercalated  $\text{MoS}_2$  in water or alcohols, has been deposited on various supports, and x-ray diffraction patterns show that the restacking of the  $\text{MoS}_2$  layers can be perfectly turbostratic. The restacked  $\text{MoS}_2$  may or may not have water or organic bilayers between them, depending on the deposition conditions.

Order No.: JA607-019

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#### Evolution of mechano-chemistry and microstructure of a calcium aluminate-polymer composite: Part II. Mixing rate effects

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(University of Illinois at Urbana-Champaign)

Microstructure, microchemistry and mechanical properties of hardened macro-defect free (MDF) composites processed at various rotor rates in a Banbury mixer were investigated. A quiescently formed calcium aluminate-polyvinyl alcohol composite served as a substitute for an unmixed system. Results from the Banbury studies in conjunction with microchemical analysis of the unmixed composite showed evidence that the polymer-particle interaction is a mechanically-induced crosslinking reaction. The rate of the mechano-chemistry increases with mixing speeds. SEM and TEM micrographs of hardened composites mixed for 15 minutes at 30, 50, 100 and 200 rpm indicate that much of the mechanical strength of MDF is due to the crosslinked interphase zones which blanket the cement grains. Stresses in the paste due to mixing can destroy the interphase layer leading to a weaker hardened composite. Microchemical analysis revealed that the mechano-chemistry of the system did not vary with changes in the mixing conditions studied.

Order No.: JA607-020

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#### A new insight on alkaline hydrolysis of calcium aluminate cement concrete: Part I. Fundamentals

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In this work a hypothesis to explain the alkaline hydrolysis degrada-

tion process of calcium aluminate cement concrete (CACC) is presented. The hypothesis is based on x-ray diffraction (XRD) data of some samples taken from real Spanish CACC structures. The identification from XRD data of a hydrated alkaline aluminate could serve as a guide to differentiate both normal carbonation and alkaline hydrolysis processes.

Order No.: JA607-021

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#### A quantitative analysis of cavitation in Al-Cu-Mg metal matrix composites exhibiting high strain rate superplasticity

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Specimens of two Al-Cu-Mg (2124) composites, reinforced with 20 vol % of either  $\text{Si}_3\text{N}_4$  particulates or  $\text{Si}_3\text{N}_4$  whiskers, were tested under experimental conditions close to those for optimum high strain rate superplasticity. Both composites developed extensive internal cavitation during testing, but quantitative measurements show that significant cavity growth occurs throughout the test in the whisker-reinforced composite but only at strains  $\geq 1.0$  in the particulate-reinforced composite. This difference in behavior is attributed to differences in the extent of a discontinuous liquid phase at the grain boundaries and at the matrix/reinforcement interfaces. It is concluded that the presence of an extensive liquid phase in the particulate-reinforced composite is beneficial for attaining high ductility because it relieves the stress concentrations from grain boundary sliding and thereby limits the growth of cavities.

Order No.: JA607-022

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#### Examination of the material properties and performance of thin-diamond film cutting tool inserts produced by arc-jet and hot filament chemical vapor deposition

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Thin diamond film coated WC-Co cutting tool inserts were produced using arc-jet and hot-filament chemical vapor deposition. The diamond films were characterized using SEM, XRD and Raman spectroscopy to examine crystal structure, fracture mode, thickness, crystalline orientation, diamond quality and residual stress. The performance of the tools was evaluated by comparing the wear resistance of the materials to brazed polycrystalline diamond tipped cutting tool inserts (PCD) while machining A390 aluminum (18% silicon). Results from the experiments carried out in this study suggest that the wear resistance of the thin diamond films is primarily related to the grain boundary strength, crystal orientation and the density of micro-defects in the diamond film.

Order No.: JA607-023

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#### Comparative measurement of residual stress in diamond coatings by low-incident-beam-angle-diffraction and micro-Raman spectroscopy

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Two experimental techniques for the quantitative measurement of residual stress in thin polycrystalline diamond coatings have been developed. The x-ray low-incident-beam-angle-diffraction (LIBAD) allows measurement of the lattice strain with well-defined in-depth information, while micro-Raman spectroscopy permits accurate measurement of the frequencies of the zone-center optical phonons of diamond which are related to the lattice strain. The interpretation of the measured information in terms of residual stress is outlined for both techniques. The residual stress data obtained by either method in thin CVD diamond coatings were found to be in excellent agreement. The sign and magnitude of the balanced bi-axial stress in the coating plane depend mainly on the substrate material used for the diamond deposition. Compressive stress was present in diamond coatings deposited on WC-Co substrates, whereas tensile stress was found in those on SiAlON substrates.

Order No.: JA607-024

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**Electron microscopic interfacial analysis of diamond film grown on silicon substrate**N. Jiang\*, A. Hatta\*, T. Ito\*, Z. Zhang\*, T. Sasaki\*, A. Hiraki\*  
(\*Osaka University, \*Chinese Academy of Science)

We have investigated the near-interface characterization of diamond films grown on Si (100) substrates by means of a hot-filament chemical-vapor-deposition (HFCVD) method using high-resolution electron microscopy (HREM). Atomic scale study of the diamond/Si interface reveals that on the top of amorphous intermediate layer, there exists a precursor phase seeming to be the diamond-like structure, which provides a suitable site for subsequent diamond nucleation. High-density crystal defects directly originate from the precursor phase. HREM images also reveal that during the deposition, Si recrystallizes in some damaged areas left by pretreatment, such as scratching grooves. In the recrystallization process twins, microtwins can be formed, and amorphous solid is left in the Si crystals.

Order No.: JA607-025

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**Effects of secondary pretreatments of substrate on the nucleation of diamond film**

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The effects of secondary pretreatments on diamond nucleation were investigated for the Si substrates pretreated by the diamond abrasion. When the substrate was just abraded with diamond powder, the nucleation density of diamond was  $7 \times 10^8/\text{cm}^2$ . However, the nucleation density was found to be greatly decreased by various secondary pretreatments except by one wet chemical etching method. The nucleation density was reduced to  $3 \times 10^7/\text{cm}^2$  by the chemical etching (I), to  $7 \times 10^6/\text{cm}^2$  by the  $\text{H}_2$  plasma etching, and to  $\sim 10^4/\text{cm}^2$  by the Ar sputtering, or  $\text{O}_2$  plasma etching. It was very slightly reduced to  $3 \times 10^8/\text{cm}^2$  by the chemical etching (II). The effects of secondary pretreatments in reducing the nucleation density were found to be very closely related to the removal of diamond seeds rather than topographic sites or structural defects. Therefore, diamond seeds generated by the diamond abrasion are considered as the main nucleation sites of diamond.

Order No.: JA607-026

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**Phase analysis of seeded and doped PMN prepared by organic solution of citrates**

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PMN prepared by organic solution of citrates was analyzed by Rietveld Method to determine the influence of seeds and dopants on the perovskite and pyrochlore phase formation. It was observed that pyrochlore phase formation increases with increased calcination time when no additives are included during the preparation. It was also observed that a greater amount of perovskite phase appeared in doped or seeded samples. The fraction of perovskite phase increased from 88 mol% in pure sample to ~95 mol% in doped and seeded samples calcined at 800°C for 1 h. It is clear that the addition of dopants or seeds during PMN preparation can enhance the formation of perovskite phase.

Order No.: JA607-027

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**A model for evaluating and predicting high-temperature thermal expansion**

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In this paper, a new set of experimental data,  $\alpha_V K_T V$ , representing the partial temperature derivative of the work done by the thermal pressure of the solid, is fitted by  $n$  terms of a modified Einstein model. Experimental data show that  $\alpha_V K_T V$ , not  $\alpha_V K_T$ , approaches a constant value at high temperature. Based on the observed linear relationship of

isothermal bulk modulus with temperature at high temperature, thermal expansion can be evaluated by fitting  $\alpha_V K_T V$  data. Our previous results have shown that at low temperature or for materials with less variable bulk modulus and expansivity, thermal expansion data can be simply approximated by an  $n$  term Einstein model. More generally and for most materials,  $\alpha_V K_T V$  data resemble an isochoric specific heat curve. With this method, thermal expansion can be predicted at high temperatures from low and intermediate temperature range data. With accurate thermal expansion data, high-temperature bulk moduli can also be predicted.

Order No.: JA607-028

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**Spontaneous ferromagnetism at room temperature in oxygen-rich dicalcium cuprate  $\text{Ca}_2\text{CuO}_{3+\delta}$** 

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Stoichiometric  $\text{Ca}_2\text{CuO}_3$ , having square-planar Cu-chains,<sup>6,7</sup> is expectedly antiferromagnetic due to 1-D intrachain superexchange.<sup>1</sup> Nonetheless we report remarkable spontaneous ferromagnetism at 293 K after sintering, prominently in oxygen. This apparently introduced excess oxygen at vacant quasi-octahedral sites, promoting spin-flip and ferromagnetic interchain coupling. Thermogravimetry (TGA) revealed excess oxygen,  $\approx 0.17 \text{ O/Cu}$ . XRD yielded a comparatively smaller unit cell. Ferromagnetism disappeared by oxygen depletion, mimicking reported nonmagnetism of  $\text{Ca}_2\text{CuO}_{3-\delta}$ .<sup>1</sup> Elemental analysis showed insignificant magnetic impurity traces.  $T_c$  ranged between 680 K–723 K, depending on freshness and purity. Saturation magnetization varied with processing, optimally 0.30 A.m<sup>2</sup>/kg at 1.0 T applied field. Coercivity and remanence varied with purity.

Order No.: JA607-029

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**Aluminum nitride buffer layer for diamond film growth**

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The role of aluminum nitride (AlN) as a buffer layer on the nucleation and growth of diamond on silicon and steel substrates during hot filament chemical vapor deposition (HF-CVD) has been investigated systematically. The scanning Auger electron microscopy (AES) is employed to study chemistry and content of carbon on the surface and in subsurface regions of AlN as a function of HF-CVD parameters. It is found that AlN offers an excellent diffusion barrier for carbon over a wide range of temperature and hydrocarbon content of CVD gas environment, with simultaneous inhibition of graphitization. It also facilitates nucleation of diamond phase. The surface reactions between AlN and carbon are discussed in terms of hydrogen-assisted phase transformations. We have developed a two-step procedure to obtain a continuous diamond film on steel substrates. The characteristic features of AlN have been exploited to obtain adherent and graphite-free diamond deposits on various types of steels including low-carbon steel, tool steel, high-speed steel, and bearing steel.

Order No.: JA607-030

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**Ion beam amorphization of muscovite mica**

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The microstructure of a muscovite mica exposed to a rare gas ion beam has been studied by transmission electron microscopy. The investigation of damage without implantation was carried out using argon and helium ions of sufficient energy to traverse the 100–150 nm mica specimens. For 340 keV Ar<sup>++</sup> irradiation, amorphization of mica occurred at a fluence as low as  $3.5 \cdot 10^{14}$  ions.cm<sup>-2</sup> which corresponds to 0.29 dpa.

Muscovite can be amorphized using 80 keV helium ions, but this requires a much higher fluence and damage production of  $4.6 \cdot 10^{16}$  ions. $\text{cm}^{-2}$  and 0.60 dpa, respectively. Since helium irradiation results principally in ionization energy loss, it indicates that amorphization of muscovite results mainly from nuclear interactions. Complete amorphization of muscovite mica is found to take place for all ions at approximately the same amount of nuclear energy transfer to energetic primary knock-on atoms assuming a recoil energy greater than 500 eV. This suggests that amorphization occurs directly in dense displacement cascades. A significant amount of helium, 100 ppm, can be implanted into muscovite mica without destroying the crystal structure.

Order No.: JA607-031

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#### The self-propagation high-temperature synthesis of ultrafine high-purity tungsten powder from Scheelite

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(Chungnam National University)

High-purity tungsten was prepared by self-propagating high-temperature synthesis (SHS) process from a mixture of  $\text{CaO} \cdot \text{WO}_3$  and Mg. The complete reduction of  $\text{CaO} \cdot \text{WO}_3$  required a 33% excess of magnesium over the stoichiometric molar ratio  $\text{Mg}/\text{CaO} \cdot \text{WO}_3$  of 3:1. The Mg and CaO in the product was leached with an HCl solution. The product tungsten had a purity of 99.980%, which was higher than that of the reactants. The high purity results because the non-tungsten reactants and products are volatilized by the high-temperatures generated during the rapid exothermic SHS reaction and are dissolved during HCl leaching of the product.

Order No.: JA607-032

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#### Structure and physical properties of sodium antimony germanate glasses

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The structure and physical properties of sodium antimony germanate glasses with compositions  $10 \text{Na}_2\text{O} \cdot x \text{Sb}_2\text{O}_3 \cdot (90-x) \text{GeO}_2$ ,  $x = 10-30$  mol%, prepared by melt-quenched route have been studied. It is observed from x-ray diffraction, SEM, density and oxygen molar volume, IR, DTA and optical absorption that single phase homogeneous glasses with a random network structure can be obtained in this system. The strength and connectivity of the glass network increase with  $\text{GeO}_2$  content. The main Ge-O stretching vibration also shifts to higher wavelength

side. Two oxidation states of antimony,  $\text{Sb}^{3+}$  and  $\text{Sb}^{5+}$ , are present while the so-called "germanate anomaly" is absent in these glasses. In this study, we have discussed the probable structural reasons behind this type of behavior of these glasses.

Order No.: JA607-033

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#### Thermal expansion of bulk amorphous $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ alloy

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The linear thermal expansion of the bulk amorphous  $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$  (atomic percent) alloy has been measured from 80 K to 773 K. The data for  $T < T_g$  were fitted by a model based on the Grüneisen relation and a Debye expression for the heat capacity. From the fit, we deduced the Grüneisen parameter,  $\gamma = 1.25$ , and the Debye temperature,  $\Theta_D = 400$  K. Annealing the amorphous alloy at 663 K, which is between the glass transition temperature  $T_g = 623$  K and the crystallization temperature  $T_x = 693$  K, causes viscous flow in the sample. This is due to the small viscosity in the undercooled liquid.

Order No.: JA607-034

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#### A new method for fabricating high-performance polymeric thin films by chemical vapor polymerization

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A vacuum deposition method is presented in which copolymer films are grown from a vinylic monomer chosen for desirable properties and paraxylylene. The concentration of paraxylylene in the final copolymer can be negligibly small if proper deposition conditions, presented here for the first time, are employed. Films of paraxylylene with *N*-phenyl maleimide deposited at 40°C, for example, showed thermal stability and FTIR spectra nearly identical with homopolymers of poly(*N*-phenyl maleimide). Different rate limiting steps are proposed to explain film composition; paraxylylene is under surface reaction control, while the comonomer obeys mass flow control. This results in a deposition environment extremely rich in comonomer. Growth rates and compositions were consistent with predictions. The initiation reaction did not appear different than for homopolymerization of paraxylylene. The general method presented here allows fabrication of vapor deposited thin films with properties limited primarily by the comonomer employed.

Order No.: JA607-035

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