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Ceramic Microstructures '86: Role of Interfaces

JULY 28-31, 1986

INTERNATIONAL
MATERIALS SYMPOSIUM

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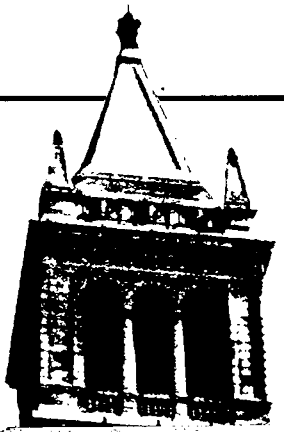
22nd University
Conference on Ceramics
Berkeley, California



**Department of Materials Science and
Mineral Engineering, College of Engineering**

●

**Materials and Molecular Research Division
and
Center for Advanced Materials
Lawrence Berkeley Laboratory**

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**University of California
Berkeley, California**

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July 1986

Prepared for the U.S. Department of Energy Under Contract No. DE-AC03-76SF00098

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SYMPOSIUM PROGRAM

Sunday, July 27, 1986

4:00–8:00 pm — Registration, Clark Kerr Campus
Informal Reception, Clark Kerr Campus

Monday, July 28, 1986

8:00 — Registration, Clark Kerr Campus
8:15 — First Call for Assemblage

A. Introductions and Reviews

Session Chair — Joseph A. Pask, *Chairman of Symposium*

8:30 — Welcoming Remarks
David A. Shirley, *Director, Lawrence Berkeley Laboratory*
8:40 — Progress in the Understanding of Ceramic Microstructures and Interfaces Since 1976
H.F. Fischmeister, *Max-Planck-Institut für Metallforschung, Stuttgart, Federal Republic of Germany*
9:25 — Ceramic Microstructures
R.J. Brook, *University of Leeds, England*

10:00 — Coffee

B. Microstructure Designing

Session Chair — Anthony G. Evans, *University of California at Santa Barbara*

10:20 — Role of Grain Boundaries and Interfaces
G. Thomas, *University of California, Berkeley, California*
10:45 — Rational Design of High Thermal Expansion Glass-Ceramics through Microstructural Control
R.E. Loehman, *Sandia National Laboratories, Albuquerque, New Mexico*
11:10 — Microdesigning of Ceramic-Metal Composites
I.A. Aksay, M. Sarakaya, and A.J. Pyzik,
University of Washington, Seattle, Washington
11:35 — Creating and Exploiting Maximum Interfaces in Diphasic-Xerogel Nanocomposites
R. Roy, *Pennsylvania State University, University Park, Pennsylvania*

12:00 — Lunch in Clark Kerr Campus Dining Hall

C. Characterization of Interfaces

Session Chair — Ronald Gronsky, *Lawrence Berkeley Laboratory*

1:10 — TEM Observation of Coherent and Incoherent Interfaces in ZrO_2-Containing Ceramics
A.H. Heuer, *Case Western Reserve University, Cleveland, Ohio*

1:35 — Grain Boundary Energy of Twisted MgO Bicrystals on (100)
E. Yasuda, S. Kimura, M. Sakaki, and H. Kim, *Tokyo Institute of Technology, Yokohama, Japan;* and Y. Moriyoshi, *National Institute for Research in Inorganic Materials, Ibariki, Japan*

1:50 — The Influence of Fe Solute on the Structure of (001) Twist Boundaries in MgO
J.A. Eastman and S.L. Sass, *Cornell University, Ithaca, New York*

2:05 — Structure of High-Angle Grain Boundaries in NiO
K.L. Merkle, J.F. Reddy, and C.L. Wiley, *Argonne National Laboratory, Argonne, Illinois;* and D.J. Smith, *Arizona State University, Tempe, Arizona*

2:20 — HRTEM Analysis of Ordered Grain Boundaries in High Purity Alpha-SiC
H. Ichinose and Y. Ishida, *University of Tokyo, Japan;* and Y. Inomata, *National Institute for Research in Inorganic Materials, Ibaraki, Japan*

2:35 — Atomic Structure of Interfaces in Sialon Ceramics
A. Thorel and D. Broussaud, *Centre des Matériaux, Ecole des Mines de Paris;* and J. Y. Laval, *CNRS, Laboratoire des Microstructures, Paris, France*

2:50 — Coffee

D. Characterization of Microstructures

Session Chair — Dieter Wolf, *Argonne National Laboratory*

3:10 — Theory of Oxide-Oxide and Oxide-Metal Interfaces
A.M. Stoneham, *Harwell Laboratory, Oxon, England*

3:35 — Segregation of Cation Impurities at Ceramic Boundaries
W.C. Mackrodt, *I.C.I., Runcorn, Cheshire, England*

4:00 — The Distribution and Influence of Minor Constituents on Ceramic Formulations
W.D. Kingery, *Massachusetts Institute of Technology, Cambridge, Massachusetts*

4:25 — Consideration of Interfaces as a Statistical Microstructure Parameter
R. Raj, *Cornell University, Ithaca, New York*

4:45 — TEM Statistical Characterization of Grain Boundaries in Polycrystalline NiO Coatings Obtained by High Temperature Oxidation of Nickel
A. Marrouche, F. Barbier, and M. Déchamps, *Université Paris-Sud, France*

5:05 — Quantitative Characterization of Microstructural Geometry of Interfaces
H.E. Exner, *Max-Planck-Institut für Metallforschung, Stuttgart, Federal Republic of Germany*

6:00 — Official reception at Clark Kerr Campus

Tuesday, July 29, 1986

8:00 — Registration, Clark Kerr Campus

E. Ceramic-Metal Interfaces

Session Chair — Thomas J. Whalen, *Ford Motor Co.*

8:15 — Diffusion Bonding, Chemistry, and Structure of Metal/Ceramic Interfaces
M. Rühle, M. Backhaus-Ricoult, K. Burger, and W. Mader, *Max-Planck-Institut für Metallforschung, Stuttgart, Federal Republic of Germany*

8:40 — Copper-Glass-Ceramic Interfaces and Composites: Reactions, Microchemistry, and Electrical Properties
S.H. Risbud, G.D. Allen, and J.E. Poetzinger, *University of Illinois at Urbana-Champaign, Urbana, Illinois*

9:05 — The Ceramic-Metal Reaction and Its Effect on Microstructure Production
J.T. Klomp, *Philips Research Laboratories, Eindhoven, The Netherlands*

9:30 — Bonding Ceramic-Metal Interfaces and Joints
M.G. Nicholas, *Harwell Laboratory, Oxon, England*

9:55 — Coffee

F. **Microstructure Development**

Session Chair — Frederick F. Lange, *Rockwell International Science Center*

10:15 — Powders, Interfaces, and Processing: Alumina as a Case Study
A. Roosen, S. Sumita, and H.K. Bowen, *Massachusetts Institute of Technology, Cambridge, Massachusetts*

10:40 — Role of Powder Consolidation on Microstructure Evolution
I.A. Aksay, *University of Washington, Seattle, Washington*

11:05 — Role of Powder Packing in Sintering
L.C. DeJonghe, M.N. Rahaman, and M. Lin, *Lawrence Berkeley Laboratory, University of California, Berkeley, California*

11:30 — Effect of Pores on Microstructure Development
M.P. Harmer, *Lehigh University, Bethlehem, Pennsylvania*

11:55 — Lunch in Clark Kerr Campus Dining Hall

Session Chair — Andreas M. Glaeser, *University of California Berkeley*

1:10 — Controlled Grain Growth in Ceramics
F.F. Lange, *Rockwell International Science Center, Thousand Oaks, California*

1:35 — Grain Growth in TiO_2
M.F. Yan and W.W. Rhodes, *AT&T Bell Laboratories, Murray Hill, New Jersey*

2:00 — Wetting and Dewetting of Grain Boundaries in Polyphase Ceramics
D.R. Clarke, *Thomas J. Watson Research Center, Yorktown Heights, New York*

2:25 — Microstructure Development of Hydrothermal Powders and Ceramics
S. Somiya and M. Yoshimura, *Tokyo Institute of Technology, Yokohama, Japan;* and Z. Nakai, K. Hishinuma, and T. Kumaki, *Chichibu Cement Co., Kumagaya, Japan*

2:50 — Vapor Transport and Microstructure Development in Ceramics
D.W. Readey, *Ohio State University, Columbus, Ohio*

3:15 — Coffee

Session Chair — Robert F. Davis, *North Carolina State University, Raleigh*

3:35 — Sintering Theory for Crystalline Solids
A.W. Searcy, *University of California, Berkeley, California*

4:00 — Selective Sintering Conditions for SiC and Si_3N_4
C. Greskovich and S. Prochazka, *General Electric Corporate Research and Development, Schenectady, New York*

4:25 — Sintering of Whisker Reinforced Ceramic Composites
T.N. Tiegs, P.F. Becher, and L.A. Harris, *Oak Ridge National Laboratory, Oak Ridge, Tennessee*

4:45 — Interfacial Chemistry and Bonding in Fiber Reinforced Glass and Glass-Ceramic Matrix Composites
J.J. Brennan, *United Technologies Research Center, East Hartford, Connecticut*
5:10 — Anion Controlled Microstructures in the Al_2O_3-AlN System
J.W. McCauley, *U.S. Army Materials Technology Laboratory, Watertown, Massachusetts;* K.M. Krishnan, R.S. Rai, and G. Thomas, *University of California, Berkeley, California;* A. Zangvill and R.W. Doser, *University of Illinois, Urbana, Illinois;* and N.D. Corbin, *Norton Co., Northboro, Massachusetts*

6:00 — Official Barbecue Banquet at Clark Kerr Campus
Banquet Speaker — Richard M. Spriggs, *National Research Council*

Wednesday, July 30, 1986

G. Electrical Properties

Session Chair — Robert J. Eagan, *Sandia National Laboratories, Albuquerque, New Mexico*

8:15 — Electrical Properties and Microstructures
L.E. Cross, *Pennsylvania State University, University Park, Pennsylvania*
8:45 — Electrical Conductivity in Ceramics: A Review
D.M. Smyth, *Lehigh University, Bethlehem, Pennsylvania*
9:10 — The Crystallographic and Chemical Relationship Between Intergranular and Bulk Resistivity in Semiconductor Oxides
M.H. Pinet and J.Y. Laval, *Laboratoire des Microstructures, CNRS, Paris, France*
9:30 — Electrical Properties and Microstructure of ZnO-Nb_2O_5 Ceramics Sintered in the Liquid Phase
K. Hamano, Z. Nakagawa, A. Sayano, and T. Mitsudome, *Tokyo Institute of Technology, Yokohama, Japan*
9:50 — New Composite PTC Materials Based on $PbTiO_3$-TiO_2
M. Okada, T. Iijima, and M. Homma, *Tohoku University, Sendai, Japan*

10:10 — Coffee

Session Chair — Donald M. Smyth, *Lehigh University, Bethlehem, Pennsylvania*

10:30 — Effect of Microstructure Control of Ferroelectric Ceramics
K. Okazaki, H. Igarashi, K. Nagata, T. Yamamoto, and S. Tashiro, *National Defense Academy, Yokosuka, Japan*
10:55 — Optical Effects of Grain Boundaries in PLZT Ceramics
Z.W. Yin, *Shanghai Institute of Ceramics, Shanghai, China*
11:20 — Interface Effects in Zinc Oxide Varistors
L.M. Levinson, *General Electric Corporate Research and Development, Schenectady, New York*
11:45 — The Role of Interfaces and Interphases in Dielectric Ceramics
D.A. Payne, *University of Illinois at Urbana-Champaign, Urbana, Illinois*

12:10 — Lunch in Clark Kerr Campus Dining Hall

1:10–4:00 — **Poster Session**

Thursday, July 31, 1986

H. Mechanical Properties and Behavior

Session Chair — Katherine T. Faber, *Ohio State University*

8:15 — Mechanical Properties: Effects of Microstructure
A.G. Evans, *University of California at Santa Barbara, Santa Barbara, California*
8:45 — Influence of Microstructure on Creep-Rupture
B.J. Hockey, S.M. Wiederhorn, and R.F. Krause, Jr., *National Bureau of Standards, Gaithersburg, Maryland*
9:10 — Mechanisms of Dynamic Failure
D.G. Brandon and Y. Yeshurun, *Technion, Israel Institute of Technology, Haifa, Israel*
9:35 — Effect of High Temperature Oxidation on the Microstructure and Mechanical Properties of Whisker-Reinforced Ceramics
W.M. Kriven, *University of Illinois at Urbana-Champaign, Urbana, Illinois;* and T.N. Tiegs and P.F. Becher, *Oak Ridge National Laboratory, Oak Ridge, Tennessee*

9:55 — Coffee

Session Chair — Koichi Niihara, *Tohoku University, Sendai, Japan*

10:15 — Interfacial Dependent Strength and Properties of Transformation Toughened Ceramics
M.V. Swain, R.H.J. Hannink, and J. Drennan, *CSIRO Division of Materials Science, Clayton, Victoria, Australia*
10:45 — Precipitation in a (Mg) Partially Stabilized Zirconia During Aging at 1000°C
K.H. Westmacott and U. Dahmen, *Lawrence Berkeley Laboratory, University of California, Berkeley, California;* A. Thorel, *Centre des Matereaux, Ecole des Mines de Paris;* and J.Y. Laval, *CNRS, Laboratoire Physique et Chimie, Paris, France*
11:05 — Temperature-Dependent Toughening in Whisker-Reinforced Ceramics
M.C. Shaw and K.T. Faber, *Ohio State University, Columbus, Ohio*
11:25 — Interfacial Delamination Toughening and Toughness Anisotropy in Ceramics
M. Sakai, *Toyohashi University, Toyohashi, Japan;* and R.C. Bradt, *University of Washington, Seattle, Washington*
11:40 — Fine Microstructure and Toughness of SiC
K. Niihara and T. Hirai, *Tohoku University, Sendai, Japan*

12:00 — Lunch in Clark Kerr Campus Dining Hall

Session Chair — Richard C. Bradt, *University of Washington, Seattle*

1:10 — Ceramic Composites
D.B. Marshall and B.N. Cox, *Rockwell International Science Center, Thousand Oaks, California;* and A.G. Evans, *University of California at Santa Barbara, Santa Barbara, California*
1:35 — On the Fracture Behavior and Microstructure of Metal-to-Ceramic Joints
M. Turwitt, G. Elssner, and G. Petzow, *Max-Planck-Institut für Metallforschung, Stuttgart, Federal Republic of Germany*
1:55 — Solid State Bonding of Alumina and Steel by HIPing
M. Shimada, *Tohoku University, Sendai, Japan;* and K. Suganuma, T. Okamoto, and M. Koizumi, *Osaka University, Osaka, Japan*

2:15 — Structure and Chemistry of Interfaces in Silicon Carbide-Containing Materials
C.H. Carter, Jr., and R.F. Davis, *North Carolina State University, Raleigh, North Carolina;* and S.R. Nutt, *Brown University, Providence, Rhode Island*

2:35 — Structure of Second Phases in Silicon Nitride Grain Boundaries
D.A. Bonnell, *University of Michigan, Ann Arbor, Michigan*

2:55 — The Impact of Compositional Variations and Processing Conditions on Secondary Phase Characteristics in Sintered Si_3N_4 Materials
W. Braue, G. Wötting, and G. Ziegler, *Deutsche Forschungs und Versuchsanstalt für Luft- und Raumfahrt, Köln, Federal Republic of Germany*

3:15 — Closing Remarks — Anthony E. Evans, *Co-Chairman of Symposium*

POSTER SESSION — WEDNESDAY, JULY 30, 1:10 pm

Grain Boundary Characterization

1. Fractal Morphology of Ceramic Polycrystal and Powder Grain Boundaries and Interfaces: Diffractal Universal Dielectric, Electrical, and Noise Functional Properties' Analytic Dependence upon Diffraction Pattern via Static Synergetics
   E. Siegel, *Static Synergetics Research Ltd., San Francisco, California*
2. Diffraction from a Natural Grain Boundary in a Magnetite Bicrystal
   S. Stock, S. Ahn, and J.B. Cohen, *Northwestern University, Evanston, Illinois*
3. The Structure of Tilt Grain Boundaries in NiO
   J.A. Eastman, M.D. Vaudin, and S.L. Sass, *Cornell University, Ithaca, New York;* and K.L. Merkle, *Argonne National Laboratory, Argonne, Illinois*
4. Green Function Method for Calculation of Atomistic Structure of Grain Boundary Interfaces in Ionic Crystals
   V.K. Tewary, E.R. Fuller, Jr., and R.M. Thomson, *National Bureau of Standards, Gaithersburg, Maryland*
5. On the Role of the Interface Plane in the Selection of "Special" Grain Boundaries in Ceramic Oxides
   D. Wolf, *Argonne National Laboratory, Argonne, Illinois*
6. High Angle Grain Boundaries in Sheet Silicates (Biotite/Chlorite): A TEM Study
   R. Wirth, *Universität des Saarlandes, Saarbrücken, Federal Republic of Germany*
7. Diffusion Induced Interface Migration in Ceramics
   J.E. Blendell and C.A. Handwerker, *National Bureau of Standards, Gaithersburg, Maryland*
8. Grain Boundary Self-Diffusion in Polycrystalline NiO: Is There Some Possible Artifact?
   M. Déchamps and F. Barbier, *Laboratoire de Chimie Appliquée, Université Paris-Sud, Orsay, France;* and F. Moya and J. Bernardini, *Laboratoire de Métallurgie, Marseille, France*
9. Grain Boundary Migration and Grain Boundary Nonstoichiometry in Ternary Oxides
   Y.M. Chiang, C.J. Peng, and J. Hahn, *Massachusetts Institute of Technology, Cambridge, Massachusetts*

Characterization of Microstructures

10. Unit Cell Distortion of $Pb(Zr,Ti)O_3$ by $Pb(Co,Nb)O_3$
    J.K. Lee and H.J. Jung, *Korea Advanced Institute of Science and Technology, Seoul, Republic of Korea*
11. Gas Transport as a Tool for Structural Characterization of Interfacial Phases
    J.F. Shackelford, *University of California at Davis, Davis California*

Characterization of Interphase Reactions

Electrical Behavior

Mechanical Properties and Behavior

PROGRESS IN THE UNDERSTANDING OF CERAMIC MICROSTRUCTURES AND INTERFACES SINCE 1976

H.F. Fischmeister

Max-Planck-Institut für Metallforschung,
Stuttgart, Federal Republic of Germany

After a resumé of the evolution of phenomenological understanding of the role played by internal boundaries in the formation and the design of ceramic microstructures, attention is focused on the atomic structure of the boundaries, and on relations between boundary structure and properties. Both ceramic and metal-ceramic systems are considered.

The crystallographic basis for the description of internal boundaries in crystalline materials is summarized, starting with the concepts of dichromatic patterns and the coincidence site lattice. The special consequences of ionic charge interactions for the structure of ceramic boundaries, as compared to boundaries in metals, are discussed. The contributions of high resolution electron microscopy and diffraction studies and of computer simulation techniques to the elucidation of boundary structures are reviewed.

Current hypotheses and experimental results on bonding and adhesion between metals and ceramic phases are surveyed, with emphasis on structural and chemical effects.

Finally, the role of interlayers between ceramic crystal grains is discussed in terms of their structure, composition, and influence on aggregate properties. A special section is devoted to solute segregation at internal boundaries.

CERAMIC MICROSTRUCTURES

R.J. Brook

Department of Ceramics, University of Leeds, United Kingdom

An increasing diversity of application and an enhanced control of processing methods have extended the range of microstructures that is now sought for ceramics. The long recognized tendency to move to more uniform microstructural design in the quest for reproducible properties has now been coupled with the tendency to propose designs of more deliberate complexity; these have emerged in response to specific property requirements which can only be met by the full realization of precise microstructural arrangements.

These developments are reviewed with examples drawn from both mechanical and electrical components. Emphasis is given to the benefits which can be derived from a close interaction between programs of microstructural design and of processing.

ROLE OF GRAIN BOUNDARIES AND INTERFACES

Gareth Thomas

National Center for Electron Microscopy,
Materials and Molecular Research Division,
Lawrence Berkeley Laboratory

and

Department of Materials Science and Mineral Engineering,
University of California, Berkeley, California 94720

The microstructure of many various types of ceramics, whether for refractory, structural, or electronic applications, can be quite complex, especially when additives are used to facilitate densification during processing or for specific property requirements. In particular, the morphology and chemical composition of phases at grain boundaries and interphase interfaces are critically important in controlling various properties.

This paper will discuss the characterization of such boundaries and interfaces, with illustrations of several systems such as oxide additives with silicon nitride and sialons, glass-ceramic interfaces in oxynitrides, zirconia mullite interfaces resulting from reaction sintering to produce toughened composites, ceramic ferrites, and ferroelectric materials such as titanates and zirconates. Emphasis will be placed on applications of modern electron microscopy, microdiffraction (CBD), and microanalysis.

RATIONAL DESIGN OF HIGH THERMAL EXPANSION GLASS-CERAMICS THOUGH MICROSTRUCTURAL CONTROL

Ronald E. Loehman

Sandia National Laboratories,
Albuquerque, New Mexico 87185

Recently, Headley and Loehman discovered the crystallization mechanism for a particular lithium silicate glass-ceramic [J. Am. Ceram. Soc. 67, 620 (1984)]. All the crystalline phases were observed to grow epitaxially on preferred faces of small (0.1–0.5 μm) Li_3PO_4 crystallites that precipitate during the heat treatment. The resulting glass-ceramic has a high thermal expansion coefficient (145×10^{-7}/C) because cristobalite is one of the phases that crystallizes epitaxially. Further work has shown that there is a fairly wide range of glass-ceramic compositions for which the crystallization mechanism holds. The critical step for those compositions is heat treating the parent glass to precipitate Li_3PO_4 and then growing the crystallites to develop faces favorable for epitaxial growth of the desired phases. The formation of silica polymorphs such as cristobalite, tridymite, and α-quartz favors high thermal expansion, and all of those phases have been produced by proper heat treatments of different parent glasses. Heat treatments in which the Li_3PO_4 crystallites are small and poorly faceted give phase mixtures without the silica polymorphs, and the expansion coefficients are much lower (90×10^{-7}/C, for example). Increasing the size of the Li_3PO_4 crystallites increases the volume fraction of silica crystallized, and the expansion coefficients also increase. Thus, our understanding of this crystallization mechanism allows us to vary the phases, microstructures, and the resulting properties of glass-ceramics over wide ranges with a significant degree of control.

MICRODESIGNING OF CERAMIC-METAL COMPOSITES

I.A. Aksay, M. Sarikaya, and A.J. Pyzik

Department of Materials Science and Engineering,
University of Washington, Seattle, Washington 98195

In processing of ceramic-metal composites with particulates or fibers, problems associated with microstructural design can be analyzed with respect to two thermodynamic criteria: (i) capillarity and (ii) chemical compatibility. With respect to capillarity, wetting conditions are required in order to achieve intimately mixed multiphase combinations. We first illustrate that in most systems this requirement can be satisfied by taking advantage of the chemical reactions between the metal and the ceramic phases. We also illustrate that the degree of wetting plays an important role on the extent of short range phase segregation. Chemical compatibility of the metal with the ceramic phase is essential if the retention of the metal at elevated temperatures is a requirement. Approaches leading to the optimization of processing parameters, as related to these criteria, will be illustrated with case studies on B_4C/metal composites.

CREATING AND EXPLOITING MAXIMUM INTERFACES IN DIPHASIC-XEROGEL NANOCOMPOSITES

Rustum Roy

Materials Research Laboratory, The Pennsylvania State University,
University Park, Pennsylvania 16802

Since 1982 the solution-sol-gel method has been used in our laboratories to prepare materials not with the usual maximum homogeneity, but instead with the maximum heterogeneity; i.e., materials having the greatest possible interfacial areas. Such materials typically have randomly oriented interfacial areas in excess of 100 m^2/gm.

This paper will describe several methods for the production of these di- or multi-phasic xerogels and ceramics with compositions ranging from SiO_{2NCS}-SiO_{2qtz}, Al_2O_{3NCS}-$Al_2O_{3corundum}$, TiO_2-ZrO_2, Al_2O_3-Ni, TiO_2-Cu, etc.

It will then describe the remarkable properties exhibited by such maximum interface composites:

(a) The accelerated sintering of compositionally di-phasic vs. monophasic gels or any other precursor.

(b) The exhibition of the generalized phenomenon of solid state epitaxial growth in the systems: Al_2O_3, TiO_2, $3Al_2O_3:2SiO_2$, $Na_2O \cdot ZrO_2 \cdot 3P_2O_5$, etc., when the two phases differ not in composition but only in structure.

(c) The radical effect on microstructure, phase transitions, and sintering of such epitaxial growth in oxides.

(d) The control of crystal morphology and microstructure simultaneously by use of doubly di-phasic nanocomposites.

TEM OBSERVATION OF COHERENT AND INCOHERENT INTERFACES IN ZrO_2-CONTAINING CERAMICS

A.H. Heuer

Department of Metallurgy and Materials Science,
Case Western Reserve University, Cleveland, Ohio 44106

A variety of coherent and incoherent interfaces occur in ZrO_2-containing transformation-toughened ceramics. These include martensite/variant and precipitate/matrix interfaces in precipitate-toughened ceramics such as MgO–partially stabilized ZrO_2 (Mg-PSZ) and Y-PSZ, interphase interfaces in dispersion-toughened ceramics such as ZrO_2-toughened Al_2O_3, and twin boundary interfaces in "colony" precipitates in Y-PSZ. The structures of these various interfaces have been studied by conventional and high-resolution transmission electron microscopy.

GRAIN BOUNDARY ENERGY OF TWISTED MgO BICRYSTALS ON (100)

E. Yasuda, S. Kimura, M. Sakaki, and H. Kim

Research Laboratory of Engineering Materials,
Tokyo Institute of Technology, Yokahama, Japan

and

Y. Moriyoshi

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MgO bicrystals with a twist boundary on (100) were made at 2400°C without pressure. The boundary energy of the twist boundary was compared to that of the tilt boundary around <100> and that of the tilt boundary around <110>. The relative boundary energy (σ_b/σ_i) was measured by a thermal grooving technique at 1500°C. The σ_b/σ_i of the twist boundary increased from zero at 0° to 0.3 at 15°. Between these twist angles the relative boundary energy followed the Read and Shockley (R&S) model well, which indicates that the twist boundary is constructed of a screw dislocation arrangement. Above 15° there were three minimum points in boundary energy, at about 22°, 28°, and 36°. These angles correspond to $\Sigma = 13$, $\Sigma = 25$, and $\Sigma = 5$, respectively, on the coincident site lattice (CLS) theory. The relative boundary energy of the tilt boundary around <110> increased from zero at 0° to 0.6 at about 15°, which also followed the R&S model well. This result showed three minimum points, at (221), (111), and (113) of twin boundaries. The relative boundary energy of the tilt boundary around <100> also followed the R&S model well up to 22°, but no remarkable minimum point was observed above 22°. Dislocation arrangements were observed by TEM. The structures of the twist grain boundaries were discussed using a schematic model.

THE INFLUENCE OF Fe SOLUTE ON THE STRUCTURE OF [001] TWIST BOUNDARIES IN MgO

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The structure of [001] twist boundaries in pure and Fe-doped MgO was examined by electron imaging and diffraction techniques in order to study the influence of solute on grain boundary structure. In addition, the effect of the oxidation state of the Fe on the boundary structure was also examined. The [001] twist boundaries were produced in the form of bicrystals, by the hot pressing of cleaved single crystals of pure MgO and MgO containing Fe. In pure MgO the [001] twist boundaries are planar and, for small misorientation angles, contain a square array of screw dislocations with Burgers vectors of the type a/2<110>. In the presence of solute, for both small and large misorientation angles, the original interface becomes wavy and dissociates into subboundaries. In small angle boundaries in Fe-doped MgO, distorted hexagonal dislocation networks as well as square arrays of screw dislocations are often observed. These observations are evidence that [001] twist boundaries in MgO undergo a structural transformation induced by the presence of Fe solute. The influence of the Fe oxidation state on boundary structure is less well understood. It appears that when the [001] twist boundaries are produced using crystals containing a substantial amount of Fe^{3+} ions, the resulting boundary structure is more likely to contain distorted hexagonal dislocation networks than when the boundary is produced from crystals containing a substantial amount of Fe^{2+} ions.

STRUCTURE OF HIGH-ANGLE GRAIN BOUNDARIES IN NiO

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The atomic structures of a number of <001> high-angle tilt grain boundaries in NiO have been studied by high-resolution electron microscopy (HREM). Crystallinity is always maintained right up to the grain boundary (GB). Grain boundary planes bounded by a (100) plane are preferred; however, symmetrical facets are also found at each misorientation. A tendency to match atomic planes across the GB is not only observed in symmetrical, but also in asymmetrical GB's. Structural units can be clearly recognized in symmetrical GB's. Contrast differences suggest that a multiplicity of structural units exists for some GB configurations. Frequently symmetric GB's also show deviations from mirror symmetry. These results will be discussed and compared to current theoretical grain boundary models.

HRTEM ANALYSIS OF ORDERED GRAIN BOUNDARIES IN HIGH PURITY α-SiC

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The grain boundary structure of high purity silicon carbide (SiC) was analyzed by high resolution transmission electron microscopy in order to investigate the most stable atomic arrangement.

SiC bicrystal was produced by sublimation recrystallization in free space without any applied restriction which prevented the boundary from keeping the lowest energy atomic arrangement during the growth. Donor concentration in the crystal was below 1×10^{-17}.

The HRTEM employed was an improved version of the JEM-200CX equipped with a cryogenic pumping system and a small bore pole piece for the objective lens. The cryogenic pumping system is powerful enough to prevent the specimen from contamination by hydrocarbons. The spherical and chromatic aberration constants were 0.7 mm and 1.2 mm, respectively. The resolution, 0.09 nm in the lattice image at the highest power, was sufficient to investigate the boundary structure of SiC.

Almost all boundaries of the bicrystal showed the same geometric characteristics, suggesting that the growing condition was suitable for the formation of a stable boundary. Two crystals of 6H structure were rotated by 70.5° about the <110> axis and joined at the {0001} plane of one crystal and the {1010} plane of the other. The atomic arrangement was asymmetrical and coincided with the structure model[1] constructed so that the number of dangling bonds was lowest in the boundary. Various polycrystalline boundaries were also investigated and will be presented.

Reference:

1. Y. Inomata, Z. Inoue, and Y. Uemura, Yogyo Kyoukai-si 90, 87 (1982).

ATOMIC STRUCTURE OF INTERFACES IN SIALON CERAMICS

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Our previous work on a β'-yttria doped sialon exhibiting an intergranular Si rich glassy phase showed a transition phase between crystal and glass. This phase is made of a peculiar sequence of layered oxynitride and silica tetrahedra. This ordered sequence results from a topotaxy relationship between the two phases due to the very close similarity between SiN_4 and SiO_4 tetrahedra. An atomic model based on a silicate structure--the dalyite--was proposed to describe the first few layers of SiO_2 at the immediate vicinity of the β' grains. This model was confirmed by HREM imaging and contrast simulations. We suggested that the same model could be extended to represent the atomic structure of a vitreous intergranular film (VIF).

In the present work we confirm and refine our atomic model of VIF in substituted silicon nitrides by combining HREM observations, simulations, and chemical information via EELS experiments. This model has been established for the simple case of prismatic planes on both sides of the VIF but can be applied to more intricate orientations. Then attention must be paid to the interfacial energy variations related to the chemical bonding (dangling bonds versus reconstructed bonds and segregation).

The stable equilibrium width of a VIF has been explained by Clarke via two approaches which are essentially a continuum description of an atomic scale phenomenon: one is based on the interfacial energy concept and the other on the force equilibrium normal to the boundary. Thus our work gives a new interfacial description which takes into account the discrete nature of the competing forces transmitted by the tetrahedral arrangement of this type of interface.

THEORY OF OXIDE-OXIDE AND OXIDE-METAL INTERFACES

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Oxide-metal adhesion is one of the complex phenomena which underly many technical programs. Theoretically, the complexity comes both from the chemical and morphological complication of the real interface and from the many distinct theoretical contributions to the interfacial energy. Recent work has shown that one of these--the image term--is of special importance because it varies greatly from case to case and because its trends are relatively simple to estimate. This allows one to understand observed systematics in oxide/(non-reactive) adhesion, the occurrence of oxide-rich layers near the metal in oxidation, and some aspects of radiation-enhanced adhesion.

Work on the structure of oxide-oxide interfaces will also be surveyed, since this allows one to identify systematic structural features.

SEGREGATION OF CATION IMPURITIES AT CERAMIC BOUNDARIES

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It has been recognized for some time that cation impurities distribute unequally between interfaces, including free surfaces, and bulk lattice, with consequent effects on the evolution and properties of ceramic microstructures. In the present paper, results are reported of a theoretical study of this phenomenon, with reference to the segregation of isovalent and aliovalent impurities in MgO, CaO, α-Al_2O_3, Fe_2O_3, c-ZrO_2, and Li_2O. Free surfaces are the major interest, though reference is also made to segregation at special boundaries in α-Al_2O_3 and to impurity domain formation in bulk c-ZrO_2.

Coverage (concentration)-dependent heats of segregation are calculated using the methods of atomistic lattice simulation based on interatomic potentials derived from electron-gas theory: the relevant procedures have been described in full previously. Heats of segregation, thus calculated, are incorporated in a recently derived, nonlinear segregation isotherm which is evaluated numerically to yield equilibrium coverages (concentrations) of impurity. Attention will focus on the following aspects:

(i) The energetics (heat) of segregation, with an emphasis on the coverage-dependence, its implications for non-Arrhenius behavior, and the interpretation of experimental measurements.

(ii) Equilibrium coverages.

(iii) The composition and structure of segregated boundaries, including a description of coherent second phases which calculations suggest might form in α-Al_2O_3 and c-ZrO_2.

(iv) The energetics of segregated surfaces, including the hypothesis that the surface energy of an impure surface might be negative, thereby acting as a thermodynamic barrier to sintering.

Where possible, comparisons will be made with such data that exist. Finally, suggestions will be made as to where experiments might vindicate, or otherwise, theoretical predictions.

THE DISTRIBUTION AND INFLUENCE OF MINOR CONSTITUENTS ON CERAMIC FORMULATIONS

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In real life it is virtually impossible to manufacture ceramics free from some significant concentration of widespread contaminants such as calcium oxide, silicon oxide, and frequently iron oxide, which are among the most common constituents of the earth's surface. In addition, small amounts of other materials are intentionally added to obtain improved processing or properties. In principle, these minor constituents may be present in the final ceramic as solid solutions in the major phase, may be present as segregants at the grain boundary and surface planes, may be present in an extended space charge layer adjacent to grain boundaries or the surface, or form separate amorphous or crystalline phases at the surface, at grain boundaries, or within the bulk phase. Examples of each of these distributions will be described and the factors leading to a particular distribution analyzed. The effect of these distributions on ceramic processing and properties of ceramic products will be discussed.

CONSIDERATION OF INTERFACES AS A STATISTICAL MICROSTRUCTURE PARAMETER

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Recent fundamental work on interfaces has shown that their structure varies with the misorientation between the adjacent crystals and with the orientation of the grain boundary plane. Indeed, the mechanical properties of interfaces have been shown to vary with structure. The structure is usually characterized in terms of the nearest coincidence-site-lattice, the sigma value.

The question addressed in this paper is how the properties of a polycrystal are influenced by the distribution in the properties of the grain boundaries. In some cases (for example, brittle fracture) the extreme value statistics will be important, while at other times (electrical conductivity) the average statistics may be more relevant.

TEM STATISTICAL CHARACTERIZATION OF GRAIN BOUNDARIES IN POLYCRYSTALLINE NiO COATINGS OBTAINED BY HIGH TEMPERATURE OXIDATION OF NICKEL

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This paper presents some results of a statistical study carried out by TEM upon the geometrical features of a sampling of more than 100 grain boundaries observed in polycrystalline nickel oxide coatings. For each boundary the following features have been determined: the orientation relationship between both adjacent crystals, the possible coincidence index (within the limit of $\Sigma = 41$), the mean crystallographic plane of the grain boundary and its orientation in relation to the surface, and the plane of the thin foil (which was assumed to be parallel to the oxide-atmosphere interface of the coating). These sets of data are collected in such a way as to give a statistical insight of the NiO coating which develops during oxidation of nickel in oxygen between 1100 and 1200°C. The conclusions are as follows:

1. The results precisely evidence the columnar growth of the coating during the oxidation, as well as the existence of an equiaxial area close to the Ni-NiO interface. Moreover some information on the oxidation texture is given.
2. The grain boundary planes are randomly distributed, with the exception that there is not any interface in the vicinity of the {011} crystallographic planes. The reason why this occurs is not understood, and investigations are currently under way to try and clear up the point.
3. The orientation relationships were used to determine a possible coincidence index Σ, within the deviation range from CSL exact misorientations defined according to Brandon's criterion. It is shown, by comparing with the theoretical estimate of Warrington and Boon (Acta Metall., 1975), that grain boundary orientation relationships are randomly distributed. In other words, despite their low energy, the special grain boundaries apparently do not play any role during the growth of the coating.

QUANTITATIVE CHARACTERIZATION OF MICROSTRUCTURAL GEOMETRY OF INTERFACES

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The geometry parameters of interfaces are important for the quantitative description of the kinetics of sintering, grain growth, and particle coarsening, as well as for the establishment of quantitative relationships between microstructure and properties. Difficulties in measuring local variations of interface curvature and stereometric techniques for fracture surfaces or for internal surfaces in transparent materials are outlined. Three-dimensional local information on internal surfaces in opaque materials can be obtained by serial sectioning but is usually too tedious and is substituted by descriptors obtained from one section. The relevant equations and techniques for the assessment of some important global parameters describing the geometry of interfaces are outlined. These are the area per unit volume and the mean curvature for each individual type of interface and statistical parameters for the interaction of various types of interfaces (grain boundaries, phase boundaries, and internal surfaces).

Case studies (sintering of glass, discontinuous grain growth) are discussed which demonstrate the advantage of using global stereological parameters in place of idealized shapes for particles, grains, or pores (usually spheres).

DIFFUSION BONDING, CHEMISTRY, AND STRUCTURE OF METAL/CERAMIC INTERFACES

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The mechanisms of diffusion bonding between Nb and Al_2O_3 are studied using a special technique. The Nb surfaces are prepared so that arrangements of well-defined defects (flaws) are included. Subsequently, bonding is performed under well-defined conditions (temperature, vacuum, loading, etc.), and the change of the structure of the flaws is analyzed after decohesion of the partially bonded interface. Bonding occurs primarily in the areas of close contact between Al_2O_3 and Nb. Experimentally, it can be shown that chemical reactions occur at the interface if the temperature during bonding exceeds a certain value. The closing of the flaws depends on the chemical reaction rate as well as on the (volume) diffusion within Nb. The shape of the interface stays flat for the selected bonding conditions. This observation is in agreement with theoretical expectations. Bonding conditions which result in a wavy interface can be derived. The chemical compositions of the interface near regions in Al_2O_3 and Nb can be determined with high spatial resolution by utilizing analytical electron microscopy. Direct lattice imaging (through high resolution electron microscopy) is used for studying the atomistic structure of the interface. Defects (facets, dislocations, etc.) at and near the interface can be identified. The observations are extended to other systems.

COPPER-GLASS-CERAMIC INTERFACES AND COMPOSITES: REACTIONS, MICROCHEMISTRY, AND ELECTRICAL PROPERTIES

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Interface microchemistry, dissolution-precipitation, and crystallized phases were investigated in a copper thick film–cordierite (MgO-Al_2O_3-SiO_2) glass ceramic system. Interfacial reactions between copper and the glass ceramic were studied after processing samples at temperatures of 800°C and 1000°C in reducing atmospheres ($P_{O_2} \simeq 10^{-10}$ atm). Copper diffusion to distances of $\simeq$ 150 μm was observed by electron microprobe analysis, and the dissolution of Cu^+ in the glassy solution at the interface was revealed by the bright blue fluorescence observed via cathodoluminescence. A diffusion coefficient of ~10^{-11} cm^2/sec at 800°C was estimated from the copper concentration profiles. Continued reactions in samples processed at 1000°C ($P_{O_2} \sim 10^{-10}$ atm) resulted in crystallization to a multiphase ceramic accompanied by the formation of a reddish pink reaction zone at the interface. Crystallization in the 1000°C samples also reduced the intensity of the blue fluorescence seen in the 800°C samples (precrystallized cordierite type glass). TEM, STEM, and EDS analyses of the glass ceramic showed considerable complexity in the microstructure of the ceramic; α-cordierite, enstatite, minor amounts of forsterite, α-alumina, and phase separated areas were identified. Precipitates of metallic copper of various sizes ($\simeq$ 100 to 200 nm) were observed in the reddish pink interface zone in the crystallized 1000°C samples.

The effects of copper or Cu_2O on the dielectric and resistive properties of the ceramic were studied. Bulk samples with compositions in the range observed in the above interface characterization results were processed. These consisted of a dozen glass ceramic matrix composites with Cu and Cu_2O dispersions at levels in the range 0 to ~3 wt% Cu or Cu_2O. Samples were fired at 1000°C in air (group 1), and reducing atmospheres of $P_{O_2} \simeq 10^{-11}$ atm (group 2) and $P_{O_2} < 10^{-15}$ atm (group 3). Dielectric constants of all samples in groups 1 and 3 were measured to be ~5.9 at 25°C in the frequency range 1 KHz to 3.5 MHz. Cu or Cu_2O additions did not significantly affect the dielectric constant, but the presence of some porosity decreased the dielectric constant to 4.7 to 5.2. The ac resistivity (at 25°C) of samples from all three groups was greater than $\simeq 10^9$ ohm-cm at frequencies from 1 to 100 KHz and was not changed significantly by the small copper additions.

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THE CERAMIC-METAL REACTION AND ITS EFFECT ON MICROSTRUCTURE PRODUCTION

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Interfacial ceramic-metal reactions can drastically affect the properties of the interface. It is therefore of interest to know the conditions for reaction in a ceramic-metal system to proceed. Since such reactions are of irreversible nature, the thermodynamics of irreversible processes should be applied in the calculation of the reaction conditions, but the lack of relevant data makes it impossible.

The equilibrium thermodynamics are useful to calculate the conditions required for a ceramic-metal reaction to occur. In this paper equilibrium thermodynamics are discussed and applied to obtain the conditions that are favorable for reaction in oxide ceramic-metal systems. Experimental verifications are presented. The structural buildup of the interface depends on the chemical nature of the materials and on the reaction conditions. A qualitative correlation between the structure and the strength of reactive and non-reactive bonded interfaces is given.

BONDING CERAMIC-METAL INTERFACES AND JOINTS

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Our understanding and control of both liquid and solid phase processes for bonding ceramics to metals has improved significantly in recent years. The prerequisite for bonding is intimate contact between the ceramic and metal surfaces, achieved by liquid wetting or deformation and creep of solids. The extent of wetting can depend critically on reactions at the contacting surfaces, to form hypostoichiometric or complex compounds, and particular reference will be made to the role of titanium in the active metal brazing of ceramics. Wetting can be promoted by increasing formation of beneficial compounds, and bonding is also initially promoted. However, compound formation ultimately can cause weakening, due to increasingly severe growth stresses. Hence there is an optimum extent of reaction, and in some cases the resultant strength maxima can be related to chemical stability parameters.

The strengths of joints in macroscopic components depend on the maintenance as well as the formation of bonded interfaces. Thus thermal contraction and design factors may be of overriding importance, but detrimental effects may be mitigated by the development of ductile joining materials for mismatched workpieces and compliant joint configurations.

POWDERS, INTERFACES, AND PROCESSING: ALUMINA AS A CASE STUDY

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The characteristics of ceramic powders are very significant to the overall powder processing methodology. Particularly important are the characteristics which relate to or control the surface of interfacial characteristics in as much as these influence the green microstructure, the firing processes, and microstructure evolution. The interrelationships of the many variables (e.g., bulk composition, surface chemistry, particle coordination number, pore size, powder size distribution, and green density) are complex, yet some progress is being made by studying model systems.

In this report, we give results for processing alumina powders which have different surface/interface related properties (size distribution, pH, organic dispersants, etc.). The green microstructures and fired microstructures are related to the powder characteristics and to the powder-solution interface chemistry. Examples of the correlations which result from these studies are the pore size distribution as a function of forming method and surface chemistry, effects of interfacial chemistry on binder burnout, effects of interfacial chemistry and green density on the sintering–grain growth curves, etc.

ROLE OF POWDER CONSOLIDATION ON MICROSTRUCTURE EVOLUTION

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Recent research results have illustrated the advantages of using colloidal dispersion and consolidation methods to control the degree of packing uniformity in the 10^{-9} to 10^{-6} m range. In this presentation we will first review the role of (i) powder characteristics, (ii) dispersion methodology, and (iii) the consolidation methods on the packing density variations. We will illustrate that packing density variations ultimately determine the character of the sintered microstructure. A specific example will be on the low temperature sintering of ceramics by approaching a state of monosize pore distribution and by maximizing the overall packing density. The advantages of (i) using polydisperse particle size systems, (ii) shear deformation techniques, (iii) amorphous powders, and (iv) inorganic polymers will be discussed.

THE ROLE OF POWDER PACKING IN SINTERING

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The densification of powder compacts containing larger pores in a fine grain, homogeneous matrix is considered. Homogenization of the porous microstructure is possible in the intermediate stage of densification due to grain growth driven coalescence of the finer pores, while the coarser pores grow less. The conditions are identified for which homogeneity can be achieved at the end of the intermediate stage. It is found that for finer powders the initial packing perfection has to increase rapidly.

The effects of temperature and the relative merits of monodispersed versus multidispersed powders are also discussed.

EFFECT OF PORES ON MICROSTRUCTURE DEVELOPMENT

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The effects of pores on the final-stage sintering behavior of ceramic materials will be discussed. Lithium fluoride will be used as a model material to demonstrate the effects of pore drag. A simultaneous model of densification and grain growth will be used to demonstrate the effects of pore number density and pore size distribution on microstructure development during final stage sintering. Factors governing the prevention of pore-breakaway and abnormal grain growth will also be reviewed, with emphasis on the use of solid solution additives and transient solid second phases.

CONTROLLED GRAIN GROWTH IN CERAMICS

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Controlling grain size and eliminating abnormal grain growth can be critically important to advanced ceramics. An inclusion phase can control grain size. As long as the inclusion is less than a critical size, microcracks that could arise during either fabrication or subsequent stressing can be avoided. For ceramics, the inclusion phase must be either included in the major phase powder prior to sintering or by a partitioning reaction while sintering in a two-phase field. The effect of the inclusion phase on hindering grain growth will be discussed in relation to Zener's initial concept, energetics of grain junction location, junction to junction relocation for immobile and mobile inclusions, and inclusion phase distribution. Experimental results will be presented and discussed for the cases where ZrO_2 is the inclusion phase in Al_2O_3 and where Al_2O_3 is the inclusion phase in ZrO_2. Partitioning reactions in the ZrO_2-rich portion of the ZrO_2-Y_2O_3 system that results in exceptionally small grain size will also be presented and discussed.

GRAIN GROWTH IN TiO_2

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During the preparation of TiO_2 ceramics, we have observed a significant microstructural difference in samples doped with various types of dopants. In this paper, we shall report the grain growth in doped TiO_2 ceramics to elucidate the effects of ionic sizes and valences of the dopants on the microstructural development of TiO_2. In particular, we investigated the grain growth kinetics in undoped TiO_2 and TiO_2 doped with ≤2 mole % Nb, Al, Sn, and Zr. We found that the grain growth exponents in the growth kinetics ranged from 1.5 to 3.1 depending on the type and concentration of dopants. In general, the Nb dopant suppressed the grain growth kinetics and the Al dopant increased the grain size of TiO_2. The Sn and Zr dopants did not have a significant effect on the grain size. Impurity drag theory and defect chemistry were used to elucidate the observed dopant effects on microstructural development.

WETTING AND DEWETTING OF GRAIN BOUNDARIES IN POLYPHASE CERAMICS

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The presence of thin (~1–10 nm) interconnected, noncrystalline phases separating crystalline grains is now widely accepted as being responsible for a variety of degradation phenomena in structural ceramics, particularly at elevated temperatures. Intergranular phases have been shown to promote subcritical crack growth, creep deformation, chemical and environmental attack, and in nonoxide ceramics, to accelerate oxidation. In view of its detrimental effects, and faced with the dilemma that it is often present as a consequence of the liquid phase sintering process necessary to produce the ceramic in the first place, attention has recently been given[1] to the thermodynamic stability of such thin films. Consideration of the balance between the surface forces acting across the intergranular phase at high temperatures suggests conditions under which the phase will be stable and the temperature dependence. One of the findings is that intergranular phases that are stable (viz., continuous) at high temperatures characteristic of liquid phase sintering conditions, can in principle become unstable at lower temperatures and break up into discrete, unconnected pockets. However, as will be discussed, there is a nucleation barrier that must be overcome before a grain boundary with an intergranular phase will dewet on cooling. In addition to such a thermodynamic barrier, whether a boundary dewets on cooling will also be shown to depend on kinetic factors, such as the rate of diffusional and viscous transport.

Reference:

1. D.R. Clarke, "On the Equilibrium Thickness of Intergranular Glass Phases in Ceramic Materials," J. Am. Ceram. Soc.

MICROSTRUCTURE DEVELOPMENT OF HYDROTHERMAL POWDERS AND CERAMICS

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ZrO_2 and Y-PSZ powders were prepared by the hydrothermal method. Among the hydrothermal precipitation, hydrothermal crystallization, hydrothermal hydrolysis, and hydrothermal oxidation methods, hydrothermal precipitation is an excellent method for producing Y-PSZ powder. The average crystallite size is 13–23 nm, and the surface is 89–23 m^2/g. The content of tet. ZrO_2 is 75%. Hydrothermal Y-PSZ powder is sinterable at 1400°C and/or 1500°C for 2 hours. The relative density is over 99%, and the bending strength is 920–1050 MPa. The fracture toughness is 6–8 $MNm^{-3/2}$. The average grain size is 0.4–0.8 μm, which depends on sintering temperature. We will discuss the effect of preparation and sintering processing, especially the effect of different washing liquids, and of calcination temperature on microstructure development.

VAPOR TRANSPORT AND MICROSTRUCTURE DEVELOPMENT IN CERAMICS

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An understanding of microstructure development during sintering of porous ceramic powder compacts has been extremely difficult to obtain. One of the main reasons for this has been the lack of quantitative and accurate mass transport data with which to compare experimental observations and models. In contrast, mass transport via vapor transport is relatively easily modeled and the gaseous diffusion coefficients are readily available or calculable from kinetic theory. As a result, a study of the effect of vapor transport, which can be easily enhanced to be the dominant mass transport process by atmosphere control, can lead to an improved understanding of microstructure development during sintering. Vapor transport has been investigated for a number of ceramic systems, both oxides and nonoxides. The effects of enhanced vapor transport on the resulting microstructure development can be compared to that predicted by simple sintering models. In some cases model and experiment are in good agreement. In others, interaction among transport processes introduces complications and leads to different paths of microstructure development

SINTERING THEORY FOR CRYSTALLINE SOLIDS

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A well known defect in most sintering models for crystalline ceramics is the assumption that sintering is driven by differences in curvatures of surfaces of isotropic bond energies. A more serious defect may be the usual assumption that the rate limiting step is mass transport over distances of the order of the particle radii. Some published micrographs show essentially all particles to grow during early stages of sintering. Such observations suggest that matter is supplied from outside the fields of the micrographs.

A new model for surface thermodynamics [J. Chem. Phys. 83, 3095 (1985)] provides general expressions for the driving force for isothermal sintering and for exaggerated grain growth. Because the driving force for isothermal sintering is very small, for dislocation-free particles the rate limiting process should often be the nucleation of new ledges. Screw dislocations should increase sintering rates by permitting crystal growth without a ledge nucleation step, much as for growth from a vapor.

Generalization of the conditions for dynamic equilibrium at constant temperature yields an expression for sintering in a temperature gradient. This expression is used to show that temperature gradients through a specimen may sometimes be more important than local differences in particle shapes in driving mass transport. In particular, temperature gradients could produce relatively uniform particle growth in central portions of a test specimen during early stages of sintering.

SELECTIVE SINTERING CONDITIONS FOR SiC AND Si_3N_4

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This paper will review and discuss certain selective sintering conditions for two important ceramic materials, SiC and Si_3N_4. Most emphasis will be placed on competitive sintering processes (surface diffusion and evaporation/condensation) that do not lead to macroscopic densification and on chemical reactions that may or may not contribute to macroscopic densification of compacts with submicron powders. It is important to understand the high temperature stability of SiC and Si_3N_4 and the chemical and phase changes that can take place at/near surfaces and grain boundaries during the sintering process. The establishment of sintering conditions which lead to a high relative ratio of macroscopic densification-to-grain growth (coarsening) permits the overall development of desirable microstructures for useful properties.

SINTERING OF WHISKER REINFORCED CERAMIC COMPOSITES

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SiC whisker reinforcement has been shown to significantly improve the mechanical properties of hot-pressed alumina and mullite. For example, typical fine-grained alumina has fracture toughness, K_{Ic}, and flexural strength values of 4 to 5 MPa•m$^{1/2}$ and 350 to 450 MPa, respectively. We have demonstrated that, by the addition of 20 vol% SiC whiskers to the alumina, corresponding values of 8 to 8.5 MPa•m$^{1/2}$ and 650 MPa are obtained. In addition, we have found that these toughness and strength values are essentially maintained up to temperatures of at least 1000°C. Analysis has indicated that crack deflection by the whiskers is the major toughening mechanism.

While hot pressing of the alumina-SiC whisker composites produces dense materials with attractive mechanical properties, the ability to pressureless sinter the composites to near-net-shape will ensure wider commercial utilization. Fabrication of high toughness composites by pressureless sintering was found to be a viable process for alumina-based composites with whisker contents <20 vol%. High density composites were fabricated with yttria as a liquid phase sintering aid. Transmission electron microscopy shows the formation at the grain boundaries of a yttrium aluminate, which is liquid at the sintering temperature. Little interaction between the SiC whiskers and the alumina matrix or the liquid phase was observed.

INTERFACIAL CHEMISTRY AND BONDING IN FIBER REINFORCED GLASS AND GLASS-CERAMIC MATRIX COMPOSITES

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The fiber/matrix interfacial region between Nicalon Si-C-O fibers and a variety of glass and glass-ceramic matrices was examined, primarily through the use of the scanning transmission electron microscope (STEM) and the Scanning Auger Multiprobe (SAM). From the analyses of strong and fracture tough composites, it was found that the chemistry of the Nicalon fibers within a few hundred angstroms of the fiber surface undergoes a rather profound change when the fibers are incorporated into certain glass or glass-ceramic matrices. Among the changes noted for certain lithium aluminosilicate (LAS) glass-ceramic and aluminosilicate glass matrix composites is that a thin (~500 Å) interfacial zone forms that is extremely carbon rich, being almost totally devoid of Si and O. From SAM analysis of Nicalon fiber surfaces from extremely weak and brittle glass and glass-ceramic matrix composites where the fiber and matrix appear to be rather strongly bonded, this carbon-rich layer is either nonexistent or much reduced in carbon content. It appears, therefore, that the formation of this carbon-rich interfacial zone in the glass and glass-ceramic matrix composites under study leads to quite weak bonding at the fiber/matrix interface that directly contributes to the high toughness observed for these systems.

It has also been found that many of the weakly bonded, tough glass and glass-ceramic matrix/Nicalon fiber composite systems undergo an embrittlement and concurrent strength and toughness degradation when either stressed at elevated temperatures in an oxidizing environment or thermally aged in an unstressed condition for relatively long periods of time in a static oxidizing environment at elevated temperature. In either case, it appears that embrittlement occurs when the fiber/matrix interface is exposed to oxygen either through matrix microcracking under stress or from the "pipeline" oxidation of the carbon-rich layer at the interface that is primarily initiated at the cut ends of fibers intersecting the composite surface. The glassy oxide layer that forms on the exposed fiber surfaces tends to form very fast and appears to either bond the fibers very tightly to the matrix or cause the fibers to become weak and brittle due to the apparent extreme notch sensitivity of Nicalon fibers with glassy surface coatings. Evidence for this phenomenon from TEM and scanning Auger analysis of the fiber/matrix interface will be presented.

ANION CONTROLLED MICROSTRUCTURES IN THE Al_2O_3-AlN SYSTEM

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The phase equilibria of the pseudo-binary Al_2O_3-AlN composition join has been extensively investigated, especially with respect to the processing of ALON--a nitrogen stabilized aluminum oxide spinel phase that can be sintered into transparent polycrystalline ceramics. The system exhibits a wide variety of features and resulting microstructures: two spinel phases, vapor-solid and liquid-solid eutectics, AlN polytype-like structures, and α-Al_2O_3/spinel modulated structures. This system provides a unique perspective to a series of quite different materials based on a constant cation chemistry, with a continuous variation in the O/N anion ratio. The addition of nitrogen into Al_2O_3 drives part of the Al into fourfold coordination, causing the formation of α-Al_2O_3/spinel modulated structures and two spinel phases--ALON and ϕ'-ALON; a ς-Al_2O_3 or $LiAl_5O_8$, a distorted spinel phase exhibiting extremely complicated twinning and intergrowth microstructures. The substitution of oxygen for nitrogen in AlN results in a series of polytype-like structures based on AlN: 32H, 27R, 16H, 21R, and 12H. In these cases the stable coordination of aluminum is driven from four to six by the replacement of nitrogen with oxygen. These materials exhibit the tendency to form in lenticular morphologies, creating an interlocking fibrous-like microstructure. The microstructures in the AlN part of the system result mainly from solid-vapor equilibria, whereas those on the Al_2O_3 side are controlled by solid-liquid equilibria.

ELECTRICAL PROPERTIES AND MICROSTRUCTURES

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In ferroelectric and "near ferroelectric" materials, which find wide application in dielectric, pyroelectric, piezoelectric, electrostrictive, and electro-optic applications, microstructure at many levels plays a most important role and in many instances has a controlling influence upon the properties of interest.

For dielectric ceramics using ferroelectric phases, the absence of a strong grain size effect in the paraelectric phase is expected. New evidence of the role of nanometer scale heterogeneity upon the polarization behavior in lead-based perovskites will be presented and its effect upon the properties of the important relaxor ferroelectrics discussed. Evidence for the control of aging by the defect structure in these ceramics will be presented and its importance in electrostrictive application underscored.

In the ferroelectric phases, new evidence suggests a much more important role for ferroelastic-ferroelectric domain motion than was heretofore suspected, both for dielectric and piezoelectric responses. Recent evidence which requires our reassessment of the role of wall motion will be discussed.

For pyroelectric and electro-optic applications, domains are generally a terrible nuisance, and methods which seek to use the defect structure to control, eliminate, or immobilize domains will be discussed.

Both in pyroelectric and electro-optic devices, it is the intrinsic properties of the single domain ferroelectric states which are of most interest. Techniques for manipulating the intrinsic properties by judicious use of solid solution behavior will be briefly considered and phenomenological aids for property optimization reviewed.

ELECTRICAL CONDUCTIVITY IN CERAMICS: A REVIEW

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The electrical conductivities of ceramic materials cover an enormous range of values and may have significant contributions from both electronic and ionic components. Depending on the specific application, either very high or very low conductivities of either type may be required. In addition to the properties of the bulk, the electrical conductivity of the grain boundaries or of intergranular phases may be crucial for device performance; e.g., they may need to be highly insulating (boundary-layer or surface-layer capacitors), highly temperature dependent (PTC resistors), or highly voltage dependent (varistors). It is thus of the utmost importance to understand the relationships between composition, microstructure, and conductivity.

The material parameters that determine the conductivity characteristics of ceramics will be reviewed. These will include the electronic structure of the atomic constituents and the resulting band gaps of the resulting solids, the nature and concentration range of ionic defects, the stability of alternative valence states of the constituents, and the depths of acceptor and donor states in the band gap.

THE CRYSTALLOGRAPHIC AND CHEMICAL RELATIONSHIP BETWEEN INTERGRANULAR AND BULK RESISTIVITY IN SEMICONDUCTOR OXIDES

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We have shown previously that polycrystalline semiconductor oxides such as ferrites processed by liquid phase sintering with additives such as CaO and SiO_2 exhibited three main types (i) of grain boundaries:

1. low Σ boundaries
2. vitreous-film-coated boundaries
3. high Σ or general boundaries with Ca segregation.

From microelectrode measurements, as well as _in situ_ measurements and crystallochemical analyses in TEM, we have interpreted the electric barrier mechanism for each case.

In this work we have first completed quantitatively the correlation between _in situ_ measurements of the voltage dropoff ΔVi at grain boundaries and the intergranular structure and composition. This leads to the typical values:

$$\Delta V_2 = 10\ \Delta V_1$$

$$\Delta V_3 = 40\ \Delta V_1.$$

Furthermore we have related the wetting rate of the grain boundaries by the vitreous phase to the grain boundaries' crystallochemical distribution. By thorough mapping of the grain boundary distribution it is then possible to explain the relationship between the grain boundaries' electrical properties and distribution on the one hand and bulk electrical properties on the other hand. For instance it is shown that few but percolating low Σ grain boundaries can greatly impair the high bulk resistivity resulting from the other types of grain boundaries.

It is to be emphasized that the described methodology can be used to elucidate the electric barrier mechanism of several polycrystalline simple or mixed oxides.

ELECTRICAL PROPERTIES AND MICROSTRUCTURE OF $ZnO-Nb_2O_5$ CERAMICS SINTERED IN THE LIQUID PHASE

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$ZnO-Nb_2O_5$ ceramics fired at 1305°C and accompanied by some melts are composed of ZnO grains and intergranular layers which are $3ZnO \cdot Nb_2O_5$ and high resistivity. The third component was added to the $ZnO-Nb_2O_5$ ceramic in order to alter the property of melts formed at high temperature. The addition of alkaline earth metal oxides improved the wettability of intergranular layers to ZnO grains and increased the room-temperature electrical resistivity. SiO_2 also improved the wettability but did not change the electrical resistivity. CoO did not affect appreciably the microstructure and electrical property. The addition of MnO markedly increased the electrical resistivity and gave rise to a nonlinear V-I relation, though it did not markedly affect the microstructure. The concentration of Mn^{2+} in intergranular layers was higher than that in ZnO grains, while Co^{2+} was distributed uniformly among them. The increase in cooling rate of fired specimens containing MnO improved the wettability of intergranular layers and the characteristic of the nonlinear V-I relation. Since some ZnO precipitated epitaxially on the ZnO host grain surface from the melt during cooling, the grain boundary region or very thin surface layer of the ZnO grains came to have electrical properties different from those in the inner part, and such a difference caused high resistivity and a nonlinear V-I relation.

NEW COMPOSITE PTC MATERIALS BASED ON $PbTiO_3$-TiO_2

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Semiconducting $BaTiO_3$ ceramics show a positive temperature coefficient of resistivity (PTC) above the Curie temperature (T_c = 120°C). PTC materials are used for many applications such as self-regulating heating elements, and ones for high temperature applications are in strong demand. In order to design the high temperature PTC materials, the Curie temperature of PTC materials must be increased by substituting $PbTiO_3$ for $BaTiO_3$. But the resistivity (ρ) of $(BaPb)TiO_3$ increases with increasing $PbTiO_3$ content, and it limits the maximum substitution content of $PbTiO_3$. Up to now PTC ceramics with $T_c \simeq$ 300–416°C are produced on a manufacturing scale or laboratory scale.

The PTC property is believed to originate from the grain boundary potential barrier between ferro-ferroelectric crystal interfaces. The present paper describes the new approach to design the new PTC materials in utilizing the ferro-nonferroelectric crystal interface. We chose $PbTiO_3$ as the ferroelectric ceramic with high T_c (490°C) and TiO_2 as the semiconducting nonferroelectric ceramic, since $PbTiO_3$ and TiO_2 are not soluble in each other according to the phase diagram. The starting materials were PbO, TiO_2, and Nb_2O_5, which were weighed in making the nominal compositions as $Pb(Ti_{0.998}Nb_{0.002})O_3$-[$\simeq$10–50 mole% $(Ti_{0.998}Nb_{0.002})O_2$]. The compact bodies were sintered at ~1000–1075°C for various times in Ar atmosphere. The samples showed PTC characteristics of $\rho_{max}/\rho_{200°C} \simeq 3$ at ~490°C, which corresponds to the Curie temperature of $PbTiO_3$. This is the highest value among reported usable PTC materials. The microstructure of the samples is such that $PbTiO_3$ and TiO_2 with around 0.5 μm size are interconnected to each other. This indicates that the origin of the PTC property in present developed composite PTC materials is due to the interface potential barrier between ferroelectric $PbTiO_3$ and nonferroelectric TiO_2 ceramics.

EFFECT OF MICROSTRUCTURE CONTROL ON FERROELECTRIC CERAMICS

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For the microstructural control of ferroelectric ceramics, hot-pressing technology was applied to some bismuth layered structure ceramics such as $PbBi_2Nb_2O_9$, $(Pb_{1-x}Sr_x)Bi_2Nb_2O_9$, etc., and some tungsten-bronze type ceramics such as $(Pb,Ba,La)Nb_2O_6$, and the anisotropies in dielectric, piezoelectric, and electrooptic properties were systematically measured and discussed. Using two-stage hot-pressing or one-stage hot-pressing with a special doctor blade method, one-directionally grain oriented $(Pb,Ba,La)Nb_2O_6$ ceramics were successfully prepared, and the anisotropic dielectric and piezoelectric properties were measured with the microstructure observation using a SEM. Using microindentation techniques, the fracture toughness was measured for some microstructure controlled PLZT, some grain oriented samples, and some composites such as SiC whisker reinforced PZT ceramics, and their mechanical properties were discussed. Also $Pb_5Ge_3O_{11}$ was hot-pressed and the dielectric and pyroelectric properties were measured with an improved pyroelectric coefficient and figure of merit.

OPTICAL EFFECTS OF GRAIN BOUNDARIES IN PLZT CERAMICS

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PLZT transparent ferroelectric ceramics are one of the most promising materials for studying the role of interfaces in ceramics due to the following advantageous factors:

1. Transparent, no pores, single phase system.
2. Granular shape grains, very thin grain boundaries.
3. The properties of PLZT ceramics are sensitive to external forces--temperature, stress, or electric field. It is profitable to study the effects of grain boundary on the properties of the material.
4. The phase transition temperature of PLZT ceramics can be regulated by modification of chemical composition. It will be convenient to do experimental work when the phase transition temperature of the material is around room temperature.

In this paper, the effects of grain boundaries on the optical and electro-optical properties of the PLZT ceramics will be presented with emphasis on the following aspects:

1. Method of preparation of grain grown specimens and 10 μm thick single grain slides for investigation.
2. Quantitative stereology of different grain size PLZT ceramics by using the Quantimet 900, Micro Image Automatic Quantitative Analyzer.
3. Measurement of optical and electro-optical properties of the different grain size PLZT ceramics and the property of single grains in PLZT ceramic slides.
4. Grain boundary movement and other phenomena were observed under optical microscopes or by means of electron microscopes.
5. The role of interfaces on optical and electro-optical properties of PLZT ceramics will be discussed with the results of the above experiments.

INTERFACE EFFECTS IN ZINC OXIDE VARISTORS

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Zinc oxide varistors are electronic ceramic materials whose electrical behavior is dominated by grain boundary interface states. The varistor exhibits a highly nonlinear current-voltage relationship, with a 5% change in voltage serving to increase the current flow an order of magnitude or more.

The unique properties of varistor ceramics are determined by the segregation of certain impurity atoms to the grain interface, creating electrical barriers to current flow. At low voltages electrons transfer over these barriers by thermionic emission. At a critical voltage electrons transferred over the grain interface have sufficient energy to create minority carriers (holes). These holes act to dramatically decrease the grain boundary electrical barriers, leading to the observed rapid increase in current flow. Hole creation has recently been verified by optical means.

This talk will review our understanding of varistor microstructures, grain boundary properties, and electrical behavior. Varistors currently have widespread application in protecting power and single level electrical circuits against dangerous voltage surges, and a brief overview will be given of the applications of this material.

THE ROLE OF INTERFACES AND INTERPHASES IN DIELECTRIC CERAMICS

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The properties of ceramic materials are greatly influenced by the boundary conditions that exist within polycrystalline microstructures. This is especially so for dielectric ceramics, where variations in chemical composition and discontinuities in periodicity affect electric flux passage through the microstructure. Examples are given for the purposeful manipulation of electric flux passage by the control of resistivity and permittivity distributions at internal surfaces. Data are reported for the characterization of the boundary conditions by impedance analysis, microscale electrical measurements, STEM, SAES, SIMS, etc. The results are discussed in the context of the role of interfaces, and interphases, on the dielectric properties of polycrystalline ceramics. Examples are given for the microstructural engineering of unique properties, which are strictly a function of polycrystallinity and, therefore, interfacial characteristics, and which are not available in perfect single crystals. The examples include enhanced apparent dielectric constants for internal boundary layer capacitors, and electric-field splitting in high voltage capacitors.

MECHANICAL PROPERTIES: EFFECTS OF MICROSTRUCTURE

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The last decade has witnessed a dramatic enhancement in the strength and toughness properties of ceramics, as well as a correspondingly enlightened understanding. The developments during this period are chronicled, emphasizing the vital role of multidisciplinarity. Particular emphasis is placed upon the properties of fiber and whisker reinforced materials, transformation and microcrack toughening, and strengthening and the effect of ductile dispersions. Finally, some properties for the next decade are presented.

INFLUENCE OF MICROSTRUCTURE ON CREEP-RUPTURE

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Creep deformation and creep rupture processes in multiphase ceramics were investigated by studies on two microstructurally different vitreous-bonded aluminas, each containing appreciable but different volume fractions of intergranular binder material. Results for the two aluminas are described not only in terms of flexural creep data, but also in terms of microstructural characterization by analytical electron microscopy. Quite generally, creep behavior is found to strongly depend on the nature of the intergranular binder phase, which can be either entirely glassy or part crystalline and part glassy. In this regard, even partial devitrification of the binder phase, by pre-test annealing, leads to improved creep resistance, as indicated by a reduction in strain rate and increases in the total strain and time to failure. Because of this dependence, intergranular deformation processes leading to eventual cavitation and crack formation are discussed on the basis of the complex distribution of intergranular phases that develop within flexural test specimens during creep.

MECHANISMS OF DYNAMIC FAILURE

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The term "dynamic failure" is here taken to exclude simple strain-rate dependence of the failure process and is therefore limited to strain rates exceeding 10^3 s^{-1}, for which shock-wave propagation events dominate the material history. Three regions of material response can be defined. Above 10 kms^{-1} the kinetic energy may be sufficient to vaporize material at the point of impact. Between 1 and 10 kms^{-1} localized melting leads to a drastic loss of shear strength, but below 1 kms^{-1} localized melting cannot occur. It is in this lower velocity, high strain-rate regime that microstructural features can play a dominant role.

Current models of dynamic failure in this third regime fall into two groups. Those based on crack propagation from a critical defect represent extensions of linear elastic fracture mechanics into the dynamic regime which take into account interaction of the impinging shock waves with the release waves generated by a high velocity propagating crack. Theories of cumulative damage, on the other hand, assume that damage centers are generated by the impinging shock waves, which then modify the elastic response of the material and lead to eventual failure by damage agglomeration.

Ceramic specimens can be recovered from planar shock-wave experiments, in which the stress history is essentially one dimensional. Post-mortem examination of such specimens reveals a wealth of microstructural detail related to the mechanisms of dynamic failure, but since the stress pulse in a typical experiment is very short (~1 μs) it is difficult to guarantee that the subsequent loading history ("reverberation") introduces no further damage.

Each volume element of the specimen in a planar impact test suffers a unique loading cycle which may lead to both compressive damage and tensile ("spall") fracture. The compressive damage depends on the velocity and physical properties of the impactor, and the physical properties and microstructure of the target. The ballistic properties include the ballistic impedance, the Hugoniot elastic limit, the dynamic yield strength, and the tensile spall strength. The spall strength is observed to decrease with increasing compressive stress, even below the Hugoniot elastic limit, indicating that microstructural damage is introduced well below the point at which the material loses shear resistance. On the other hand, both the Hugoniot elastic limit and the residual spall strength are strong functions of composition and microstructure.

Preliminary examination of alumina specimens recovered from planar impact experiments strongly indicate that dynamic failure occurs by a process of microstructural degradation, particularly in regions of residual porosity. Subsequent spall fracture then seems to occur by the linking up of these regions, but is itself characterized by extensive breakup of the microstructure in the region of the spall plane. The intergranular glass appears to play an important role both in determining the ballistic properties and in controlling the path of failure. Localized melting of the glass is a possibility, and the impedance mismatch between the crystalline and glassy phases seems to be important.

EFFECT OF HIGH TEMPERATURE OXIDATION ON THE MICROSTRUCTURE AND MECHANICAL PROPERTIES OF WHISKER-REINFORCED CERAMICS

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Silicon carbide whisker reinforcement has been shown to significantly improve the mechanical properties of polycrystalline alumina (Al_2O_3) and mullite ($3Al_2O_3 \cdot 2SiO_2$). Increases of approximately 100% in toughness and 60% in strength can be achieved up to temperatures of 1000°C, by 20 vol% additions of SiC and judicial processing procedures. Crack deflection by the whiskers appears to be the major toughening mechanism.

Since such composite materials are currently under consideration for high temperature applications, samples were annealed for prolonged times (1000 hours) at temperatures of 1000–1400°C. The alumina and mullite composites were compared for weight gain, formation of a surface scale, and subsequent degradation of room temperature strength. Unlike mullite, alumina showed appreciable weight gain and surface strength losses.

The microstructure of the oxidized surface layer in both materials was examined closely by electron microscopy and microanalysis techniques (SEM, TEM, STEM, EDS). Significant changes, such as mullite or glass formation, were observed in whisker-matrix interfacial regions, due to the changes in phase equilibria at high temperatures resulting in incorporation of oxygen. Straining stage experiments were performed in a 1 MeV HVEM to study the effect of the modified interfacial region on the micromechanics of fracture.

INTERFACIAL DEPENDENT STRENGTH AND PROPERTIES OF TRANSFORMATION TOUGHENED CERAMICS

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Recent studies have shown that the strength of tough PSZ materials appears to be limited by the critical stress to initiate the t- to m-ZrO_2 transformation. Detailed observations suggest in the case of Mg-PSZ that microcracks initiate at grain boundaries which extend and eventually link up resulting in complete failure. The inability of the anisotropic transformation strains within favorably disposed grains to be accommodated by adjacent grains in the tensile field results in grain boundary failure. Compression testing and deformation about a Vickers hardness impression leads to more extensive t- to m-ZrO_2 transformation and some degree of transgranular continuity of the transformation.

Other areas where interfacial conditions modify the properties of PSZ ceramics include the addition of Al_2O_3 to Y-TZP, and SrO together with sub-eutectoid aging of Mg-PSZ materials. Alumina appears to modify the wettability of t-ZrO_2 by silica, leading to much enhanced strength and better electrical conductivity. The addition of small quantities of SrO eliminates undesirable grain boundary impurities such as silica and forsterite and imparts better resistance to decomposition above 1000°C. Sub-eutectoid heat treatment of Mg-PSZ results in the formation of a magnesia enriched δ phase that exists in a number of variants and causes severe localized strains to develop where two such variants impinge on the t-ZrO_2 precipitate interface. Such internal straining of the precipitates modifies the M_s temperature of the material and thereby the toughness. These aspects along with experimental evidence will be discussed.

PRECIPITATION IN A (Mg) PARTIALLY STABILIZED ZIRCONIA DURING AGING AT 1000°C

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The generally excellent strength and toughness properties of a partially stabilized zirconia (PSZ) product can be compromised if it is used at a service temperature at which its initial microstructure has not been fully equilibrated. In a recent study, transmission electron microscopy was used to relate an observed deterioration in both the rupture strength and fracture toughness of a (Mg) PSZ to subtle changes in the microstructure. The evidence suggested that the presence in the material of a noncubic "(O)" grain boundary silicate phase combined with the progressive precipitation of a glassy phase at interphase boundaries during aging at 1000°C was responsible for the property degradation. Because of the small lateral dimensions of the glassy film, a variety of experimental techniques are required to verify its presence. In the present contribution the (O) phase is characterized further by analytical electron microscopy and convergent beam diffraction; the results of a hot stage HVEM study will be given; and the results of studying the glassy phase by high resolution and electron beam—induced effects will be presented.

TEMPERATURE-DEPENDENT TOUGHENING IN WHISKER-REINFORCED CERAMICS

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The mechanical response of whisker-reinforced ceramics, which is dominated by interface chemistry and residual stresses, would be expected to vary substantially over the useful temperature range (room temperature to 1500°C). To examine the temperature dependence of toughening processes, three silicon carbide whisker-reinforced systems have been studied: alumina, mullite, and silicon nitride. The systems represent a broad range of thermal mismatch conditions and potential crack-whisker interactions including crack bridging, whisker pullout, and crack deflection.

For each system, both the fracture toughness and hardness are measured as a function of temperature. Post-mortem fractography was used for samples tested at elevated temperatures, where residual stresses were minimized and degradation of the whiskers and enhanced chemical reaction between whisker and matrix were possible. In addition, controlled crack growth at room temperature fracture has been optically monitored using a video system to provide insight into the toughening mechanism(s).

INTERFACIAL DELAMINATION TOUGHENING AND TOUGHNESS ANISOTROPY IN CERAMICS

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A special form (perhaps the ultimate form?) of process zone microcracking, that of interfacial delamination, occurs in several types of common ceramic material systems. Toughening by interfacial delamination processes can readily create order-of-magnitude toughness increases for crack propagation perpendicular to the planar interfaces. Accompanying that marked toughness increase is the presence of a pronounced toughness anisotropy. This paper addresses delamination toughening and toughness anisotropy, reporting measurements in several systems including pyrolytic carbon, laminated carbon felt/carbon matrix composites, SiC woven fabric/CVI-SiC matrix composites, and several textured ceramic systems including oriented hexaferrites and beta-aluminas. The case of pyrolytic carbon as a "pure" model system for comparison with laminated felt carbon/carbon composites is a particularly interesting contrast. The base matrix material toughness anisotropy is accented as it compares directly with the macrostructural scale-up of the carbon/carbon composite to engage additional microstructural toughening factors. Conclusions from this comparison are extended to the other ceramic systems of interest.

FINE MICROSTRUCTURE AND TOUGHNESS OF SiC

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Effects of grain boundaries and stacking faults on fracture toughness and strength have been investigated for highly pure and dense β-SiC ceramics. The plates (1 to 3 mm thick) of β-SiC were prepared by CVD from a mixture of C_3H_8 and H_2-carried $SiCl_4$. The density of stacking faults was controlled by changing CVD conditions such as total gas pressure and C_3H_8 flow rate. The grain boundary structure, crack tip/stacking fault interactions, and crack tip deformation were observed by high resolution electron microscopy.

TEM observations revealed that there exist no glassy layers or secondary phases at any grain boundaries. As expected from this fact, the crack deflection by the grain boundaries was not observed for almost all cases. However, the strong crack tip deflection and/or microcrack formation associated with stacking faults were revealed by TEM observations, which suggests the fracture toughness of SiC may be improved by incorporating the stacking fault into the grains. In fact, the toughness increased from 3.2 to 6.8 $MN/m^{3/2}$ with increases in the stacking fault density. Above ~1000°C, the nucleation of dislocations was identified at crack tips. Therefore, the observed increase in toughness and strength above ~1000°C is attributed to the stress relaxation by small plastic deformation at crack tips.

CERAMIC COMPOSITES

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The role of the fiber-matrix interface in determining the mechanical properties of ceramic composites will be discussed. Weak interfaces allow sliding between the matrix and fibers and can result in composites with very large strains to failure. Increasing the sliding resistance changes the failure mechanism to a more catastrophic mode. Explicit relations for strength, toughness, and the condition for failure transition in terms of interfacial properties and other microstructural properties have been obtained from fracture mechanics analysis. Several methods have been devised for measuring the mechanical properties of the interface. These measurements in glass and glass-ceramic matrix composites will be compared with the fracture mechanics analysis.

ON THE FRACTURE BEHAVIOR AND MICROSTRUCTURE OF METAL-TO-CERAMIC JOINTS

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Small sandwich-like four-point bend test specimens cut from solid-state bonded alumina-niobium joints and other oxide-metal joints are notched at one interface situated in the middle of the specimens. They are used to study the microstructure and the fracture of metal-ceramic transitions. The bond strength is characterized by the fracture energy G_C calculated from the measured fracture load and a correction function Y_G depending on the geometry of the specimen and the elastic constants of the bonded materials.

Solid-state bonding of polycrystalline and single crystalline materials is performed in the case of Nb-Al_2O_3 joints in a high vacuum at 1700°C under an applied load of 10 MPa. For joints between polycrystalline alumina and niobium the interface fracture energy depends on the surface geometry of the ceramic before welding. Experiments with joints between single crystalline ceramic and polycrystalline metal show that the interface fracture energy is influenced by the amount of metal grain growth during welding. The results are discussed with respect to the interface structure.

SOLID STATE BONDING OF ALUMINA AND STEEL BY HIPING

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and

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A study has been conducted to examine the effects of interlayers on the internal stress resulting from the thermal expansion mismatch, the bonding strength, and the resistance to thermal cycling for alumina/steel joints. Both niobium and niobium/molybdenum laminated layers less than 1.5 mm thick were used to control the thermal stress between alumina and steel, and the bonding was carried out by means of HIPing under the conditions of 100 MPa and 1000–1400°C for 30 minutes. It was found that the internal stress in the joint area significantly decreased by using the laminated layer. The room temperature bending strength of the joint with 0.5 mm niobium and 0.5 mm molybdenum laminated layers was 500 MPa. From the results of change in the bending strength by thermal cycling from room temperature to 500°C, the strength degradation of the joint with a 1 mm niobium layer due to the formation of cracks in alumina was found. On the other hand, no strength degradation was found after 100 cycles for joints with 0.5 mm niobium and 0.5 mm molybdenum laminated layers.

STRUCTURE AND CHEMISTRY OF INTERFACES IN SILICON CARBIDE-CONTAINING MATERIALS

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Transmission electron microscopy has been employed to investigate the structural character of high and low angle boundaries in both crept and uncrept reaction-bonded and sintered silicon carbides as well as the interfaces occurring in silicon carbide whisker-containing silicon nitride matrix composites and in ion implanted or laser annealed nickel coated silicon carbide. The reaction of Si vapor with excess carbon during the formation of reaction-bonded SiC results in epitaxial growth of additional SiC on the existing SiC matrix and subgrain boundary formation. Climb-controlled deformation above 1773 K causes additional and unique subboundary formation in this material. In sintered α-SiC containing B and C as densification aids, an amorphous grain boundary phase is occasionally reported; however such a phase was not discerned in the material studied in our program using a combination of high resolution TEM as well as SAM analyses. This controversy will be discussed in detail. In the Si_3N_4 composites an amorphous layer derived from the reaction of the oxide additives with the native SiO_2 results in the formation of an amorphous phase between the SiC whiskers and the Si_3N_4 matrix. In addition an MgO-containing silicate phase crystallized epitaxially on the SiC whisker during cooling. Finally ruby or excimer laser annealing of the Ni-coated SiC caused melting of the Ni and diffusion of SiC into this molten phase; whereas ion implantation of Si^+ at the dose and an energy of 10^{17} cm^{-2} and 140 keV, respectively, resulted in the sequential formation of numerous layers of varying chemistry. These include polycrystalline Ni, amorphous Ni_xSi_y, a mixture of amorphous Ni_xSi_y and crystalline Ni_3Si_2, and amorphous SiC. A detailed description of these several SiC-containing materials and their interfaces will be presented and supported by extensive pictorial results.

STRUCTURE OF SECOND PHASES IN SILICON NITRIDE GRAIN BOUNDARIES

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The structure of grain boundaries often determines the deformation mechanism in ceramics. In highly covalent materials (Si_3N_4, SiC, etc.), this structure is controlled by second phases which are necessary to densification processes. This investigation compares the grain boundary structure resulting from controlled crystallization of these second phases in silicon nitride. TEM is used to characterize the grain boundary structure which is related to glass structure, crystal growth anisotropy, and grain boundary stress state. Periodicity at the silicon nitride/silicate interface is considered. Property data can also be discussed in terms of grain boundary structure.

THE IMPACT OF COMPOSITIONAL VARIATIONS AND PROCESSING CONDITIONS ON SECONDARY PHASE CHARACTERISTICS IN SINTERED Si_3N_4 MATERIALS

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Further improvement of dense Si_3N_4 properties, especially of the high temperature strength, requires careful evaluation of several items such as

- the characteristics of the Si_3N_4 powders processed by different techniques,
- the nature and amount of additives, and
- the sintering and post–heat treatment conditions on the composition/viscosity relationship of the liquid phase during microstructural development.

These topics are discussed for Y_2O_3 + Al_2O_3-fluxed sintered Si_3N_4 in the light of systematic sintering experiments and TEM studies.

Besides residual porosity, room temperature strength is mainly a function of the β-Si_3N_4 grain morphology as revealed by quantitative stereological analysis. Idiomorphic β-grains with high aspect ratio are favored by a highly viscous liquid. Reduction of viscosity and/or prolonged soaking times change grain morphology from idiomorphic to globularized particles, which results in decreased strength and K_{IC} data. High temperature strength, however, depends on the constitution of the grain boundary phases, e.g., the interaction between the residual liquid and Y-Al bearing oxynitride phases. Improvement of high temperature properties is achieved by devitrification of the glassy phase due to a post-heat treatment by using dopants promoting crystallization. Different processed Si_3N_4 powders (Si-nitridation, CVD-processes, carbothermal reduction, diimide precipitation) exhibit a pronounced effect on high temperature properties, too, due to their typical impurity patterns.

FRACTAL MORPHOLOGY OF CERAMIC POLYCRYSTAL AND POWDER GRAIN BOUNDARIES AND INTERFACES: DIFFRACTAL UNIVERSAL DIELECTRIC, ELECTRICAL, AND NOISE FUNCTIONAL PROPERTIES' ANALYTIC DEPENDENCE UPON DIFFRACTION PATTERN VIA STATIC SYNERGETICS

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The critical importance of ceramic polycrystal and powder grain boundaries' and interfaces' fractal morphology in dominating ceramic dielectric, electrical, optical, and noise functional properties militates for a universal analytic real-time technique for computation as a consequence of fractality. Appreciation of Berry's "waves that have encountered fractals" diffractals, Johscher's universal dielectric and electrical properties, universal explanation in terms of universal infrared divergence of Ngai and Handel, explanation of infrared divergence in terms of Brillouin-like symmetry-breaking "disorder" modulation/filtering of collective-mode (phonon,...) dispersion relations by Siegel, and unification into the Static Synergetics universality principle by Siegel has put this goal into the reality of a new universal, analytic, flexible, versatile tool for use on any ceramic microstructure at any and all stages of its processing. Static Synergetics, the reexpression of the inescapable very basic three laws of thermodynamics in the $\underline{r}$-, $\underline{k}$-, and w-domains, the equivalence of w-domain signal-processing to $\underline{r}$-domain microstructure pattern recognition (SEM, TEM, photomicrography), or to Fourier transform $\underline{k}$-domain small-angle-scattering (SAS) diffraction-pattern/static structure factor $S_{SAS}(\underline{k})$ in analytic 1:1 mapping, is expressed as a mathematical algorithm "software," with $S_{SAS}(\underline{k})$ "hardware" measurement input. Outputs are w-domain universal function properties:frequency-dependent FM (implicitly processing-parameter set dependent):dielectric:constant/function, dispersion, dissipation/loss, loss tangent, capacitance, admittance, impedance, conductance, AC and DC electrical conductivities, 1/f flicker noise power spectrum (voltage and/or current), signal-to-noise ratio, optical:refractive index, reflectivity, and extinction coefficient. Application and implementation provide the first opportunity, heretofore unknown, for during-processing real-time Q.A. and, in parallel with a specific process-model, interactive real-time Q.C. and quality and quantity yield optimization for any and all ceramics.

DIFFRACTION FROM A NATURAL GRAIN BOUNDARY IN A MAGNETITE BICRYSTAL

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The structure of a natural small angle boundary in a magnetite bicrystal was investigated for the first time by x-ray diffraction. This boundary was a "general" one with a mixed twist and tilt character. The grain boundary reflections observed around an 040 matrix reflection were in good agreement with those predicted by Bollmann's O-lattice theory. These extra reflections appear to arise from a predominantly planar dislocation network. The structural width of the boundary, determined from the length of the relrods of the extra reflections, was of the order of four unit cells, close to the spacing of the predicted dislocation network. Sample preparation, x-ray techniques, and the methods for calculating the expected dislocation network will be briefly reviewed, as well as the results.

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THE STRUCTURE OF TILT GRAIN BOUNDARIES IN NiO

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The structure of tilt grain boundaries in NiO was studied with an electron microscopy technique that is sensitive to the change in mean inner potential at the cores of dislocations, and an electron diffraction technique that provides information on fine scale faceting. Boundaries possessing a wide variety of rotation axes were examined, and it was shown that in all cases the boundaries are faceted. It is suggested based on these observations that in NiO a tilt boundary with an arbitrary rotation axis will be faceted. Bollmann's O-lattice theory was applied to determine the geometry and dislocation content of the faceted boundaries. For certain of the boundaries, the predictions of the theoretical analysis agreed with all details of the observed structure, while for other boundaries, disagreements were noted. The origin of the disagreements is not understood at present. The value of electron diffraction techniques for the study of faceting will be discussed.

GREEN FUNCTION METHOD FOR CALCULATION OF ATOMISTIC STRUCTURE OF GRAIN BOUNDARY INTERFACES IN IONIC CRYSTALS

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A lattice statics Green function method is described for calculating the atomistic structure of grain boundary interfaces in ionic crystals. The method fully accounts for the discrete structure of the lattice and uses the zero frequency limit of the phonon Green function.

The grain boundary is taken along coincidence lattice sites which are obtained by rotating two imaginary halves of a crystal relative to each other. Perfect translation symmetry is assumed in directions parallel to the axis of rotation and the grain boundary line. The periodicity of the coincidence lattice is exploited by taking a partial Fourier transform of the Green function.

The method is applied to a tilt boundary in an ionic crystal of rock salt structure. A shell model based potential is used which accounts for the polarizability of the ions. It is shown that Coulomb interactions between ions across the grain boundary line can be represented in terms of effective dipolar and higher order polar interactions, which makes them relatively short range.

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*On attachment from Ohio State University; on leave from Birla Institute of Technology and Science, Pilani, India.

ON THE ROLE OF THE INTERFACE PLANE IN THE SELECTION OF "SPECIAL" GRAIN BOUNDARIES IN CERAMIC OXIDES

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Within the framework of Bollmann's coincident-site lattice (CSL) model, grain boundaries with the lowest values of Σ, the inverse density of CSL sites, are usually assumed to have lower energies than the more general high-Σ boundaries. However, it has been known for some time that whereas certain low-Σ boundaries show, indeed, especially low energies, other low-Σ interfaces do not. In order to elucidate the selection criteria for the identification of "special" boundaries, the calculated energies of twist grain boundaries on the (100), (110), and (111) planes in metal oxides with NaCl structure have been computed by means of lattice-statics techniques. A detailed comparison with similar calculations for fcc metals shows the role in the selection of low-energy boundaries of the spacing between lattice planes parallel to the grain-boundary plane. However, in addition to metals, the planar charge on the interface plane in ionic materials is also found to have a strong influence on the energy and stability of ceramic grain boundaries. In particular, it is found that boundaries on the charged (111) planes in the NaCl structure are considerably more stable than the boundaries on the neutral (100) and (110) planes. The theoretical analysis of these results leads to the formulation of rather simple selection criteria for the identification of special interfaces in ceramics, based on Pauli's principle and on the planar charge of the interfacial plane.

HIGH ANGLE GRAIN BOUNDARIES IN SHEET SILICATES (BIOTITE/CHLORITE): A TEM STUDY

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The morphology of high angle grain boundaries in two different sheet silicates (mica, chlorite) has been studied using a lattice-fringe imaging technique. Mica and chlorite are very common and important rock-forming minerals. The lattice-fringe images of biotite (symmetrical 21° tilt boundary, asymmetrical 37° tilt boundary) and chlorite (asymmetrical 10° tilt boundary) show that the fringes come into contact at the grain boundary, without forming a narrow, contrast-free zone. A glass-like or a liquid-like structure of the grain boundary with a grain boundary width up to 100 nm (quartz[1]) is in contradiction to the observations reported here. A glass- or liquid-like structure of a grain boundary with a width of the boundary in the range of 100 nm would result in a total loss of the Bragg diffraction and, thus, should generate no lattice fringes in an area the width of which could be comparable to the boundary thickness.

The observed behavior of the lattice fringes may be interpreted in terms of a narrow distorted zone of mismatch (width about 1 nm or less) in the vicinity of sheet silicate grain boundaries.

Reference:

1. R. Joesten, Amer. J. Sci. 283-A, 233 (1983).

DIFFUSION-INDUCED INTERFACE MIGRATION IN CERAMICS

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Diffusion-induced interface migration is an interesting and potentially useful mechanism for controlling the microstructure of polycrystalline ceramics. In this process, interfaces--grain boundaries and thin liquid films separating grains--are induced to migrate as a result of the diffusion of a solute into the sample. The strain in the alloyed region due to the change in the lattice parameter with composition has been identified as a driving force for the boundary migration. A critical test of this model is the absence of boundary migration when there is no change in the lattice parameter upon alloying, but with the free energy of mixing finite. In this case, even though there is a lowering of the free energy of the system by mixing, there is no coupling of the energy to the boundary. This absence of migration under these conditions has been observed previously by Yoon and coworkers for liquid film migration in several ternary metallic systems.

We have studied diffusion-induced interface migration over a range of compositions in the MgO system. Experiments have been done for both Diffusion-Induced Grain-boundary Migration (DIGM) and Liquid Film Migration (LFM). NiO, CoO, SrO, Cr_2O_3, or Y_2O_3 and mixtures of these compounds have been used as alloying elements to achieve changes in the lattice parameter difference between MgO and the alloy, and V_2O_5 has been used as the liquid phase. The composition profiles in the alloyed regions have been measured using quantitative SEM x-ray microanalysis and electron microprobe analysis, and the rate of boundary migration has been determined as a function of the composition of the alloy.

The results are in agreement with a coherency stress model as the driving force for boundary migration. The model is being extended to predict the microstructures that develop under a range of experimental conditions.

GRAIN-BOUNDARY SELF DIFFUSION IN POLYCRYSTALLINE NiO: IS THERE SOME POSSIBLE ARTIFACT?

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Grain-boundary diffusion in NiO is presumably enhanced in relation to lattice diffusion. However contradictory results have been observed by several authors. In a previous paper it has been shown qualitatively that diffusion in the vicinity of grain boundaries is very sensitive to surface preparation processes. New experiments and quantitative exploitation of our results show that results which were considered as typical of grain-boundary diffusion could, at least partially, result from the initial surface condition.

GRAIN BOUNDARY MIGRATION AND GRAIN BOUNDARY NONSTOICHIOMETRY IN TERNARY OXIDES

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In spinels and in perovskite-structure titanates, large concentrations of lattice defects are generated by either aliovalent doping or deviations in lattice stoichiometry. Marked changes in the grain growth rates of polycrystalline materials often parallel these changes in the lattice defect structure. Examples include: 1) the variation of boundary mobility with cation stoichiometry in magnesium aluminate spinel; 2) the effects of electronic vs. ionic donor compensation on grain growth in barium titanate and strontium titanate; and 3) the influence of lanthanum additions on grain growth rates in PLZT. In these systems, STEM analyses of grain boundary impurity segregation, cation stoichiometry, and oxygen/cation stoichiometry suggest solute-drag controlled grain boundary migration rates which vary as intrinsic lattice defects segregate to or deplete from the grain boundary region. The influence of aliovalent dopants appears to be one of inducing changes in near-boundary defect distributions through the lattice defect structure, rather than directly reducing mobilities through solute segregation. Background impurities seem unimportant, unlike the case in highly stoichiometric oxides and halides.

UNIT CELL DISTORTION OF $Pb(Zr,Ti)O_3$ BY $Pb(Co,Nb)O_3$

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Crystallographic aspects of the $Pb(Zr,Ti)O_3$-$Pb(Co,Nb)O_3$ system were investigated by x-ray diffraction methods. The system contains rhombohedral, tetragonal, and pseudocubic phases at room temperature.

Crystal symmetry was changed from 4-fold to 3-fold symmetry by adding $Pb(Co_{1/3}Nb_{2/3})O_3$ to $Pb(Zr_{0.52}Ti_{0.48})O_3$. When the sintering temperature was higher, a smaller amount of $Pb(Co_{1/3}Nb_{2/3})O_3$ changed symmetry. When the symmetric forms changed, the lattice parameters varied; that is, an increase in the a-axis direction and a decrease in the c-axis direction occurred simultaneously. And tetragonal distortion, c/a, varied by sintering temperature. The higher the sintering temperature, the higher was the rate of increase of the lattice parameter in the a-axis direction resulting from adding $Pb(Co_{1/3}Nb_{2/3})O_3$.

GAS TRANSPORT AS A TOOL FOR STRUCTURAL CHARACTERIZATION OF INTERFACIAL PHASES

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At the previous conference in this series, the principles of using gas transport as a structural characterization tool for glasses were outlined.[1] In the subsequent decade, substantial effort has been devoted to refining the experimental and analytical bases of this technique. The central point of these studies is that information about the interstitial structure of materials can be obtained by careful analysis of the solution and diffusion of unreactive gas atoms and molecules small enough to percolate through that structure. In recent years, the utility of this method for characterizing the structure of interfacial phases has been demonstrated. In this paper, two such areas will be discussed: (i) grain-boundary structure and (ii) the surface oxide layer on semiconductor silicon.

The grain boundary phase in crystalline metals and ceramics can be modeled in a way comparable to that used for noncrystalline solids of the same composition. Gas transport can be a sensitive probe of this interfacial structure, as the interstitial structure in the grain boundary region is generally more open than in the bulk crystalline region.

The growth of a vitreous silica surface layer on semiconductor silicon is generally limited by the diffusion of molecular oxygen. This important component of MOS device technology can be more clearly understood by correlation of the thin film growth kinetics with results on gas transport in bulk vitreous silica.

Reference:

1. J.F. Shackelford and J.S. Masaryk, "The Gas Atom as a Microstructural Probe for Amorphous Solids," in Ceramic Microstructure 76, R.M. Fulrath and J.A. Pask, Eds., West View Press, Boulder, CO, 1977, pp. 149–159.

INTERFACE MORPHOLOGY IN CERAMICS

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In ternary and higher order systems initially planar interphase boundaries can become morphologically unstable during isothermal interdiffussion processes, although no metastable phases are present.

Diffusion experiments are carried out for the Fe-Mn-Cr-oxide system in air at 1400°C. In this model system only two phases, spinel and sesquioxide, exist, which are separated by a miscibility gap. After annealing of spinel-sesquioxide couples with an initially planar interface, various interface morphologies were observed, ranging from planar, wavy, and dendritic to globulitic structures. Experiments show that the morphology is independent of cooling rate, grain size, and pretreatment of the crystals, but dependent on the starting compositions of the diffusion couple and, of course, on the thermodynamic and kinetic properties of the system.

To explain these observations, linear transport theory has been applied to the diffusion processes in ternary two-phase systems with a nonplanar interface. For small deviations from the planar interface coordinate, the time evolution of the interface coordinate is calculated: a critical parameter was found to determine the time evolution of small pertubations. If it is smaller than zero, every perturbation will decrease and the planar interface is stable. If it is larger than zero, perturbations can grow and yield a nonplanar interface. In agreement with the experimental results the critical parameter depends on the starting compositions of the diffusion couple, the thermodynamic properties, and the transport data of the system.

ELECTRON MICROSCOPY STUDIES OF $BaTiO_3$-$NaNbO_3$ CERAMICS

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Dielectric mixtures in the system $BaTiO_3$-$NaNbO_3$ were prepared by both (i) solid state and (ii) liquid-phase sintering. Data are reported for the dielectric compositions and the evolution of ceramic microstructures. Particular attention is paid to the role of chemical heterogeneities on dielectric properties. Results are given for TEM and STEM studies on the ceramic microstructures. For fast-fired (unequilibrated) liquid-phase sintered mixtures, a very thin intergranular phase was detected by Fresnel imaging. In addition, EDX analysis identified a chemically modified Nb diffusion layer extending into the grain interior, the width of which was dependent on composition and thermal processing conditions. The grain interior remained unmodified $BaTiO_3$. For comparison purposes, microstructural analysis of equilibrated (Ba,Na) (Ti,Nb)O_3 ceramics determined Nb to be homogeneously distributed throughout the grain and boundary regions. The results are discussed in the context of the role of chemical heterogeneities on microstructure development and dielectric properties, for materials of constant composition which have been prepared by different thermal processing conditions.

ANALYTICAL MICROSCOPY OF THE GLASSY PHASE IN MULLITE/ZIRCONIA COMPOSITES

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Mullite/zirconia composites have been produced by the reaction sintering of alumina and zircon with 0.25 and 1 mol% titania added as a sintering aid. The addition of titania enhances sintering rates by the formation of an intermediary liquid. The glassy phase present primarily at mullite/zirconia interfaces is the unreacted liquid phase retained at room temperatures. The compositional variation of the glassy phase has been studied as a function of annealing time and its role in the evolution of the microstructure and mechanical properties discussed.

MICROSTRUCTURE CHARACTERIZATION OF BASALT GLASS-CERAMICS

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Glasses and basalt glass-ceramics were obtained from spanish basalt rocks from the Canary Islands. TTT devitrification curves of original glasses were determined and scanning electron microscopy with energy dispersive x-ray microanalysis was performed in order to characterize the microstructure. Crystalline volume fraction (mainly diopside) and other microstructural parameters were determined by image automatic analysis. Potential applications of these basalt glass-ceramics are as good abrasion resistant materials and as a candidate matrix for immobilization of nuclear wastes.

EFFECTS OF INTERFACIAL DIFFUSION BARRIERS ON THERMAL STABILITY OF CERAMIC FIBERS

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Ceramic fibers used as reinforcement for high-performance composites require good retention of mechanical properties after extreme thermal exposures. Strength retention of the fibers depends on growth of their critical flaws which, in turn, can depend on the extent of decomposition reactions. These reactions require gas transport through the outer fiber surface and are subject to control by effective diffusion barriers at this interface. Examples are given of barrier coatings applied to high-strength Si-C-O-N fibers pyrolyzed from polymer precursors. Barrier coatings of SiO_2 can be produced by passive oxidation in controlled atmospheres. The effectiveness of these barriers is reported in terms of strength retention and, in some cases, flaw growth and extent of chemical decomposition. This is related to the permeability, porosity, thickness, and continuity of the barriers. New techniques are reported to study the growth of critical flaws.

INTERFACIAL REACTION BETWEEN BIOACTIVE GLASS AND SYNTHETIC PHYSIOLOGICAL SOLUTION

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It has been found that direct biochemical bonding can occur between the glass implant and the surrounding bone tissue when the glass of the system Na_2O-RO-P_2O_5-SiO_2 is used as artifical bone material. A hydroxyapatite (HAP) layer was found to form on the glass surface with a silica-rich layer existing between the formed HAP layer and the bulk glass in either synthetic or natural physiological solutions. These layers are considered to play an important role in the bonding of bioglass to bone tissue of a living body.

Therefore, a kinetic study was carried out on the formation of HAP on the surface of bioglass of the system Na_2O-RO-P_2O_5-SiO_2 in a synthetic physiological solution, a buffer solution with pH = 7.4, consisting of trihydroxymethyl aminomethane, $(CH_2OH)_3CNH_2$, and hydrochloric acid, HCl.

The data concerning the weight loss of the glass samples showed that the reaction could be divided into three stages. In the first stage the weight loss was found to be proportional to the time of the reaction. In the second stage the weight loss was found to slow down gradually. During the third stage weight loss was found to reach maximum and did not change with the time of the reaction.

It was verified by the experiments with IRRS, SEM-EDAX, and x-ray diffraction that the beginning of the silica-rich layer occurred during the first stage. During the beginning of the second stage, the HAP crystal phase appeared on the silica-rich layer, and simultaneously, calcium decreased from the silica-rich layer. During the entire second stage the concentrations of Na, Ca, and Si in the reacted solution increased gradually according to determination by AAS, and the concentration of P also increased according to determination by ICPE. The system reached equilibrium during the third stage, since the weight of the bioglass samples did not continue to change. All the samples followed the same rule regardless of chemical composition. The critical time t_c of the reaction relating to the turning point from the first to the second stage depended on the properties of the materials. The t_c decreased with the increase of CaO in the bioglass of the same components and increased with MgO and BaO substituting for CaO as CaO < BaO < MgO. There was no obvious change in t_c when a small amount of CaF_2 was added.

Under the same experimental conditions for different samples, the shorter the critical time, the longer the saturation time when compared with each other, which meant biologically more active but chemically less durable. These phenomena were satisfactorily explained with the theoretical model of the double electrolytic layer forming between bioglass and synthetic physiological solution.

COLLOIDAL CHEMISTRY OF GROWING SILICA SPHERES

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Recipes are available for the preparation of monodisperse oxide powders, and these materials are seeing increased use in the preparation of low flaw density green bodies and in the reduction of sintering temperatures. Despite growing demand for these single sized powders, little is known about the physicochemical processes which determine particulate morphology. Due to the precipitation techniques employed, interfacial chemistry of the growing powders becomes an important concern in understanding particulate size distributions.

Here we report studies aimed at elucidating the mechanisms which control particle size and monodispersity. As a model system we choose silica spheres prepared through the hydrolysis of silica alkoxides in basic alcoholic solutions. The diameters of these particles can be varied in a reproducible fashion from 10–1,000 nm with standard deviations of 3–8%. In this work we question the origins of the precipitate monodispersity and show that the interaction between growing precipitate particles is of fundamental importance to the resulting particle morphology. Classical nucleation and growth theory suggests that monodispersity is controlled by limiting the period of nucleation to a short time. The resulting particles then grow at the same rate, maintaining a monodisperse size distribution throughout the course of the reaction. In experimental tests of this mechanism, we find that nucleation proceeds over a substantial period of the reaction and that as the reaction proceeds, the particle size distribution sharpens. Extensive electron microscope studies reveal that the particles have an internal structure which suggests that an aggregative growth mechanism is operating whereby colloidally unstable primary particles (nuclei) aggregate to form large stable particles. Under these conditions, monodispersity is determined by the surface properties of the growing particles, not by the time period of the nucleation stage.

The importance of this observation lies in its application to methods employed to control precipitate morphology. Rather than attempting to limit the time period of nucleation to achieve monodisperse particles, one looks, instead, to control particle interaction potentials. The aggregative growth mechanism predicts an increase in particle size as the interaction potential becomes less repulsive. If the particles experience no repulsion, however, than a heterodisperse precipitate will be observed. These interaction potentials are determined by the state of the particulate's interfacial region. Consequently, the solid/solution interface is important not only in rates of nucleation and growth by monomeric addition, but also in determining the colloidal stability of the precipitate.

EFFECT OF DEVIATIONS FROM STOICHIOMETRY ON SINTERING AND MAGNETIC PROPERTIES

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Toroidal samples of nonstoichiometric NiZn ferrites were obtained by sintering of the reagent-grade corresponding oxides, according to the formula:

$$(0.36\ NiO_{0.64}ZnO) + xFe_2O_3\ ,$$

with $0.90 \leq x \leq 1.2$. The density and grain growth of sintered samples showed a clear dependence on deviation from stoichiometry; the highest density and grain growth values were obtained for $x \cong 0.96$, that is, a small excess of divalent oxides. This behavior can be explained on the basis of a cation-vacancy-controlled diffusion mechanism.

Magnetic properties, in particular initial magnetic permeability, ferromagnetic hysteresis, and Curie point, were also measured and exhibited a dependence with composition; the highest permeability value was obtained for the stoichiometric sample, as well as the lowest coercive field and Curie temperature. These results are explained on the basis of a dissolution of Fe_2O_3 excess through a reduction mechanism:

$$3Fe_2O_3 \rightarrow 2Fe^{2+}Fe_2^{3+}O_4 + \frac{1}{2}O_2$$

for $x > 1.0$. For $x < 1.0$, it is necessary to postulate a different dissolution mechanism, involving the oxidation of Ni^{2+} to Ni^{3+}, which could explain the observed magnetic properties.

SINTERING OF ACICULAR NiZn-FERRITE POWDER

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An acicular NiZn-ferrite powder was prepared by the reaction of acicular Fe_2O_3 with ZnO and NiO in the presence of molten KCl. The sintering behavior of the acicular powder was compared with that of an ordinary equiaxed powder. Green compacts were made by uniaxial pressing or extrusion and sintered between 800° and 1300°C for different time periods. The sintered density was calculated from dimensions and weight. The pore size distribution was measured by Hg porosimetry. The acicular powder densified faster than the equiaxed powder, and the maximum densities obtained were 99% and 95% of theoretical for the acicular and equiaxed powders, respectively. The acicular powder changed to an equiaxed shape at an early stage of sintering. The high sinterability of the acicular powder is explained by pore shape in the green compact. The green compact of the equiaxed powder had a larger hysteresis in Hg porosimetry than that of the acicular powder, indicating a complex pore shape in the former compact. During sintering, closed pores were formed at a low density for the equiaxed powder. It is concluded that the densification rate depends on pore size and shape, which is determined by the particle shape and forming method.

SINTERING OF MULLITE WITH CVD PROCESSED POWDER

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Colloidal dispersion characteristics of submicrometer CVD processed mullite powder were studied in electrostatic and sterically stabilized suspensions. The isoelectric point of mullite suspensions was pH ≈ 7.7, which is closer to that of Al_2O_3 than that of SiO_2. Electrostatic stabilization in an acid medium of pH < 4.0 was effective in the dispersion of sintered particle clusters formed during powder processing. The large clusters could be broken to submicron size range (average size ≈ 0.1 μm) at pH ≈ 4.

Sintering behavior and microstructural evolution of colloidally consolidated mullite compacts formed with CVD-processed powders were investigated at temperatures up to 1600°C. We show that the pore size distribution of the compacts plays the most crucial role on the densification behavior during sintering. Factors that affect the pore size distribution were identified as: (i) the degree of dispersion in the colloidal suspension stage, (ii) the structure of the particle clusters that form during casting as affected by the type of dispersant and the forming technique used, and (iii) the physical characteristics of the powder. When the pore size distribution approached a monosize state, compacts could be densified to relative densities above 97% by sintering at 1500–1600°C for 2 hours. Pore size distribution in the green compact was correlated to the densification behavior. Average grain size of mullite sintered at 1600°C ranged from 0.36 to 0.72 μm.

THE MICROSTRUCTURAL EVOLUTION AND VARIATION OF INTERGRANULAR POROSITY IN SWELLING UO_2

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A major problem in the structural evolution of porous ceramics during sintering, hot-pressing, and swelling or cavitation is the variability in the microstructure, including pore size and spacing variations, and pore distributions on grain boundaries and within grains. The evolution of grain boundary pores, cavities, and bubbles is especially important in controlling swelling and gas release from the pores as well as in stress rupture, sintering, and hot-pressing. Although simple models do not usually consider such variations, they can strongly affect the evolution of the microstructure.

To study this problem, UO_2 compacts were first sintered under high ambient pressure to entrap gas, then hot-pressed at 1410°C. The 96% dense specimens were then allowed to swell under the entrapped gas pressure for various times, and cooled rapidly. To obtain intergranular fracture surfaces, the specimens were thermally quenched from relatively low temperatures. The fracture surfaces were finally studied and quantified from scanning electron micrographs using new analytical procedures.

The results indicate that the intergranular pore size and spacing distributions during swelling are roughly log normal. During hot-pressing, and especially during swelling, nonequilibrium-shaped or interconnected pores were commonly observed. Finally, the partitioning and size of pores on grain faces, edges, and corners and in the bulk are dependent on grain growth.

OXIDATION AND MICROSTRUCTURE OF SINTERED SILICON NITRIDE

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For various sintered silicon nitride (SSN) samples, the microstructural changes resulting from oxidation were investigated. After oxidation, the formation of an oxide layer containing elements of sintering aids and the depletion of the grain boundary near the surface were observed in SSN samples with grain boundaries in the glassy phase. For SSN samples with grain boundaries crystallized to Mg-sialon, both the decomposition of Mg-sialon and the formation of a glass phase at the grain boundary near the surface were observed. For SSN samples with grain boundaries crystallized to nitrogen-diopside, almost no changes in microstructure were observed. The oxidation mechanism in the SSN was discussed in terms of thermodynamic stability of the grain boundary phase and the diffusion rate of grain boundary constituents.

CONTINUOUS SiC FIBER/GLASS COMPOSITES

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A method of producing continuous SiC fiber/glass matrix composite materials will be described. The method involves continuous pulling of pretreated SiC fibers through molten glass. Large pieces of excess of 1 m and with a variety of cross sections can be made in this way. Pieces can be consolidated to form larger, more complex shapes. The volume fraction of fibers can be varied over a wide range. The effects of pulling rate and residence time at temperature on the fiber/matrix interface have been investigated. Important factors affecting the integrity of the composite are the thermal expansion mismatch between the matrix and the fiber, the reactivity of the glass and the fiber, and the volume fraction of fibers. SiC fibers produced by different manufacturers and having different diameters, compositions, and surface properties have been investigated.

COMPOSITION EFFECTS AT THE CARBON FIBER/GLASS MATRIX INTERFACE

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The effect of glass composition upon the physical and chemical characteristics of carbon fiber/glass matrix interfaces is being studied A simple sodium-borosilicate glass (4% Na_2O, 14% B_2O_3, 82% SiO_2) forms the basis of this investigation, and the incorporation of reactive oxides including TiO_2, MoO_3, Nb_2O_5, Cr_2O_3, V_2O_5, and WO_3 is then evaluated. Some of these oxides have been shown to be surface active in silicate glasses, and so even small additions (1%) to the bulk glass can lead to high interfacial concentrations and large decreases in surface tension.

A computer algorithm called SOLGASMIX has been used to define the thermochemical equilibria at the carbon fiber/glass interface. The calculations show that substantial interfacial activities of carbides and oxycarbides are expected due to these additions in the temperature ranges where glass matrix composites are typically processed. The interfaces are experimentally investigated using a sandwich of glass plates between which isolated carbon fibers have been encapsulated. The encapsulation is effected at a low temperature using a hot press, and then these specimens are annealed at higher temperatures to evaluate the time and temperature dependent formation of interfacial reaction zones. The interfaces are characterized with electron microscopy and surface analysis techniques. These tailored glass matrix compositions are also being used to fabricate fiber reinforced composites for mechanical property testing.

MICROSTRUCTURAL DEVELOPMENT IN HOT PRESSED CaO: DENSITY DECREASE AND PORE GROWTH DURING POST SINTERING

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Calcium oxide derived from calcination of calcium acetate was vacuum hot pressed at 1543–1618 K under 17–34 MPa in a graphite die. Grain growth and pore growth studies were performed on low density (85%) and high density (99.8%) specimens.

The grain growth of CaO followed the square law with time, and in both cases the grain growth rate increased with increasing temperature. This was attributed to an increase in both surface energy and diffusion coefficient. Microstructural studies demonstrated that grain growth at intermediate temperatures was accomplished by a swift grain boundary movement and that pores lay mainly on the grain boundaries.

During post sintering of hot pressed samples, a decrease in bulk density was accompanied by an increase in pore size and a decrease in the number of pores. It was concluded that transfer of gas occurs from high pressure to low pressure, which causes expansion of the specimen with an increase in pore size, resulting in the decrease of density.

INTERFACES IN HETEROGENEOUS DISSOLUTION OF OXIDES IN MOLTEN Ca-Al-SILICATES

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The dissolution of Al_2O_3, $MgAl_2O_4$, $Y_3Al_5O_{12}$, MgO, and other refractory oxides in molten Ca-Al-silicates is heterogeneous over significant temperature and silicate composition ranges with the formation of at least one solid reaction product at the oxide-silicate interface. Mass transport through the interfacial solid reaction phase by diffusion determines the dissolution rates. The composition of the reaction product is dependent on the composition of the silicate, the test temperature, and the oxide. For Al_2O_3, $MgAl_2O_4$, and $Y_3Al_5O_{12}$ in 20% Al_2O_3–80% $CaSiO_3$, the reaction product is $2CaO{\bullet}Al_2O_3{\bullet}SiO_2$, and at higher SiO_2 contents, the product is $CaO{\bullet}Al_2O_3{\bullet}2SiO_2$. At high temperatures, $CaO{\bullet}6Al_2O_3$ is also formed at the Al_2O_3-$2CaO{\bullet}Al_2O_3{\bullet}SiO_2$ interface. The heterogeneous dissolution of MgO is more complex, forming $MgAl_2O_4$, $2CaO{\bullet}Al_2O_3{\bullet}SiO_2$, and complex silicates.

The phase compositions and elemental distribution at the reaction interfaces were determined using high-resolution (1μm) quantitative SEM-EDAX. The results are related to the phase equilibria and the dissolution kinetic data.

The dissolution kinetics of single crystal and sintered Al_2O_3 and $MgAl_2O_4$ were determined in 20% Al_2O_3–80% $CaSiO_3$ between 1607 and 1782 K with and without natural convection from both geometric changes and the changes in interface reaction product thickness. The dissolution rates for Al_2O_3 and $MgAl_2O_4$ are the same, a mechanism change near 1700 K with high- and low-temperature activation energies near 111 and 48 Kcal/mole, respectively.

INTERFACES AND INTERFACE REGIONS IN MONOCRYSTALLINE β-SiC SEMICONDUCTOR THIN FILMS CREATED BY GROWTH, OXIDATION, OR ION IMPLANTATION PROCESSES

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Monocrystalline thin films of β-SiC have been grown on Si substrates by chemical vapor deposition for semiconductor applications. A chemical conversion of the Si surface via reaction with C_2H_4 is employed to partially negate the large (≅20%) differences in lattice parameters and coefficients of thermal expansion between SiC and Si. High resolution XTEM has shown that the converted layer is ≅40 Å thick and is highly faulted. Furthermore, there is a thin amorphous region between the Si substrate and the SiC film. Microtwins which originate at the interface were found to be the primary defect in the SiC films. The interfaces between SiC and thermally grown SiO_2 have also been investigated. Oxidation experiments were conducted under both wet and dry conditions. It was determined by TEM that wet oxidation preferentially attacks defects extending to the surface, whereas dry oxidation does not. The nature of the interfaces resulting from both ion implantation and implantation and annealing have been also investigated. Extensive experimental evidence of these interfaces will be presented.

THE STUDY OF MICROSTRUCTURES FOR Pt-SILICIDE INTERFACES AFTER Nd:YAG LASER IRRADIATION BY XRD, SEM, XPS, AND RBS

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The samples consisted of p-type (111) oriented silicon wafers, which were covered with sputtering deposition Pt of 540–1000 Å thickness. The substrate crystals were deoxidized by immersing in 10:1 H_2O:HF just prior to Pt deposition, which was accomplished at 10^{-5} Torr in an oil free vacuum system. The Nd:YAG laser provides a scanning localized hot spot. Scanning line overlapping was 25–30 μm. The scanning rate was, respectively, 9.3, 11.5, 14.3, 16.9, or 21.9 mm•sec^{-1}. After the laser annealing, the samples were analyzed by x-ray diffraction (XRD), scanning electron microscopy (SEM), x-ray photoelectron spectroscopy (XPS), and Rutherford backscattering spectrometry (RBS). XRD analysis generally showed the coexistence of nonuniform multiphase Pt silicides, such as Pt_3Si, $Pt_{12}Si_5$, and Pt_2Si. SEM results pointed out that there were cellular segregations by molten supercooling. XPS suggested that the chemical shifts for Pt 4f electrons were 1.0–1.3 eV. RBS also showed the formation of Pt silicides. But the component of Pt ranged from 0.19 to 1.05 among them.

HREM OF SILICON NITRIDE/METAL BONDED INTERFACES

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Bonded interfaces of β-Si_3N_4 and metals such as Cu-Ag and stainless steel containing titanium were examined by high resolution electron microscopy. A bonded interface was sliced perpendicularly, polished mechanically down to a thin specimen of ~10–15 μm in thickness, thinned by Ar^+ ion at 5 KeV, and examined in a JEM 200CX electron microscope equipped with a high resolution pole piece ($C_c = 0.7$ mm and $C_s = 1.2$ mm).

A strong segregation of titanium was noted in the bonded interface of β-Si_3N_4/Cu-Ag. The high resolution observation of the bonded interface layer showed that the titanium segregation is due to very fine crystals several nm in diameter at the ceramic/metal interface of either TiN or titanium silicide. Epitaxial orientation relationships between the basal plane of β-Si_3N_4 and a densely packed plane of the precipitate was predominant, indicating the epitaxial nucleation at the interface and the role of segregating titanium during the process.

THE INFLUENCE OF SURFACE ROUGHNESS ON INTERFACE FORMATION IN METAL/CERAMIC DIFFUSION BONDS

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The rate determining step in the diffusion bonding of nonreacting metals is believed to be determined by the time taken to achieve an intimate mechanical contact across the joint. This occurs by diffusional mass transfer along the interface and plastic deformation of the contacting surfaces in the bond region. Models of these processes, derived from prior work on sintering, indicates a strong dependence of bonding rate upon the precise geometry of the joint as determined by the roughness of the faying surfaces. The roughness amplitude effectively controls the size of interfacial voids, the closure of which will be dependent on their curvature.

An adaptation of a metal/metal diffusion bonding model is applied to the simple case of Al_2O_3/Al bonds, where no interfacial reaction occurs, and its prediction as to the importance of surface roughness compared with experiment. Current work on the effect of interfacial reactions on bonding rate predictions will be reported.

A REAPPRAISAL OF CONTACT PHENOMENA IN THE SYSTEM Al LIQUID-Al_2O_3 SOLID FROM 750 TO 1000°C

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The wetting of single crystal alpha alumina by high purity aluminum has been the subject of numerous studies. With few exceptions, however, have the studies been thorough enough to elucidate the complicated physicochemical phenomena that are operative in this relatively simple system. Therefore, the interfacial phenomena of the Al-Al_2O_3 system were reinvestigated through sessile drop experiments. Emphasis has been placed upon the establishment of equilibrium under various experimental conditions. A molten-drop dosing system has been used to determine contact angles at temperatures close to the melting point of aluminum.

The results of this study will be discussed in the context of oxide film formation and destruction, dehydroxylation of alumina surfaces, and solid surface structural transformations. Explanations are presented for contact phenomena observed in previous studies. The complex interactions observed in this relatively simple system point out the need for caution in the interpretation and application of contact angle data from high-temperature sessile drop experiments.

MICROSTRUCTURAL DEVELOPMENT AND ELECTRICAL CONDUCTIVITY OF CERIA-GADOLINIA SOLID ELECTROLYTES

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$Ce_xGd_{1-x}O_{2-x/2}$ solid solutions containing 4 or 8 mole% Gd_2O_3 were prepared by coprecipitating (a) carbonates (via urea) and (b) oxalates. Calcined powders were isostatically pressed (200 MPa), and the sintering at 1550–1600°C produced fully densified bodies, and different microstructures were developed. Sintered bodies obtained from carbonates were mechanically stronger than those obtained from oxalates. SEM analysis was performed to reveal the grain boundary and grain size distribution. By using ac complex impedance analysis, the electrical behavior of the ceria-gadolinia solid electrolytes was studied. It was found that the bulk conductivity was larger in the composition having a greater grain size; however, the grain boundary conductivity was always predominant in the global electrical conduction process. On the other hand, a very large difference in the grain boundary properties was noticed between the samples containing the same Gd_2O_3 concentration, and a good agreement in the activation energies was observed between them. Finally, the influence of the impurity distribution and the homogeneity of the samples on the electrical properties were also studied.

MICROSTRUCTURES OF HIGH DIELECTRIC CONSTANT MATERIALS

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Electron microscopy has been used to characterize the microstructures of several important classes of high dielectric constant materials. Systems that have been most studied include doped barium titanate $BaTiO_3$, lead scandium tantalate $Pb(Sc_{1/2}Ta_{1/2})O_3$, lead magnesium niobate $Pb(Mg_{1/3}Nb_{2/3})O_3$, lead zinc niobate $Pb(Zn_{1/3}Nb_{2/3})O_3$, and commercial multilayer ceramic capacitors. The microstructures of these materials will be presented, including a discussion of the formation of unconventional 90° domain boundary walls in doped $BaTiO_3$, and micro-macropolar domain formation and the degree of B-site cation ordering in lead based relaxor ferroelectrics.

ELECTRICAL BARRIERS AT GRAIN BOUNDARIES IN SILICON CARBIDE MATERIALS WITH BeO ADDITIONS

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SiC materials hot-pressed with BeO additions have a high electrical resistivity of above 10^{13} Ωcm at room temperature and a thermal conductivity higher than aluminum. These unusual properties are related to the microstructures of the SiC grain boundaries. The carrier depleted layers in the grain adjacent to the grain boundaries are formed as potential barriers, as confirmed by measuring the dielectric behavior of the materials. The electrical barriers at grain boundaries were investigated by examining the change of the microstructures and electrical properties and also the behavior of the Be in the sintering process.

The grain growth of SiC particles was observed at above 1750°C, and the relative density increased to about 98% at 1950°C. The electrical resistivity increased with the density of the materials, but above 1950°C resistivity increased rapidly as the density approached its theoretical density. To study the relation between dissolved Be atoms and electrical resistivity, the solubility of Be in the SiC grains was examined using SiC single crystals which were buried in BeO powder and hot-pressed at various temperatures. The results showed that the solubility of Be depended on the hot-pressing temperature and had low levels of about 70 ppm at 2050°C and about 10 ppm at 1800°C. These results suggest that (a) the dissolution level of Be atoms in the SiC grains affects the electrical resistivity in the hot-pressing process and (b) in the cooling process after hot-pressing, oversaturated Be atoms within SiC grains near grain boundaries diffuse to the grain boundaries. The increase of Be atoms near grain boundaries may create higher trap levels of holes to form the depletion layers, causing the high electrical resistivity at grain boundaries of these SiC materials.

MICROSTRUCTURAL ANALYSIS OF SILICON CARBIDE MATERIALS WITH BeO ADDITIONS

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Silicon carbide materials with BeO additions have a thermal conductivity higher than metallic aluminum and high electrical resistivity of above 10^{13} ohm-cm. It has been reported that the BeO addition mostly remains along grain boundaries of SiC and controls microstructures, and the high electrical resistivity has been measured along grain boundaries. Microstructural and chemical analyses on the SiC-BeO materials have been carried out using analytical electron microscopy.

The results show that SiC materials with the above physical properties have homogeneous microstructures with BeO distributed evenly and mostly in triple points. The grain sizes are controlled by basal growth of α-SiC with aspect ratios of ~2–3. Sheaths are formed along basal planes near grain boundaries of SiC grains, which have complex lamellar formation of 4H and 6H polytypes. Transition metal impurities form crystalline carbides which are epitaxially grown on the basal plane of an adjacent SiC grain. Microstructures of these materials with lower than optimal electrical resistivity show two different possible failure modes: (a) Exaggerated grain growth has been observed where small BeO grains are trapped within SiC grains. (b) Perpendicular cracks are often observed in large BeO grains, which indicates that the BeO α to β phase transformation occurred during the cooling cycle, producing multiple variants with mutually perpendicular c-axes within BeO grains.

The distribution and chemistry of the second phase formed by the BeO addition play major roles in controlling microstructures and physical properties of the materials. A possible diffusion mechanism of Be into SiC grains will be discussed by comparing the microstructure of other SiC materials.

CERAMIC-METAL INTERFACIAL FRACTURE ENERGIES

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Failure of ceramic-metal interfaces is frequently primarily brittle in nature even though appreciable plastic strain in the metallic phase or an adjoining bonding layer often adds significantly to the fracture "toughness," i.e., the energy of decohesion. Thus, the fracture toughness depends on the nature and magnitude of chemical bonding across the interface, and the plasticity and flow stress of the metal and any compounds that are present, as well as other factors, such as local residual stresses, that influence the propensity for crack tip branching, deflection, blunting, or shielding. These factors depend on the bond fabrication conditions, e.g., temperature, stress, and gas atmosphere, as well as the microstructure and composition of the ceramic-metal couple, e.g., roughness of the interface(s), thickness of any reaction products and of the metallic component, and interfacial segregant. Electron microscopy, DCB testing, and indentation-induced delamination studies of model metal-ceramic systems provide new insights into the relative importance of parameters that determine the decohesion resistance and into conditions under which ductile versus brittle behavior obtains.

THE ROLE OF INTERFACIAL REACTIONS ON THE MECHANICAL PROPERTIES OF CERAMIC BRAZEMENTS

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Ceramics show considerable promise as structural materials in a number of energy conversion and utilization applications. The technology for joining ceramics to themselves and to metals is vital to the successful use of these materials at elevated temperatures, at high stresses, and in dirty environments. We have investigated a wide range of metallic alloys for their ability to wet and adhere to structural ceramics without requiring pretreatment (coating) of the ceramic surface. The wetting behavior of the metals on ceramic substrates was determined by the well-known sessile drop technique. The strengths of the bonds were determined by room temperature shear tests, and by flexural tests of ceramic-ceramic and ceramic-metal brazements at temperatures up to 600°C. We have also developed a test, based on a modified applied moment double cantilever beam specimen, that has been successfully used to measure the fracture toughness of similar material and dissimilar material brazements. A number of brazed samples have been microscopically examined in order to determine what interfacial reaction products have been formed (as a function of alloy and ceramic composition); and to try to correlate these products, which exist on a microscopic scale, with macro or bulk mechanical properties.

CHARACTERIZATION OF NICKEL:SAPPHIRE DIFFUSION BONDS

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Diffusion bonds between 1.5-mm-thick slices of polycrystalline nickel and sapphire (basal plane parallel to the bonding plane) have been produced. Mechanically sound bonds were produced by bonding in a vacuum of 10^{-5} torr, at temperatures close to the melting point of nickel. Scanning electron microscope observations of the interfacial regions indicated that a thin (approximately one micron thick) layer of an intermediate phase was produced during bonding. Thin sections suitable for transmission electron microscopy could be prepared from the interfacial regions, and the intermediate phase was identified by electron diffraction as nickel-aluminate spinel. The spinel phase was epitaxially related to the sapphire such that the close-packed planes and the close-packed directions of the anion lattices were parallel. The spinel phase also contained a high density of microstructural defects which are being analyzed. The interface between the spinel and the nickel was often faceted, and orientation relationships between these phases are being examined.

ORIGIN OF CRACKING PHENOMENA OBSERVED IN DECOMPOSITION REACTIONS

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The development of cracks in the decomposition of $Mg(OH)_2$ and $MgCO_3$ was observed directly by transmission electron microscopy and scanning electron microscopy. Clear differences in the crack morphologies were found for the two solids. Decomposing $Mg(OH)_2$ formed a continuous network of cracks of about 2 μm mesh size, while decomposing $MgCO_3$ showed cracks to radiate from isolated centers.

Cracks formed in only partially decomposed $Mg(OH)_2$ propagated even through the undecomposed $Mg(OH)_2$. This fact was apparent from observation of both $Mg(OH)_2$ and MgO spots in electron diffraction patterns taken just after cracking. Previous investigators[1] proposed that the cracking occurred to relieve a critical strain that arose from the coherent nucleation of MgO in the $Mg(OH)_2$ matrix. However, this model is inconsistent with present experimental observations.

The only identifiable driving force for the cracking is the high excess surface energy of the product solid MgO particles of ~2 nm cross section. The cracks may form as a consequence of aggregation of these particles to reduce the surface energy.

The isolated crack centers observed in partially decomposed $MgCO_3$ do not extend into the reactant solid but are confined to the porous product solid MgO. The observed orientation relationship between $MgCO_3$ and MgO suggests that no plausible semicoherent reaction interfaces exist for the decomposition of $MgCO_3$. This fact implies that the cracking is not a consequence of an elastic strain but of the aggregation of MgO particles of ~3 nm cross section.

Detailed characteristics of the cracking observed in the decomposition of $Mg(OH)_2$ and $MgCO_3$ will be presented and discussed.

Reference:

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CREEP PERFORMANCE OF SILICON CARBIDE WHISKER-REINFORCED ALUMINA

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The creep behavior of aluminum oxide composites reinforced with silicon carbide whiskers is of interest because of the potential application of whisker-reinforced composites as heat engine components. Creep tests in four point flexure at 1773 K revealed that whisker reinforcement considerably enhanced creep resistance in polycrystalline alumina. The composites exhibited creep stress exponents close to 5 in contrast to a stress exponent close to 2 obtained in polycrystalline alumina, suggesting that different mechanisms for creep were operative in each case. The high-temperature strength of the hot-pressed composites was reduced relative to unreinforced alumina, with failure apparently originating at processing flaws, consisting primarily of whisker clumps and alumina agglomerates. Procedures to reduce the flaw population, using sedimentation techniques, have been developed. Dispersions of whiskers and powder are separated from their associated clumps and agglomerates, mixed in the correct proportion, press-filtered, and the resulting green body hot-pressed using graphite pistons without lateral constraint. Such laboratory prepared composites have high-temperature strengths significantly greater than the externally obtained hot-pressed samples.

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HIGH TEMPERATURE MECHANICAL BEHAVIOR OF ZrO_2-BASED CERAMICS

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The high temperature mechanical behavior--bend strength and toughness--of several ZrO_2-based ceramics is studied between room temperature and 1000°C. The effect of dopants like Y_2O_3 on the retention of the tetragonal phase and its influence on the mechanical values is also reported. Finally, the importance of the microstructural parameters, grain boundaries, and interfaces on the high temperature mechanical properties will be discussed.

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MICROSTRUCTURE AND MECHANICAL PROPERTIES OF Al_2TiO_5-MULLITE-ZrO_2 COMPOSITES OBTAINED BY REACTION SINTERING

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The sintering reactions of titania-alumina-zircon mixtures, according to the following reaction:

$(3 + y)Al_2O_3 + yTiO_2 + 2ZrSiO_4 \rightarrow yAl_2TiO_5 + 2ZrO_2 + Al_6Si_2O_{13}$ (y = 16.8 mol.),

were investigated in the temperature interval ranging from 1400 to 1570°C.

The kinetics of the reaction, the microstructural evolution, and the dynamic sintering of the reaction sintering mixture were comparatively studied with the corresponding stoichiometric Al_2O_3-TiO_2 (1–1 mol) mixture processed under the same experimental conditions.

The reaction sintered compact reached ~97% density with a very fine aluminum titanate (<5 μm) matrix, and with a homogeneously dispersed intergranular mullite (~3 μm) and intergranular m-ZrO_2 (~1 μm) grains.

The influence of the dispersed phases in the mechanical properties of the sintered compact is also discussed.

CONTROL OF THE TETRAGONAL-TO-MONOCLINIC PHASE TRANSFORMATION OF YTTRIA-DOPED TETRAGONAL ZrO_2 POLYCRYSTALS BY ANNEALING IN WATER

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The tetragonal-to-monoclinic phase transformation of yttria-doped tetragonal zirconia by annealing in water was investigated at 80–200°C using the sintered bodies of zirconia containing 2, 3, and 4 mol% Y_2O_3. Three approaches, alloying $ZrO_2(Y_2O_3)$ with 0–20 wt% CeO_2, dispersing 0–40 wt% Al_2O_3 into $ZrO_2(Y_2O_3)$ ceramics, and decreasing the grain size of zirconia, were examined to inhibit the tetragonal-to-monoclinic phase transformation. The amount of the monoclinic phase formed decreased with increasing the concentrations of CeO_2 alloyed and Al_2O_3 dispersed, and with decreasing the grain size of zirconia.

From the present experimental results, it is expected that the tetragonal-to-monoclinic phase transformation of the yttria-doped tetragonal zirconia is perfectly controlled by the addition of CeO_2 and dispersion of Al_2O_3, and the degradation of the fracture strength by low temperature annealing is completely inhibited.

AUTHOR INDEX

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