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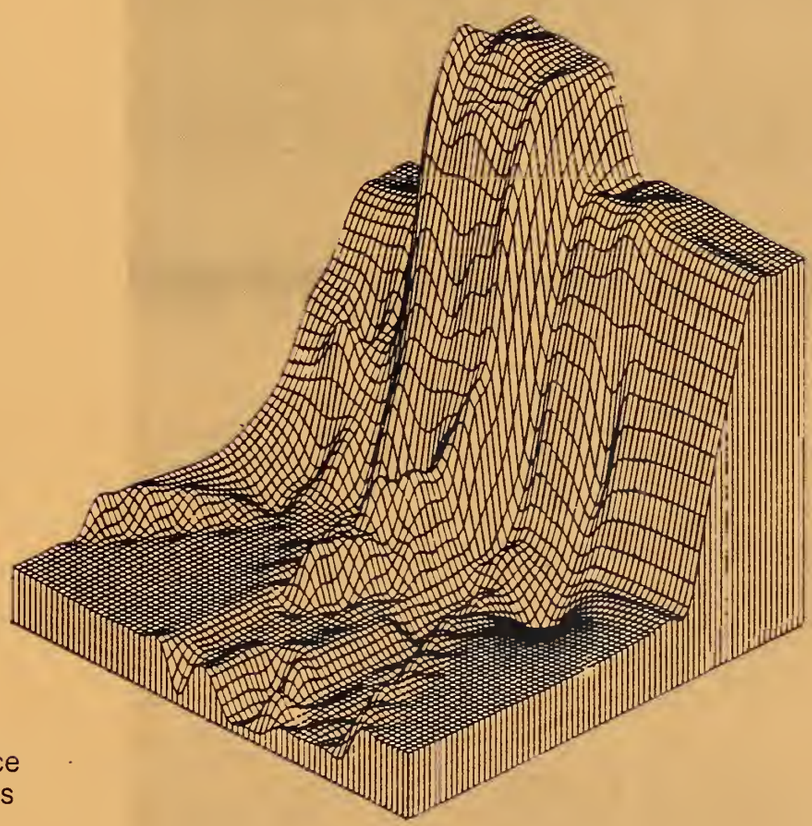

NAS-NRC
Assessment Panel
February 2–3, 1989

NISTIR 88-3840
U.S. Department of Commerce
National Institute of Standards
and Technology

Technical Activities 1988

The first three-dimensional wear map of alumina lubricated with paraffin oil showing the relationship between extent of wear (Z axis), normal force (x axis) and sliding speed (Y axis). Ceramics may undergo potentially catastrophic transitions in wear when the tribological operation conditions exceed certain limits. Wear maps are being developed to understand these limits.

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INTRODUCTION

Introduction

1988 marks the third year that the Ceramics Division has been in existence. Several events occurred in 1988 that have far reaching impact on our future activities. On August 23, 1988, President Reagan signed the Omnibus Trade and Competitiveness Act which, among other things, renamed the National Bureau of Standards to the National Institute of Standards and Technology (NIST). Besides the traditional role of standards and measurement research, NIST will also assist U.S. Industries to develop technology and enhance competitiveness. This has reinforced the objective of the Ceramics Division to provide understanding, critical data, reference materials, and measurement techniques in key technological areas to enable industry to achieve desired properties through advanced processing. In late summer, we invited senior industrial representatives to NIST to explore the technical feasibility of advanced process control through intelligent materials processing. We have also increased our already strong ties to industry through mutual visits and discussion over a wide range of technical areas for possible collaboration. This increased emphasis on awareness of industry's requirements has been manifested by increased industrial support of the Division's activities (estimated at approximately $1.5M) through both direct funding and services in kind such as Research Associates in the Division.

Concurrently, the Division has been restructured to focus on structural ceramics and functional ceramics. Within each focus area, the characterization-property activities have been augmented by a processing component. Integration of processing-structural-property activities within a class of material will increase our program impact.

We continue to expand our programs in terms of personnel and equipment. On January 1, 1988 we were converted into a Personnel Demonstration system which gave us considerable flexibility in recruitment, hiring, and salary administration. As a result, we have been successful in recruiting several key staff members who are crucial in establishing several key competence areas.

One area is in surface chemical characterization and measurement. We are in the process of setting up a solid state NMR (Nuclear Magnetic Resonance) which when coupled with existing facilities of FTIR (Fourier Transformed Infrared) microscope and micro-focused, time resolved Raman Scattering Spectroscopy, will give us an unique capability of characterizing surface chemistry, phases, and composition of powders, compact and sintered bodies.

Another area is in the surface forces facility. We are now able to measure surface forces down to molecular levels. Understanding of the nature and magnitudes of the surface forces has serious technological implications in ceramic powder dispersion, agglomeration, crack propagation, crack healing, lubrication, and the control of interface bonding.

Division output continued at a high level with the publication of 174 papers, and the presentation of 213 talks. Recognition of the many

contributions of Dr. Sheldon Wiederhorn to the field of mechanical properties measurement was manifested by his appointment as a Institute Scientist.

At this time, we are looking forward to increasing our interactions with U.S. ceramics industries, and together, we shall accomplish our goals.

S. M. Hsu
Chief, Ceramics Division

September 1988

TECHNICAL ACTIVITIES

Technical Highlights

Significant accomplishments by the Ceramics Division in 1988 include:

High Temperature Superconductors - Significant progress has been made in determining the effects of processing on the grain boundary chemistry and structure of YBaCuO superconductors. This research has provided insight which could increase the critical current density which now limits the application of these materials.

Phase Diagram for Ceramists - The Division, in cooperation with the American Ceramic Society, has completed Volume 7 of the widely used "Phase Diagrams for Ceramists". This volume contains approximately 1,000 phase diagrams of salt systems.

Diamond Film Research - Research on diamond film synthesis has emphasized the development of understanding of the effects of processing on the structure and properties of this important class of materials. Significant progress on identification of defects and impurity sites has been realized through the development of cathodoluminescence analysis techniques.

Surface Forces Laboratory - A laboratory has been constructed to study the forces present between solid surfaces in close proximity (10-100 nm). This laboratory, one of only a few in this country, will provide data required for a fundamental understanding of phenomena occurring in fracture and lubrication of ceramic materials.

Ceramic Composites - Behavior of ceramic composites, which offer the potential for widespread usage due to their damage tolerance, depends upon the properties of fiber or whisker to matrix interface properties. Research on techniques to characterize the chemical, and mechanical properties of these interfaces has resulted in the ability to optimize fiber coatings for increased composite toughness.

Ceramic Wear Maps - Wear maps which provide a comprehensive view of the wear of ceramics in terms of load and contact velocity have been developed for aluminum oxide and silicon nitride. These maps, the first characterization of wear by this technique provide design information required for wear and guidelines for avoidance of the transition to high wear.

Ceramic Tensile Tests - Inexpensive techniques have been developed to determine the creep and creep rupture properties of structural ceramics to temperatures as high as 1500°C. The use of laser techniques to measure creep displacements to accuracies of ± 2 Micrometers has allowed evaluation of silicon carbide and silicon nitride composites with potential for use in heat engine and heat exchanger applications.

A Computerized Tribology Information System (ACTIS) - The vast volume of tribological data available to designers has not been widely utilized due to both the narrow focus of tests and the wide variety of fields of research publication. ACTIS, a program sponsored by a variety of Federal and private organizations, attempts to provide a readily accessible and viable data base for the design community. Computerized formats have been

designed and demonstrated and evaluated data for selected ceramic material has been input to the program.

Time Resolved Micro Raman Analysis - A time resolved Micro Raman technique has been developed to analyze chemical reactions at tribological contacts. This facility will provide basic data to determine mechanisms of wear and lubricant behavior at wear surfaces.

Synchrotron Radiation Analyses - The NBS synchrotron radiation beamline capabilities for topographic imaging of the interior of crystalline materials have been used to observe, perhaps for the first time, defects which may be the "missing link" that materials scientists have been searching for to explain the performance limits of gallium arsenide single crystals.

STRUCTURAL CERAMICS

OVERVIEW

The major barrier facing the structural ceramic industry today is cost/effectiveness. This can be related to the technical capability to produce reliable and durable ceramics. Reliability can be defined as consistency in properties while durability is related to corrosion, wear, and environmental stability under in-service conditions. Both factors can be controlled through advanced processing and intelligent process control which requires models, test methods, and sensors capable of real time measurements. Discussions with industries have identified these needs and additional requirements in reference materials, easily accessible data, and in-service performance simulations and predictions. As a result, the division program has been structured to focus on ceramic powder characterization, mechanical properties, and wear behavior under different conditions. The underlying scientific theme is to develop models to describe the processing-structure-property relationships of monolithics and composites.

Identification and measurement of key powder properties for reliable manufacturing of ceramics is a difficult but crucial requirement for process model development for both monolithic and composite ceramics. One of our key activities in powders has been the leadership role of an international round robin to compare different methods on several powders among some 30 laboratories. This effort, under the auspices of the International Energy Agency, entailed the preparation and distribution of over 10,000 controlled samples of ceramic powders and analysis of data developed by the participants. This will be the most comprehensive compilation of methods and data on ceramic powder characterization, and would provide industry with a crucial data base for process and product development.

Research efforts in ceramic powder analysis are focused on the characterization of the surface chemistry of powders and the effect of this feature on structure and properties. FTIR and Micro Raman techniques now in use will be augmented in 1989 by solid state NMR analysis. Production of Ceramic Standard Reference Materials has continued and a standard for silicon nitride alpha/beta ratios is scheduled for completion in 1989.

Reliability of structural ceramics requires a determination of the relationship of processing to properties and structure. The availability and use of methods of property measurement and the development of these techniques has been a key element of the structural ceramics program. Development of tensile creep rupture tests has resulted in an inexpensive procedure now being examined in a round robin.

The increased reliability offered by fiber reinforced ceramic composite depends upon the behavior of the fiber to matrix interface. In 1988, a comparison of techniques of measurement of fiber to matrix bonding was conducted. The data from this project will be utilized to further the development of uniform test methodologies. In 1988, a more fundamental characterization of the nature of fracture of ceramics was initiated by the

establishment of a surface forces laboratory. Data from this latter research will aid our understanding of the influence of microstructure and environment on crack propagation.

Durability of ceramics in wear applications has been a primary reason for the development of structural ceramics. Our focus on the development of wear test methodologies and the interpretation of data has led to the development of wear maps which relate system parameters such as load, speed, and environmental factors to wear. Such maps will allow designers much better insight into selection of materials and operation conditions to avoid siezure and premature wear. We have also participated actively in standard setting activities both internationally and within the U.S. Two wear test methods have been developed and are undergoing ASTM round robin testing.

Lastly, the dissemination of critical data to the technical community has been emphasized throughout the division programs and is best illustrated by the development of A Computerized Tribology Information System (ACTIS). ACTIS is an interagency, intersociety joint effort in providing best judgment values by experts in the computerized data base. This year, approximately 5,000 evaluated data on triboligical properties of materials have been established and will undergo user trials in 1989. Similar programs in phase diagrams and fracture properties are also underway.

PROJECT LISTING

Powder Synthesis and Characterization

- Ceramic Powder Synthesis
- Powder Characterization - Physical Properties
- Electron Microscopy/Image Analysis
- X-ray Diffraction
- Chemical Characterization of Ceramics
- Small Angle Neutron Scattering
- Powder Characterization - Colloidal Processing

Mechanical Properties

- Microstructure and Toughness
- Surface Forces
- High-Temperature Deformation and Fracture
- Interfaces in Structural Ceramics
- Processing-Property Relations in Ceramic Matrix Composites
- Sintering Multi-Component Ceramic Systems
- Machining Damage of Si_3N_4
- Structural Ceramics Database

Tribology

- Advanced Ceramics
- Tribological Coatings and Composites
- Advanced Lubrication
- A Computerized Tribology System

POWDER SYNTHESIS AND CHARACTERIZATION

Alan Dragoo

The Powder Characterization and Processing Group seeks to further the reliability and reproducibility of advanced ceramic products by the development of improved starting powders, characterization procedures and standards, and the science and technology base for ceramic processing. The group is integrating a broad range of characterization methods with ceramic processing studies both to advance the understanding of processing effects and to improve and expand characterization methodology.

For chemical analysis of precursor powders and ceramic materials methods used within the group to elucidate both bulk and surface characteristics include x-ray diffraction (XRD), surface extended x-ray augmented fine structure (EXAFS), analytical scanning electron microscopy (SEM) and Fourier transform infrared (FTIR) spectroscopy; and a solid state nuclear magnetic resonance (NMR) facility is being added. These are complemented by other methods at the NIST or at universities through cooperative arrangements. During the past year a procedure was established for measuring the amount of crystalline and amorphous phases in silicon nitride powders by FTIR.

Crystalline structure and microstructure of particle ensembles are characterized with x-ray diffraction and small angle neutron and x-ray scattering (SANS and SAXS, respectively). The application of SANS to the characterization of agglomerate microstructures of particles in liquid media is being explored.

The group continues to play a key role in an international interlaboratory comparison of powder characterization methods conducted under the auspices of the International Energy Agency. The results of this program will provide an important basis for the establishment of measurement procedures and standards which are needed for the international trade of advanced ceramic powders. The group has been instrumental in the establishment of an U.S. Working Group for Powder Characterization which is composed of industrial and governmental researchers in the fields of powder characterization and ceramic processing.

Representative Accomplishments

- A numerical descriptor was developed for description of the fiber distribution in fiber-reinforced composites.
- Work was concluded on a three-year effort in which over 6000 reference powder samples of silicon nitride, silicon carbide, silicon and yttria-zirconia were prepared and certified for a international powder characterization round-robin.
- Standard Reference Material 1879, cristobalite powder, was certified as new reference material for quantitative characterization of silica phases by x-ray powder diffraction.

- o Demonstrated the application of FTIR analysis for determination of silicon nitride phase composition.

- o Demonstrated the application of FTIR analysis for the characterization of the surface chemistry of ceramic powders in aqueous slurries.

- o Development of chemical treatment for the passivation of hydrolytically unstable oxide powders.

- o Densification of microporous silica analyzed with small angle neutron scattering to determine the change in porosity.

Ceramic Powder Synthesis

J. Ritter, R. Faltynek

Families of ambiently stable organic molecules containing boron-nitrogen and silicon-nitrogen bonds were extensively studied as coating agents for alumina and mullite fibers. Although earlier research indicated that the compounds were pyrolytic precursors to boron nitride and silicon nitride, it was unexpectedly found, however, that the nonoxide ceramic precursors react irreversibly with alumina or mullite, resulting in fiber degradation and embrittlement. Decomposition was rapid at 700-800°, but solutions of the precursors in nonreactive solvents slowly attacked the oxide fibers at room temperature as well. Studies are underway to identify means of both retarding and enhancing the degradation reaction, leading to methods for successfully depositing BN or Si_3N_4 on fibers, and for removing oxide coatings from nonoxide substrates.

Powder Characterization - Physical Properties

A. Dragoo, S. Malghan, J. Kelly, D. Minor, L. Lum, C. Robbins, R. Munro[1]

[1]Ceramics Division Office

Research is carried out to develop measurement procedures and standards for powder characterization, to support national and international programs in this area, and to support research on ceramic processing. The instrumentation includes an x-ray gravitational sedigraph, centrifugal photosedimentation apparatus, photon correlation (quasi-elastic light scattering) spectrometer, Brunauer-Emmett-Teller (BET) surface area apparatus, mercury intrusion porosimeter and automatic helium pycnometer. Work sponsored under the Department of Energy Heat Engine Program has a key role in supplying powders and providing data analysis for an international interlaboratory comparison of powder characterization methods. Research on powder characterization is coupled to needs of U.S. industry through active leadership of the U.S. Working Group for Powder Characterization and through guestworker opportunities.

Electron Microscopy/Image Analysis

J. Kelly, D. Minor, J. Ritter, A. Dragoo

Direct microscopic characterization of ceramic particles provides fundamental size and shape data not accessible by indirect techniques, as well as distribution data that serve to verify the indirect measurements. The capacity for characterizing thousands of individual features has been developed through the installation of a computer controlled scanning electron microscope with EDS x-ray and image analysis distributions for ceramic powders as part of the international round-robin on ceramics characterization under the auspices of the International Energy Agency.

Small relative changes in the microstructural details of ceramic materials can result in major changes in their strength. It is therefore important to understand the relationships between fracture processes controlling material toughness and microstructure. Toward this end an in situ fracture stage has being developed to enable real time observation of crack propagation in ceramic wafers in the SEM. This capability will enable us to observe in greater detail the role of grain morphology in the mechanism of bridging ligaments behind the advancing crack tip. This work is in collaboration with the Mechanical Properties Group and is supported by the Air Force OSR.

The dependence of ceramic properties on their microstructural and compositional homogeneity is well established. Specifically this homogeneity is an important factor in the properties of YBaCuO, high T_c, superconductors. An SEM study of the particle size, shape and chemical homogeneity of chemically precipitated YBaCuO precursor powders has shown the relationship between those microscopic properties and the chemical reactor conditions of concentration and solution pH.

X-ray Diffraction

J. Cline, M. Kuchinski, A. Dragoo, C. Hubbard[1], W. Wong-Ng[2], H. McMurdie[3], B. Paretzkin[3], Y. Zhang[4], T. Nakamura[5], C. Robbins[6]

[1] Formerly Data Activities Group, Ceramics Division, now at Oak Ridge National Laboratory
[2] Electronic Materials Group
[3] Guest scientist
[4] Guest scientist, University of Maryland
[5] Guest scientist, Meiji University, Japan
[6] Formerly Powder Synthesis and Characterization Group, now retired.

Research in the field of x-ray diffraction involves its application to ceramic materials throughout the various fabrication phases for improved process modeling and process control. The aim is to increase both the number of sample characteristics that may be measured and the accuracy of such measurements as they pertain to ceramic research.

The investigation of the accuracy of quantitative analysis by XRD has led to the isolation of microabsorption and extinction effects. This work has

not only led to a greater understanding of how to obtain high quality analyses of this type, but has also lead the using of these effects to determine additional aspects of sample character. This knowledge is being used in conjunction with high temperature x-ray diffraction for in-situ measurements of grain growth during sintering. The high temperature diffraction equipment on site incorporates a high speed detection system which allows us to measure both phase equilibria and the kinetics of phase transformations. The kinetics of the formation of the BaYCuO superconducting system as a function of atmospheric composition is one of the several systems being investigated.

Conventional methods of x-ray pattern interpretation use selected areas or points of diffraction maxima. Profile refinement procedures developed here utilize peak shape for high accuracy particle size and strain measurements. Whole patterns analysis by means of the Rietveld refinement technique allows for the simultaneous elucidation of the broadest range of sample characteristics. These include the anisotropy and degree of particle size and strain, crystallographic parameters, texture, as well as quantitative analysis.

The techniques and expertise developed here are being used to produce a variety of Standard Reference Materials relevant to both the ceramic and diffraction communities. Two SRMs were certified in 1988, SRM 660, a line profile standard consisting of LaB_6, and SRM 1879, a respirable cristobalite standard. The recertification of SRM 674 is nearing completion. The Rietveld method is also being applied to the certification of an alpha/beta silicon nitride SRM. X-ray line profile analysis is being used to measure peak breadth for the certification of an ultrafine MgO powder for use as a crystallite size SRM. Additional SRMs being certified consist of a high purity alumina and respirable tridymite.

Expansion of the market for new ceramic materials and the use of computer automation combine to accentuate the needs for improved reference data in the Powder Diffraction File (PDF). NBS has carried out a two-year program, supported by the JCPDS - International Centre for Diffraction Data, to generate high-quality x-ray diffraction patterns for new phases of advanced ceramic materials. During the past year work has focused on x-ray data for phases of interested for high T_c and electronic ceramics, approximately 70 experimental patterns were produced.

Chemical Characterization of Ceramics

Pu Sen Wang, R. A. Faltynek, S. M. Hsu

Work has been started on the characterization of the surface chemistry of ceramic powders, with emphasis on detection of surface additive components. Surface components were analyzed and quantified for three Si_3N_4 powder samples by x-ray photoelectron spectroscopy (XPS). C 1s, N 1s, O 1s, Si 2s and Si 2p photoelectrons were observed. X-ray induced Si KLL Auger electron (XAES) was also detected. Surface carbon and SiO_2 layers were found on all three samples. Two of these powders were found to contain Y_2O_3 and one of these two also has Al_2O_3 additive.

Si_3N_4 tribological discs were also analyzed by XPS and AES coupled with an argon etching technique to profile the surface structure. Both techniques suggest that the carbon and SiO_2 films were limited to the first 40 Å. Normal Si_3N_4 composition was observed underneath these films. Samples after wear testing were found to contain phosphorus which is believed to come from the lubricants used.

Complete phase composition analysis of silicon nitride powders by Fourier transform infrared (FTIR) spectroscopy was improved by the introduction of a multiple linear regression program for data reduction. Typical results are shown below:

	% Composition (actual)	% Composition (FTIR)
Sample 1:	α = 56.4	α = 58.6
	β = 27.0	β = 27.0
	amorph = 16.6	amorph = 14.4
Sample 2:	α = 22.4	α = 24.0
	β = 40.8	β = 41.8
	amorph = 36.8	amorph = 34.2

The technique yields data that correlates well with independent x-ray powder diffraction analysis, and it promises to be useful in SRM certification.

FTIR measurements by attenuated total reflectance (ATR) on aqueous slurry samples of Si_3N_4 and SiC pretreated with surface modifying agents showed that the technique can directly determine the qualitative chemical environment of powder surfaces. Analyses were carried out at the request as part of our industrial collaboration. In terms of application to on-line process monitoring, it is significant that ATR measurements yield information on the condition of slurry with no further sample preparation prior to analysis.

Single-pulse FT-NMR experiments for test mixtures of ceramic powders were performed for ^{7}Li, ^{11}B, ^{29}Si, and ^{31}P nuclei. Resonance signals in forms of free induction decay and Fourier transform were observed at 116.640, 96.258, 59.620, and 121,496 MHz for these nuclei, respectively. Experiments were performed in both stationary and magic angle spinning states. The configuration for the Division's NMR spectrometer was designed, specifications written, and purchase order issued.

Small Angle Neutron Scattering

G. Long (420), S. Krueger (440), and R. Gerhardt[1]

[1]Rutgers University

The sol-gel technique can be used to prepare novel glasses, fibers, thin and thick films with chemical homogeneity and unique structural and electrical properties. High purity, crack-free silica bodies with "made-to-order" narrow pore-size distributions have been formed as model systems for the investigation of the relationships between the physical properties of this class of material and the amount and character of porosity. The present research, which is a collaboration between NIST and Prof. R. Gerhardt of Rutgers University, focuses on the characterization of such porous bodies by small angle neutron scattering (SANS) and multiple small angle neutron scattering (MSANS) since it has been demonstrated that thermal processing and the resultant microstructure bears a strong influence on the dielectric and other properties of the product material.

MSANS was used to measure the average pore sizes present during the intermediate stages of thermal processing, where the radii could be expected to be in the 0.08 - 10 μm range. Total surface areas were estimated from the single scattering Porod curves. Pore populations were studied in the late stages of processing by means of diffraction measurements with 14 Å incident neutrons.

The results indicate that densification during the intermediate stages is accompanied by pore coarsening. Although pore coarsening had previously been observed in the earlier stages of thermal processing, this result was unexpected since the pores are generally expected to undergo shrinkage in order for the body to density. The observed pore coarsening eventually levels off and by the time the material is 95% dense, one cannot detect any pores with radii greater than 0.08 μm. SANS measurements on the 95% dense sample using 14 Å incident neutrons reveal the presence of populations of pores with radii 33 nm and less.

Powder Characterization - Colloidal Processing

S. Malghan, G. Long, A. Dragoo, B. Moudgil[1]

[1]Faculty member, University of Florida, Gainesville

Ceramic components with a high degree of homogeneity and reliability can be produced from ultrafine powders using colloidal processing techniques -- slip casting, pressure casting, etc. In colloidal processing, not only physical (size, surface area, morphology, etc.) but also chemical (bulk, surface chemical) properties are found to play an active role in obtaining homogenous dispersions. The specific colloidal properties based on electrochemical phenomena under investigation are electrokinetic behavior, rheological behavior, and dispersability. To complement existing equipment capabilities, efforts are underway to establish high energy attrition mill for dispersion and size reduction, and acoustophoretic mobility measurement

facilities. Some of the powders and whiskers to be included in these studies are alumina, silicon nitride, zirconia and silicon carbide.

Primary goal of this research is to relate microstructural changes influenced by the colloidal properties of the powder suspensions. This includes determination of colloidal properties of powders and whiskers in liquids of interest, and relationships between colloidal properties and processing response in green state and after consolidation.

Since particulate arrangements in dense slurries may have an important bearing on pore size and structure in green state ceramics, and hence on strength limiting voids in structural ceramic components, a program has been initiated to investigate methods for characterizing particle assemblages in dense and flocculated slurries. Preliminary work is in progress to investigate the use of SANS for in situ characterization of such assemblages.

MECHANICAL PROPERTIES

David Cranmer

Our program on mechanical properties has as its broad objectives: (1) the generation of new theories and data to elucidate fracture and deformation mechanisms in brittle materials; (2) the development of fracture methodology for studying the fundamental forces that exist between two near surfaces; (3) the investigation of ceramic microstructures and their relationship to mechanical behavior; and (4) the understanding of the deformation and fracture properties that govern the mechanical response of ceramics at high temperatures. Specific projects are focussed on the processing-property relations between microstructural features and resulting properties including toughening behavior in structural ceramics and development of models for the fracture behavior of continuous fiber-reinforced, ceramic matrix composites. This latter work involves test development as well as preparation, characterization, and testing of composite systems.

Representative Accomplishments

- A laboratory facility for measuring the magnitude of forces between ceramic surfaces has been constructed and is now operational. The laboratory is a semi-clean room facility containing laminar flow cabinets which permit contaminant free surfaces to be prepared for examination in the surface forces apparatus.

- A semi-automated facility for investigating the creep and creep rupture behavior of ceramic materials in tension has been constructed. Data collected by laser imaging is used to calculate deflection-time curves at the completion of each run. Displacement measurements are accurate to $\pm 1\mu m$ at 1500°C, the maximum operational temperature of the equipment.

- Tensile creep specimens were designed so that alignment of less than 1% strain in bending could be achieved at a cost of approximately $80 per specimen. Creep and creep rupture behavior of carbide and nitride composite materials intended for use in high temperature structural applications are being investigated.

- An indentation-strength procedure for determining R-curves for ceramic materials has been developed. The method involves the use of a controlled flaw, where an indenter is used to place well-defined starting cracks into the surfaces of prospective strength specimens. When coupled with the theoretical model, microstructures which optimize strength and toughness can be chosen.

- Processing techniques were developed for studying residual stresses and distortions in multi-component ceramic systems, such as ceramic composites, co-fired ceramic/metal packages, and multilayer devices.

- Facilities were developed for fabricating whisker-toughened ceramic composites; and a J-integral analysis was developed to explain their fracture behavior in terms of microstructural processing variables. This will allow us to make predictions of the behavior of the material as well as to optimize the processing conditions and microstructure for a particular application.

- A fracture mechanics specimen with a simple array of fibers was developed and used to study influences of processing conditions and metallic interface layers on the toughening of ceramic matrix composites. The simplicity of the test method and specimen geometry allows us to test a broad range of composite processing variables and coating compositions/thicknesses without the necessity of producing full-scale composites.

- A fiber coating system involving the ultraviolet curing of a polymer slurry containing the powdered ceramic composition was developed. A patent has been applied for on this process which permits the uniform coating of continuous ceramic fibers with a ceramic powder which can later be consolidated to form the composite matrix.

- Thermal wave analysis was used to determine the extent of surface damage introduced into Si_3N_4 components by grinding, as well as to characterize the thermal properties of diamond films.

Microstructure and Toughness

B. R. Lawn and S. J. Bennison[1]
[1]Guest Scientist, Lehigh University

During the past year the strength behavior of a number of ceramic materials has been studied using indentation flaw techniques. In-situ microscopic observations of crack growth in alumina, revealed a radical new type of toughening process. We identified interlocking grains and ligaments of unbroken material in the wake of the crack front as the main cause of toughening. We have now developed a theory that provides a full fit of the R-curve for various alumina and other ceramics. Our model is based on a frictional pullout process in which interlocking grains exert frictional closure forces on the new crack walls behind the advancing tip. "Locked-in" thermal expansion mismatch stresses in non-cubic structures play a profound role in enhancing these frictional tractions. The output of this project has strong implications concerning the microstructural tailoring required for optimum toughness properties of ceramics. We are embarking on a systematic processing program to test these implications. A collaborative program with Dr. M. P. Harmer's ceramics processing group at Lehigh University is currently underway to explore this prospect.

Surface Forces

B. R. Lawn, S. Lathabai[1] and R. M. Thomson
[1]Guest Scientist, Lehigh University

In addition to the covalent and ionic cohesive forces that hold brittle materials together, there are weaker (but longer-range) adhesive forces which come into play when new surfaces are created, particularly in the presence of interactive environments: dispersion (van der Waals), electric double layer, solvation, and cation-site forces are examples. These are the surface forces which are of great importance in colloidal chemistry. We have shown in fracture experiments on mica, glass, and sapphire that forces of this type are important also in strength properties of ceramics. Data on the growth of cracks in both the forward and reverse directions have been collected in various environments and are being analyzed. We find that cohesive energies for the crack interfacial regions are considerably higher than might be expected from current theoretical knowledge of fundamental forces, or from measurements of adhesion in the surface forces apparatus. The reasons for these divergences are currently being investigated in terms of the accessibility of the environment species to the crack interface. These investigations are leading us to new conclusions concerning the nature of the interaction, particularly in regard to the geometrical configuration of the interaction zone in both cracks and adhesion geometries.

High-Temperature Deformation and Fracture

S. M. Wiederhorn, T.-J. Chuang, B. J. Hockey, D. E. Roberts and D. F. Carroll[1]
[1]Guest Scientist, Pennsylvania State University

The development of new ceramics provides hope for high efficiency, enhanced performance of structural systems in high temperature, stress-bearing environments. However, before ceramics can be used in industrial applications, issues concerning reliability and service life remain to be resolved. With this in mind, we have been studying the creep and creep rupture behavior of model ceramics at elevated temperatures. During the past year, the creep and creep rupture behavior of a grade of siliconized silicon carbide having a large grain microstructure was investigated and compared with a similar grade of material having a uniform fine grain microstructure. Grain size enhancement resulted in cavity formation at the boundaries between the large grains of silicon carbide and the silicon. These cavities grew along the silicon carbide interface, forming large cracks that limited the amount of deformation allowable in the material and were the eventual cause of component failure. Although the cavity nucleation process in the fine grain material was similar, the small size of the grains limited the size of the cracks that could form as a result of the creep process. As a consequence, the fine grain material was found to be more ductile, tolerating a greater degree of creep before failure. Work on the effect of microstructure on creep is being continued. During the coming year, tensile creep studies on silicon carbide whisker reinforced silicon nitride will be conducted.

Creep rupture behavior of non-oxide ceramics is also being characterized in tension and in flexure. During the past year we observed that for both modes of loading, the rupture time was roughly inversely proportional to the creep rate prior to failure. Quantitative relations between failure in flexure and tension were developed, permitting both the creep rate and the failure time in flexure to be calculated from tensile and compressive creep data using a maximum strain criterion for failure. This maximum strain criterion represents a new approach to lifetime prediction. For the coming year, this method of lifetime prediction will be applied to compressively loaded "C"-rings to determine the general applicability of the technique to ceramic materials.

Interfaces in Structural Ceramics

S. M. Wiederhorn, B. J. Hockey, Ygal Finkelstein[1] and J. E. Blendell
[1]Guest Scientist, Rafael Laboratories, Haifa, Israel

A new effort has been initiated to study the mechanical behavior of ceramic interfaces at elevated temperatures. During the past year, the interface between aluminum oxide and glass was studied in some depth. Interface migration was investigated by sandwiching presintered polycrystalline alumina between thin plates of sapphire. The type of bond formed as a consequence of the joining process and degree of migration was found to depend on the orientation of the sapphire. The kinetics of migration are believed to be interface controlled, and the morphologies of the advancing sapphire interface were rationalized in terms of the interfacial surface energies of the sapphire plane relative to the average surface energies of the aluminum oxide grains in the alumina. Work in this area will be continued to obtain a better insight into the sintering process in alumina.

Processing-Property Relations in Ceramic Matrix Composites

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The primary objective of this program is the experimental determination of the relationships between the fracture behavior of fiber-reinforced, ceramic matrix composites and the chemistry, structure, and properties of the fiber-matrix interface. A second objective is to establish mechanical test procedures appropriate for these composite systems. The increased understanding of the fracture process will be used to develop strong, damage-tolerant materials.

Low and high-temperature structural performance of ceramic matrix composites is controlled to a large extent by the structure, properties and stability of fiber-matrix interfaces. Techniques to characterize these

interfacial properties and to relate them to both processing, and macro-scale mechanical behavior are required to develop reliable ceramic composites. Experimental studies were undertaken to process and characterize such interfaces. A fracture mechanics specimen was fabricated from a model composite system of SiC monofilaments in a borosilicate glass matrix. Measurements of the change in applied stress intensity factor as the crack approaches and passes the monofilaments provided quantitative data on bridging fiber tractions and the fiber-matrix interfacial bond developed by the processing conditions.

A recently installed vacuum hot press (loads to 500 kN and temperatures to 2100°C) is being used to fabricate high-density billets of silicon carbide whisker-reinforced alumina composites. The relation of processing conditions to microstructure, mechanical properties, and performance is being evaluated with a Research Associate from Iscar Ceramics. The fracture behavior of similar materials, obtained from Advanced Composites Materials Corporation, was characterized as a function of porosity (from 0.6% to 11.5%), using a novel analytical method for interpreting the strength of indented flexure specimens. The materials exhibit a rising fracture resistance with crack extension (R-curve behavior). A J-integral analysis was developed to explain this behavior in terms of microstructural features and processing variables. The creep and creep rupture behavior of these materials were also measured at temperatures from 1000 to 1300°C. Creep rupture occurs in two distinct time-regimes, separated by a transition stress. High stresses cause failure, typically in less than 100 hours, while the material is still in a primary creep mode. Low stresses produced not only primary creep, but also a sizeable time-regime of steady-state creep, generally exceeding 500 hours before failure. Electron microscopy is used to relate microstructural behavior to these properties.

Several test methods have been used to experimentally characterize the fiber/matrix interfacial properties in continuous fiber-reinforced ceramic matrix composites. The methods include double cleavage drilled compression (DCDC), indentation push-in and push-out, and single fiber pull-out tests. The composite systems studied have included glass (borosilicate, soda-lime-silica) or glass-ceramic (LAS III) matrices reinforced by SiC monofilaments (AVCO SCS-6) or Si-C-O tows (Nicalon).

The work is divided into three parts: measurement of the fiber-matrix interfacial strength, determination of the effects of thermal expansion mismatch on fiber-matrix interfacial strength, and determination of the effects of fibers in retarding crack extension. A single fiber pull-out test was devised to directly determine the interfacial frictional stress (τ) and debond stress of fibers in a glass matrix. τ's measured using this test varied from 2-3 MPa for the SiC/borosilicate system to 4-20 MPa for the SiC/soda-lime-silica system. The larger value of τ for the soda-lime matrix is due to the greater fiber/matrix thermal expansion difference, leading to larger clamping stresses of the matrix on the fiber. An indentation apparatus instrumented to directly measure force and displacement was used to conduct fiber push-out experiments. These experiments gave values of τ between 1 and 55 MPa for the SiC/LAS-III composite. This variability in τ is directly due to differences in bonding between the individual fibers and matrix. Results of the DCDC tests showed increases in the crack tip stress intensity required to grow the crack due

to both number of fibers and coating thickness. The increase in K_I due to bridging of the crack by fibers is about 20% for a single fiber and 35-50% for two and three fibers. The thickness of Ni coating on SiC fibers was shown to have a significant effect on the bridging force.

Sintering Multi-Component Ceramic Systems

J. E. Blendell, E. R. Fuller, Jr., C. P. Ostertag, M. D. Vaudin;

Sintering multi-component ceramic systems typically results in the development of residual stresses and distortions. Important examples include fiber-reinforced composites, co-fired ceramic/metal packages, and multilayer devices. These stresses and distortions are usually undesirable, and approaches for their avoidance are a mandatory aspect of technology. Processing techniques were developed this past year to study and minimize these phenomena. In particular, small external loads, applied during the sintering cycle, were found to influence greatly the degree of residual stress and resultant distortion.

Uniaxial compressive stresses are applied through rigid platens so that the dimensions perpendicular to the stress (i.e., along the fiber axis of a unidirectional fiber-reinforced composite) remain constant during densification (constrained sintering). In this manner, the axial tensile stresses responsible for crack formations are suppressed when a critical stress is applied. The body is stress free when the constraints are released (after the heating cycle), and hence, remain undistorted during the remaining sintering process. Stresses that allowed distortion-free densification are quite small, on the order of 2 to 2.5 MPa, and thus, constrained sintering is a viable commercial option.

Machining Damage of Si_3N_4

G. White

The mirage thermal wave technique is being used to investigate Si_3N_4 surfaces as a function of grinding treatment. Si_3N_4 specimens have been ground with various grit SiC to simulate levels of machining experienced by ceramic components during fabrication. The surface finish of the Si_3N_4 is being investigated using two approaches: three dimensional images of specific surface areas and dependence of the thermal wave signal on the average thermal properties near the surface. The imaging approach has, so far, detected residual grinding grooves, many small cracks, and what appears to be a near surface inclusion. However, because flaws in brittle materials are both small and numerous, imaging of discrete defects is impractical. The second approach depends on measurements of the average surface damage rather than in discrete flaw detection. In particular, thermal diffusivity, α, appears to vary systematically as a function of surface grinding. For large thermal wave penetration depths into the material, the measured value of α is that of bulk Si_3N_4. As the penetration depth is reduced, α deviates from the bulk value and the deviation appears to depend monotonically on the coarseness of the surface damage. Since both the deviation and the ideal bulk values of α are determined on the same specimen, the system may be self-calibrating; i.e.,

no standard reference specimen may be needed. The two approaches appear to fulfill two separate needs. For small critical components or highly stressed regions in a large component, imaging may be a practical NDE tool. For general information on the quality of a surface, the averaging approach is expected to be superior.

Structural Ceramics Database

R. G. Munro, C. R. Hubbard[1], H. M. Ondik, and F. Y. Hwang[2], S. M. Hsu

Industrial innovation and competitiveness are predicated on the successful use of technical information. In materials research and development, the information is complex, and not readily accessible. In cooperation with the Gas Research Institute and the Center for Advanced Materials at Pennsylvania State University, the Ceramics Division has launched an effort to establish a computerized database on critical properties of structural ceramics. The initial data base will be targeted for use in gas-fired applications such as heat exchangers and recuperators, radiant tube heaters, prime movers, and fuel cells.

The properties of potential importance in an advanced ceramics engineering database may be divided into eight important general categories of data: (1) materials specification, (2) processing characterization, (3) structural and microstructural characterization, (4) intrinsic properties, (5) dislocation and vacancy-dependent intrinsic properties, (6) microstructural dependent properties, (7) performance properties, and (8) failure characterization.

Based on the accumulated information, a preliminary computerized database system, focused on ceramic heat exchangers, has been developed. The information gathered for heat exchangers and recuperators considered current candidate materials, processing methods, and other required characterization information, typical operating conditions, and key design properties required in these applications.

The preliminary system consists of modules for materials specification, thermal expansion, thermal conductivity, thermal diffusivity, specific heat, thermal shock resistance, and a bibliography of data references, along with program elements for queries and output. Currently, the query and output programs are rather general, for development purposes, and need to be streamlined before being used in the eventual prototype. The other modules are ready for testing in their current forms.

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TRIBOLOGY

Said Jahanmir

The primary objective of the Tribology Group is the development of the science and technology base to provide scientific understanding, critical data, and design guidelines for new and improved tribomaterials. This information is needed for mechanical systems requiring high performance, durability, and cost effective designs. Tribology is the science that deals with friction, lubrication and wear of interacting surfaces that are in relative motion. The output from the tribology program will allow wider usage of engineered ceramics, coatings, self-lubricating composites and advanced liquid lubricants, as well as realistic models for prediction of performance and reliable data and information for design and selection of new materials for advanced applications. The research program is divided into three thrust areas: 1) advanced ceramics, 2) tribological coatings and composites, and 3) advanced liquid lubricants. The primary focus in these areas is on the characterization of the tribological interface including analysis of chemical reactions and formation of tribochemical films, physical and mechanical behavior of surface films, and the deformation and fracture process leading to wear and failure. A comprehensive computerized information system is being established as an effective vehicle for technology transfer.

Representative Accomplishments

- A wear test procedure was developed and used to obtain reliable design data and to define the limits and requirements of ceramics under various conditions of load, speed, temperature and environmental factors. The data has been represented in a useful and simple-to-use "Wear Map" configuration.

- A time-resolved micro-Raman test system was developed to analyze chemical reactions at tribological contacts. The system uses a Nd-YAG laser to provide periodic pulses of monochromatic light which are focused on the surface to be analyzed. This unique facility can provide fundamental knowledge on complex chemical reactions and phase changes that occur on tribological surfaces.

- Wear and friction behavior of electrodeposited, composition-modulated coatings of nickel-copper on steel have been measured under both lubricated and unlubricated sliding conditions and found to offer significant improvement over the pure metals. A preliminary model explaining features of the wear of composition-modulated coatings has been developed.

- A demonstration of the ACTIS numeric data base was presented at the meeting of the Society of Tribologists and Lubrication Engineers in May and at the ASM World Congress on Materials, Chicago, IL, in September.

- A specified method for a new pin-on-disk wear test standard developed at NIST that is being balloted in ASTM. We have also developed a modified method for measuring wear of coatings using a crossed-cylinder geometry. A standard test procedure is being written for evaluation of wear performance of ceramics. These standards will be significant since previously standard methods were not available in the U.S. in these important areas.

Advanced Ceramics

S. M. Hsu, S. Jahanmir, D. E. Deckman, R. S. Gates, S. Jahanmir, R. G. Munro, and J. P. Yellets

Advanced engineering ceramics possess a number of unique physical and mechanical properties that makes them suitable for tribological applications where high temperatures, chemical inertness and high resistance to wear are important. Examples may include high speed ball bearings for machine tool spindles, valves and cylinder liners for advanced heat engines, mechanical seals in reactive environments such as food and chemical processing, and valves and flow nozzles in solid particulate handling. The primary technical problems that inhibits wide spread use of ceramics are (lack of detailed scientific knowledge on their tribological performance) reliability and cost effectiveness. Our program is focused on investigating the relationship between processing and performance, the effect of microstructure and composition on friction and wear, surface reactions and formation of lubricating films, atomistic and mechanistic models for friction and wear, and providing reliable test methods and data for design and selection of advanced ceramics for important technological applications.

The research activities on test methods have focused on the selection of appropriate test apparatus, contact geometry, specimen preparation procedure, and assessment of the effect of test variables on friction and wear performance of several advanced ceramics. Test results on alumina, silicon nitride and silicon carbide, lubricated with mineral oil have shown that at a specific load both the friction coefficient and the wear rate increase to a level comparable with the data in unlubricated tests. The fundamental mechanisms which control this transitional behavior are currently under investigation.

The selected test procedure was used to obtain reliable design data and to define the limits and requirements of ceramics under various conditions of load, speed, temperature and environmental factors. The data has been represented in a useful and simple-to-use "Wear Map" configuration. These data are being used to provide a critical step towards understanding the wear mechanisms of advanced ceramics and the establishment of predictive models of wear.

The cover illustration of this Annual Report is one of a series of three-dimensional graphs that comprise the wear map representation for alumina. The cover figure shows a dramatic transition between regions of low wear and high wear in a ball-on-three-flats wear test with a nonreactive, paraffin oil lubricant. Results, such as this figure, provide important

insights and design guides to applications of ceramic materials. For example, the operating point of a wear component in an engine is actually an operating range in which variations of both speed and load are possible. The operating range must now allow the speed and load variables to cross any portion of the wear transition zone.

Recent findings on the role of microstructure have shown that the grain size and porosity exert an important influence on wear. Experimental data suggest that there may be an optimum grain size for best wear resistance. This phenomena is being currently investigated; it may be related to the combined effects of fracture initiation and propagation.

Our extensive data on the friction and wear performance of several technologically important ceramics have confirmed that lubricants must be used to control the friction coefficient and the wear rate of ceramics. The present lubricant technology, however, is based on a vast amount of basic knowledge on reaction between lubricant species and metallic surfaces. Similar detailed knowledge for ceramics is not available. One of our projects is directed towards understanding the reaction mechanisms between lubricants and ceramics. The research during last year has provided important insights on reaction and film formation tendencies of several important chemical functionalities such as phosphates, sulfates, chlorides, as well as the normal paraffinic hydrocarbons, and moisture in the environment. Such basic understanding is indispensible for design of advanced lubricants for future applications using ceramic components.

Tribological Coatings and Composites

D. E. Deckman, L. K. Ives, S. Jahanmir, M. B. Peterson, A. W. Ruff, and E. P. Whitenton

In many applications it is not possible to use liquid lubricants and thus the materials themselves must have suitable friction and wear characteristics. Wear and corrosion resistant tribological coatings, and composites that contain solid lubricating phases are most promising for these applications. Mechanical seals, actuators and values, rolling element bearings, splines and couplings are among the tribological components where coatings and composites could be used to extend the practical operating limits. Our research in this area included wear resistant composition modulated coatings, synthesized diamond films, and self-lubricating composites.

The composition-modulated coatings made at NIST are prepared as alternate layers of nickel and copper, deposited on steel, at layer spacings from 10 nm to 100 nm. Sliding wear studies have been completed under both unlubricated and lubricated conditions. An analytical model of dislocation behavior in a layer microstructure during the plastic deformation associated with wear has been developed. The model allows for three effects associated with these unique microstructures; 1) layer spacing effects, 2) dislocation line energy difference effects, associated with composition, and 3) layer interface thickness and structure difference effects. Efforts are now underway to explore these effects systematically in different alloy systems and using different coating processing

parameters. Longer term wear experiments are planned using a different test geometry. Plans for research on additional composition-modulated alloy systems are being made and include alternate metal-ceramic coatings where improved hardness and toughness are expected.

Self-lubricating composites based on polymers are used in many low speed-low load sliding applications. Their use has been limited because of temperature limitations of polymers. To reach higher interface temperature metal or ceramic based materials are required. Such tribomaterials would have much broader applicability. Research projects include: microstructural effects on wear and strength; the effect of matrix/lubricant/counterface variables on wear; mechanics of solid lubricant film behavior; improved test methods for wear, property, and operating limits; and the fabrication and evaluation of metal and ceramic based composites.

Four models of wear behavior were formulated and evaluated in sliding experiments using copper/graphite and nickel/graphite combinations. Results showed that the dominate feature of the wear process was the capture of the copper or nickel wear particles in the graphite phase which interfered with the transfer process in forming self-lubricating layers.

Diamond is both the hardest material known and the material with the largest thermal conductivity. In addition, it is chemically inert. However, scarcity and expense have limited their use. The deposition of diamond in inexpensive thin film form might remove these limitations. Diamond films offer the possibility of superior wear resistant, low friction, and chemically protective coatings. The purpose of our research is to explore the possible use of diamond films as wear resistant, low friction materials for tribological applications. Silicon carbide disks were coated with synthesized diamond films using the hot filament CVD method, in the Optical Materials Group. Preliminary results indicate that the diamond films provide a low friction coefficient of 0.07, under unlubricated conditions, as well as excellent wear resistance. The scientific issues that are being addressed consist of the mechanisms by which low coefficients of friction are obtained, the effect of deposition parameters on the physical and chemical characteristics of the diamond films, such as surface roughness, interfacial bond strength, and the percentage of diamond bonds in the film.

Advanced Lubrication

S. M. Hsu, S. Jahanmir, D. E. Deckman, R. S. Gates, B. E. Hegemann, C. S. Ku, P. Pei, and J. M. Perez

The development of advanced lubrication systems for future applications is critical to the advancement of technology. Manufacturing processes and machining, magnetic recording devices, advanced aerospace engines, more efficient low heat rejection engines, transportation and power generation are a few examples of technologies with critical lubrication needs. High temperature lubrication efforts consist of the following: lubrication of ceramics using improved synthetic fluids, lubricant interaction with

ceramics, high temperature additive chemistry and the mechanism of oxidation and deposit formation at high temperatures.

Definition of reaction mechanisms at high temperatures involves an understanding of the relationship between molecular structure and thermal oxidative stability. Understanding how changes occur at the interface under severe tribochemical conditions is the first step in controlling the processes.

Micro-Raman and μ-FTIR spectroscopy were used to analyze the tribochemical reactions between advanced materials and lubricants. The spatial resolutions achieved in these techniques are 2 to 3 μm and 100 μm, respectively. A major area of application is in the analysis of tribochemical interaction products with ceramic substrates. An understanding of the effects of differences in ceramic composition and information on phase change, occurring under in both lubricated and unlubricated conditions, is being developed.

To further understand the role of chemical structures on effective high temperature lubrication, the role of polar constituents of base oils was pursued in light of their ability to enhance or deter the effectiveness of additives. Base oils obtained from different sources and processed by different technologies, may differ significantly in their response to essential additives. Base oils were separated into compound classes and then evaluated as to their antagonistic or synergistic effect on selected antioxidants. The fractions were also chemically characterized to determine the chemical functionality that may cause the observed effects. Recent findings indicated that most polar subfractions behave in a synergistic manner with antioxidants to increase the oxidation induction time. However, the most polar subfractions, containing hydroxyl functionalities, act in antagonistic manner and decrease the oxidation induction time.

Many advanced ceramic applications require lubrication to prevent catastrophic failure. Tribological behavior of four synthetic fluids, polyalphaolefins (PAO), trimethylolpropane tripelargonate (TMP), polyphenylethers (PPE), and tricresyl phosphate (TCP) were studied on alumina. It was found that the transition from normal wear to high wear rates can be affected by lubricant chemistry. Lubricant-ceramic interaction products were found for TMP and PPE but not for TCP and PAO, suggesting lubricant effects. Functional groups were identified by μ-FTIR and changes due to tribochemical reactions at the sliding contacts, played significant roles. Lubrication behavior on alumina is related to differences in the oxidation/thermal stabilities and relative volatility of the synthetic base fluids.

Control of the formation of deposits and thermal-oxidative degradation of materials at high temperatures is critical to developing advanced engine technologies. Cooperative studies with industry has resulted in a promising method to evaluate deposit forming tendencies of lubricants and additives. Laboratory simulation of engine test results have been demonstrated with current baseline engine oil technology. Extension of the technique to evaluate novel additives and lubricant formulations is in progress.

A Computerized Tribology Information System

S. Jahanmir, A. W. Ruff, S. Harris, R. G. Munro and S. M. Hsu

Research in tribology is attempting to reduce the estimated $100 billion cost incurred by the U.S. economy each year as a result of friction and wear processes. The Department of Energy has estimated that as much as forty percent of those losses could be saved by improved technology transfer. Research in tribology, however, is a complex, interdisciplinary effort that involves scientists and engineers of rather diverse areas of expertise. These researchers report their progress in correspondingly diverse media. As a result, advances in this field are often hindered by the inaccessibility of critical data or by the lack of awareness of parallel and concurrent research efforts.

An international effort to overcome this technological problem is being pursued through the development of A Computerized Tribology Information System (ACTIS). The central project, ACTIS, is an interagency government program sponsored by the Department of Energy/Energy Conversion and Utilization Technology/Tribology Program, the National Institute of Standards and Technology, the U.S. Army/Fort Belvoir, the U.S. Air Force/Wright Patterson Aeronautical Laboratories, and the National Science Foundation. Additional support is being provided by the American Society of Lubrication Engineers, by the American Society of Mechanical Engineers, and by two distinguished advisory committees.

The system will include six distinct components: numeric data, design programs, bibliographic search capability, references to tribological products, research in progress listings, and a newsletter. All the data bases will be linked together for easy access by the user, and interactive searches for particular data are possible.

Considerable effort has been placed this year into the implementation of the ACTIS tribology data and information system. Most of the effort has concerned the numeric data portion of the system.

A computer scientist attached to the NIST Office of Standard Reference Data (OSRD) has started working with the data bases. The selected data base management system is Advanced Revelation. A major effort was placed in developing a format for the numeric data to be used with the data base. The format consists of 49 field names in the categories 1) materials data, 2) mechanical data, 3) physical data, 4) tribodata, and 5) triboconditions. Substantial time was spent in developing entry screens for the data base using features in Advanced Revelation. Those screens provide the user with instructions and information on the system, and give the options available for selecting report output from any data search. Six of the nine numeric data base efforts underway have been received from the experts involved, and three of them installed into the prototype ACTIS system.

Additional data gathering activities are currently underway in the areas of seals and lubricants. Plans for additional activities include areas of

coatings and surface treatments, polymers, ceramic, composites, and lubricated wear.

A demonstration of the ACTIS numeric data base was presented at the Cleveland, OH, meeting of the Society of Tribologists and Lubrication Engineers (STLE) in May over a 2 1/2 day period. A second demonstration was given at the ASM World Congress on Materials, Chicago, IL, in September.

FUNCTIONAL CERAMICS

OVERVIEW

Since 75-80% of the roughly $4.4B sales of "advanced ceramics" by the U.S. ceramics industry in 1987 were in electronic and optical ceramics, the Division's efforts in functional ceramics support an established portion of the U.S. ceramics industry. The Division's program in electronic ceramics addresses superconductors, substrate and packaging materials, dielectrics, and piezoelectrics. The program on optical ceramics currently addresses thin optical films and planning is underway for possible future work in other photonic materials. There are also collaborations with other groups of the Division and other portions of NIST where appropriate.

The current program in superconducting ceramics is part of a much larger NIST-wide program aimed at providing the nation with part of the technology base needed for exploiting as soon as possible the recent discovery of ceramic superconductors with critical transition temperatures (T_c) above 77K. The Division's program currently emphasizes technology needed for producing bulk superconductors as opposed to thin films (which are addressed in efforts in other NIST divisions). The major technological barriers to the serious consideration of potential applications of these materials as bulk superconductors are ways of processing the materials into components which have high current densities (on the order of $10^5 A/cm^2$) and adequate mechanical strengths. The three divisional thrusts are: determinations of phase diagrams, explorations of chemical routes for producing powders, and methods of processing the powders into bulk superconductors with optimal properties; it is anticipated that these three thrusts will continue to be emphasized in the foreseeable future. We believe that the phase diagrams provided by the Division over the past two years have had major impacts in guiding the processing of the new superconducting compounds.

Substrate and packaging materials, dielectrics and piezoelectrics constitute about 50-60% of the U.S. advanced ceramics industry sales mentioned above and the technologies involved are multi-faceted and rather mature. The major needs are ways to more cost-effectively produce components with properties as good or better than those currently produced. The needs require materials with inherently better properties and more efficient and reliable ways of processing and testing the materials into components embodying the improved properties over longer periods of service. Our efforts in these areas, therefore, emphasize use of very strong or unique expertise within the Division, namely, phase equilibria analyses, ceramic processing, small angle neutron scattering and x-ray analyses, and mechanical properties testing and theory. With the advent of NIST and the mandate to work closely with U.S. industry, we are in the process of identifying additional activities in this area that should and could be addressed.

The current efforts in optical ceramics also emphasize applications of unique or strong divisional expertise. The major emphases are on synthesis and characterization of thin films of a variety of materials but especially of diamond. In the diamond thin film technology, the major needs are to

develop techniques for cost-effectively producing films, particularly single crystal films, with properties appropriate to the intended applications. The Division's current efforts in diamond thin films concentrate on the development of chemical vapor deposition (CVD) techniques and development and use of techniques for characterizing the films. Other work addresses the mechanical properties of infrared transmitting materials. The area of photonic materials (optoelectronic and electrooptic) has been recognized as a potential major growth area and planning is underway.

The synchrotron radiation analysis program includes the development and exploration of a unique x-ray topographic capability for nondestructively analyzing the microstructures of crystalline materials under more realistic conditions than is possible with most methods. These efforts address a generic need throughout materials science for an <u>in situ</u> capability for microstructural characterization. Current efforts emphasize the exploration and use of these techniques for analyses of defects and microstructures in electronic and electrooptic single crystals and polycrystalline ceramics. During 1988, this capability allowed observation of a type of defect not known to exist in GaAs single crystals but which may be a factor in limiting the electronic performance of the crystals. Because current sales of the U.S. semiconductor industry are on the order of $12B per year, the potential implications of this find are significant. Increased utilization of this facility by other members of the Division, NIST, and outsiders to resolve fundamental measurement issues, is being encouraged and is anticipated.

PROJECT LISTING

Electronic Materials

- Development of Superconducting Ceramics
    - Ceramic Powder Synthesis
    - Phase Equilibria Studies
    - Structural Phase Transition Studies
    - Processing-Property Relations
- Ceramic Phase Diagram Program
- Pressure Induced Sintering and Transformation Toughening
- Mechanical Failure of Piezoelectric Components
- Studies of Residual Strain and Crystallite Size
- Thermal Wave Measurements in Brittle Materials

Optical Materials

- Diamond Film Growth and Structural Characterization
- Properties of CVD-grown Diamond Films and Particles
- Photothermal Radiometry of Ceramic Films

Synchrotron Radiation Analysis

- Analysis of Polycrystalline Materials Individual Particle Imaging
- Spatial Resolution in X-Ray Image Magnification of Diffraction Images
- Diffraction Imaging for Process Control in Commercial Crystal Growth
- Pervasive Antiphase Boundaries in Gallium Arsenide

ELECTRONIC MATERIALS

Stephen Freiman

The Electronic Materials Group performs research in a number of different areas. A major effort is directed toward an understanding of the relationships between processing and properties of the high T_c superconducting ceramics. In this task, we are working closely with personnel in the Powder Synthesis Group, as well as with other scientists throughout NIST. One of the primary research objectives in the superconducting ceramics program is the development of phase equilibria data, leading to phase diagrams for the different systems. Also, phase transformations are being investigated in various systems using X-ray diffraction techniques. In addition, techniques are being developed to determine critical currents in superconducting ceramics. In somewhat related work, there is an ongoing study on the reliability of piezoelectric components under cyclic loading including possible effects of electric fields on fracture.

During this past year, the Ceramics Phase Diagram Program which is conducted jointly with the American Ceramic Society was incorporated into this group. The primary objective of this program is the publishing of edited phase diagrams for use by ceramic scientists worldwide.

Various processing techniques are being investigated for preparing multi-component ceramic systems such as electronic packages. Pressure induced densification has been studied as a means of obtaining toughened, infrared transmitting ceramics.

Work in powder synthesis new chemical routes has been explored for the preparation of precursor powders for high Tc superconductor ceramics. This work has led to several advances and patent applications in the preparation BaYCuO and Bi(Pb)SrCaCuO materials, including a ceramic material with a critical current in excess of 800 A/cm^2.

Discovery of conditions for novel chemical synthesis of precursors for high Tc superconductor materials.

Demonstrated the application of FTIR analysis for determination of silicon nitride phase composition.

Achieved significant advances in processing high T_c ceramic superconductors, particularly with regard to compositional homogeneity, the role of processing on grain-boundary properties, and the influence of sintering conditions on microstructure and critical current density.

Examined influences of heat treatment on the formation of 80 K and 110 K superconducting components, as well as regimes of partial melting, in a study of processing conditions for a new class of high-temperature oxide superconductors in the Bi-Sr-Ca-Cu-O system.
Finally, there is work ongoing in the development of non-destructive evaluation techniques for ceramics. This research involves the use of thermal wave analysis for the determination of surface flaws, possible delamination of thin films, and inhomogeneities in the thermal diffusivity of electronic ceramic components.

Representative Accomplishments

- A phase diagram for the Y-Ba-Cu-O superconducting ceramics was published. This diagram shows those compositions from which single crystals of the superconducting compound can be grown. This work has also led to important observations regarding effects of carbon impurities on the formation of particular phases in this system.

- Significant advances were made in processing high T_c ceramic superconductors in both the Ba-Y-Cu-O and Bi-Sr-Ca-Cu-O systems, particularly regarding compositional homogeneity, the role of processing on grain-boundary properties, and the influence of sintering conditions on microstructure and critical current density.

- Mechanical and magnetic processing techniques were developed to align the crystalline grains of bulk Ba-Y-Cu-O superconductors to exploit the preferred directions of current transport in these materials.

- Discovery of conditions for novel chemical synthesis of precursors for high Tc superconductor materials.

- Examined influences of heat treatment on the formation of 80 K and 110 K superconducting components, as well as regimes of partial melting, in a study of processing conditions for a new class of high-temperature oxide superconductors in the Bi-Sr-Ca-Cu-O system.

- Pressure-induced sintering and particulate inclusions were used in processing polycrystalline, infrared-transmitting ceramics to improve their structural properties, particularly their fracture toughness.

- Volume 7 of Phase Diagrams for Ceramists on salt systems was completed, and will be published in early 1989.

- Dielectric aging studies were conducted on a number of capacitor ceramics as a function the oxygen partial pressure during annealing.

Development of Superconducting Ceramics

Despite intensive worldwide research in high T_c superconducting ceramics, difficulties in reproducing materials having optimum electronic properties and lack of a thorough understanding of the origin of the superconducting mechanism still remain. A major problem limiting the technological development of these materials is the relatively small currents, Jc, that these materials will support in the superconducting state. Impurities and grain-to-grain misalignment play a large part in limiting the current carrying capability of these ceramics.

Ceramic Powder Synthesis

J. Ritter, R. Faltynek

Work within the past year has lead to the development of chemical synthesis methods for three types of high T_c superconductors. The investigations were prefaced with the synthesis of the binaries $Y_2Ba_4O_7$ and $CaCuO_2$ as intermediates important to understanding the formation of precursors in the YBaCuO and BiSrCaCuO systems respectively. Experience gained in the binary synthesis was used to develop synthetic approaches to ternary and higher systems. Considerable success was achieved in precipitating homogeneous YBaCuO hydroxycarbonate precursor to the YBaCuO superconductor. The precipitated material converts readily to the superconducting phase at 875°C and test bars made from this powder have shown critical current densities > 800A/cm^2 at 77K. In addition, two novel synthetic routes to the BiSrCaCuO and BiPbSrCaCuO superconductor systems have been developed. Each of these processes has been the subject of a patent application.

Phase Equilibria Studies

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3 Powder Characterization Group
4 Metallurgy Division

Phase equilibria studies, to determine the thermodynamic relations and the primary phase field of the $Ba_2YCu_3O_{6+x}$ superconducting compound in the Ba-Y-Cu-O system have continued. The compound $Ba_2YCu_3O_{6+x}$ was found to melt in air through a four phase field with $BaY_2Cu_3O_5$, $BaCuO_2$ and liquid gradually increasing in amounts from about 975°C to the incongruent melting point at 1002°C. As four phases cannot coexist in equilibrium, through a temperature range, a fourth component, CO_2, is required to explain the experimental melting data. The compound previously described as $3BaO:1/2Y_2O_3:2CuO$, has been shown to exist as a solid solution region between, but not including, the 3:1:2, 4:1,: and 5:1:3 compositions. A series of single phase specimens can be prepared at 950°C with the formula $Ba_{3.2}Y_{0.8}Cu_{2-x}O_{6.4-x}$ ($0.1<x<0.4$). This phase does not form at all when prepared with BaO_2 in a pure oxygen atmosphere; it is concluded that the compound is structurally and chemically an oxycarbonate. This work illustrates the importance of carbon impurities in the processing of these materials.

Phase equilibria studies in the quaternary system Ba-Sr-Y-Cu-O have also been undertaken in order to determine the extent of solid solution of Sr in $Ba_2YCu_3O_{6+x}$ and also to identify any new phases that might be present in the four component system. The results show that Sr will substitute for Ba in $(Ba,Sr)_2YCu_3O_{6+x}$ up to about 60%. There are no ternary compounds in the Sr-Y-Cu-O system equivalent to the three ternary phases in the Ba system. Collaborative X-ray diffraction studies have also been carried out with

AT&T Bell Laboratories scientists on single crystals grown from different alkaline earth/metal oxide-cuprate melts.

A systematic study of the quaternary, Bi_2O_3-SrO-CaO-CuO system is being carried out to determine the thermodynamic relations between phases as well as to develop processing routes to the superconducting phase (or phases). In the SrO-CaO-CuO system, a new binary phase, probably $CaCuO_2$ was discovered. The ternary SrO-CaO-CuO system has extensive regions of solid solution; complete solution is observed for the 2:1 series $(Sr,Ca)_2CuO_3$. Another new ternary phase with a very narrow range of homogeneity was also reported. Crystals of composition $(Ca_{0.86}Sr_{0.14})CuO_2$ have been grown, and characterized by X-ray diffraction.

Structural Phase Transition Studies

W. Wong-Ng, L. P. Cook, C. K. Chiang, L. J. Swartzendruber[1], L. H. Bennett[1] and F. Beech[2].

[1] Metallurgy Division
[2] Reactor Radiation Division

Understanding of structural phase transitions in solids is of importance for processing control, and the development of new products. In the case of $Ba_2RCu_3O_{6+x}$, where R = yttrium and the lanthanides, phase transition studies are being used to gain insight into the role of oxygen in determining the superconducting properties.

Various measurements including x-ray diffraction, thermogravimetric analysis, and determination of Meissner effects were carried out for several high T_c superconductors $Ba_2RCu_3O_{6+x}$ (where R= Sm, Y, Gd and Er; x=0 to 1) in order to correlate the phase transition temperature and oxygen content with the size of R, annealing temperature, and crystallographic data. The structural phase transition temperature appears to follow a trend anticipated from the dependence of the ionic radius of R on the f electron count. The crystal structures undergo a transformation, presumed to be second order, from orthorhombic $Ba_2RCu_3O_7$ to tetragonal $Ba_2RCu_3O_6$. The transformation for all four phases takes place in a temperature range of 625 (Sm) to 770°C (Er); and the lanthanide elements of smaller size seem to stabilize the orthorhombic phase to a higher temperature.

Oxygen stoichiometry is clearly the most important parameter affecting the T_c depression and the presence of T_c plateaus. Neutron diffraction was carried out to investigate the oxygen distribution in the basal Cu-O plane of a 60K material $Ba_2YCu_3O_{6.56}$. Within statistical error, no oxygen was found in the a-axis. When oxygens are being removed from the Cu-O chain, which possibly acts as a charge reservoir, the magnitude of Cu2-O1 distance increases and the Cu1-O1 distance decreases, which diminishes the coupling between the Cu-O plane and the Cu-O chain. By this mechanism, disruption of oxygen along the Cu-O chain is a likely cause of the depression of T_c.

Processing-Property Relations

J. E. Blendell, E. R. Fuller, Jr., C. P. Ostertag, S. A. Soulen, L. C. Stearns, M. D. Vaudin, J. S. Wallace

The interrelations between processing, microstructures, and properties are particularly important for the new high T_c ceramic superconductors. Significant advances were made in processing these materials, elucidating many of the processing-microstructure-properties interrelations. Results for the Ba-Y-Cu-O system are discussed below.

Composition control. Grain-boundary chemistry has a major effect on the current carrying capability of these materials. The presence of second phases along grain boundaries is a major impediment to current flow. Segregation of impurities below the solubility limit also can limit current flow. Clean-room processing of high-purity starting materials gave order-of-magnitude improvements in transport critical current density, J_c, as compared to conventionally processed, reagent grade materials. Values of transport J_c at 77 K increasing from tens of A/cm^2 to hundreds of A/cm^2. Transmission electron microscopy indicates that considerable amounts of second phases remain at many grain boundaries; thus further improvements are possible. Recent chemically prepared samples have had transport J_c values at 77 K of greater than 800 A/cm^2 (sample heating prevented exact measurements).

Grain Alignment. Crystallographically aligned polycrystalline samples were produced both by sinter-forging and magnetic casting. Due to the anisotropic nature of these materials, aligned materials exhibit higher critical current density as compared to unaligned materials. In sinter-forging, samples are deformed during unconstrained hot pressing. Alignment occurs as the grains rotate during the deformation. Although the samples were observed to align crystallographically, the transport current density was very low, and in some cases the samples were not conductive at all. SEM, EPMA and TEM analysis showed that this was due to large scale chemical segregation that occurred during sinter-forging. The usefulness of this technique for improving properties of Ba-Y-Cu-O superconductors is somewhat doubtful at this time.

In contrast, studies on magnetic alignment of calcined superconductor powders prior to sintering are more promising. Resulting sintered compacts tend to have their c-axes aligned parallel to the applied magnetic field, as confirmed by X-ray and neutron diffraction observations. The measured values of magnetization versus applied field at 77 K were strongly anisotropic, indicating appreciable crystallographic alignment. Critical current densities calculated from magnetic measurements were on the order of 10^3 to 10^4 A/cm^2. Transmission electron microscopy showed that the grain boundaries did not contain second phases, and that the (001) planes were aligned across most of the grain boundaries to within an angle of 10°.

Lanthanide Substitutions. The use of the lanthanide elements for Y are being investigated. The initial stages of a study on the effect of La, Gd, Ho, and Er on the nature and location of second phases in Ba-Ln-Cu-O have been completed. The effect of these substitutions on the magnetic alignment will also be investigated.

Ba Precursors. Microstructure and superconducting properties are intimately related to the processing conditions employed. It has been determined that the choice of the Ba precursor plays a critical role on the

microstructural evolution of the sintered body, particularly in relation to the density and grain size. Transmission electron microscopy showed marked inhomogeneity in these fine-grained materials with the same grain in some instances having both "clean" and "dirty" facets. Investigation of the effect of using different Ba precursors is continuing, with emphasis on obtaining clean grain boundaries and high critical current densities.

Ceramic Phase Diagram Program

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The National Institute of Standards and Technology (NIST)-American Ceramic Society (ACerS) ceramic phase diagram program completed its third full year of the expansion plan. The driving force for this joint program is industry's need for current, evaluated phase equilibria data covering a broad range of ceramic systems. Industrial contributions for the support of Research Associates at NIST have passed the $2,000,000 mark.

Volume 6 of Phase Diagrams for Ceramists was published by the Society in November, 1987. Volumes 7 and 8 are in production. Each contains approximately 1000 phase diagrams. Final review of Volume 7 on salt systems has been completed and is fully typeset. An early 1989 publication date is anticipated. Volume 8 on water containing oxide systems at elevated pressures is fully keyboarded; commentaries and diagrams have been reviewed and computer typesetting has begun. A mid-1989 publication date is anticipated. Material for Volume 9 on carbides, nitrides, and borides is in the hands of the technical editors, and should be published in late 1989.

Databases which permit direct search capability of the data sets of both graphics and text material have been developed for Personal Computers (PC). Currently, the data files for the graphics and the bibliography-commentary files corresponding to Volume 6 are in the PC databases. The graphics capabilities developed by Peter Schenck now include the ability to transfer the diagrams to a Personal Computer (PC) database, edit them for PC viewing, and manipulate them on screen.

The PC bibliography and commentary database established in 1987 on a customized commercial database management system has been upgraded. The commercial company provided a more complex system which uses menus and pop-up windows, thereby eliminating the need for the user to learn the rather tedious original query system. This PC database also contains the bibliographic data for all the diagrams being considered for future inclusion in Phase Diagrams for Ceramists.

A large effort has been expended in keyboarding the bibliography corresponding to Volumes 1-5. In early 1989, the files will undergo a final proof check by computer and will be available for data dissemination by the ACerS.

The upgraded version of the text-containing database as well as the PC graphics database were exhibited at the ACerS Annual Meeting in May. Since then, they have both been distributed to the Industrial Sponsors of the program for testing.

Pressure Induced Sintering and Transformation Toughening

S. Block, G. J. Piermarini, M. L. Balmer, V. Bean

Ceramics are typically sintered at high temperatures, occasionally with the assistance of moderate pressures. An interesting alternative for producing ceramics with potentially superior properties is "high-pressure induced sintering" at low temperature. Such a process can be accomplished by high-pressure compaction of ceramic powders, thereby enhancing interparticle contact and breaking down aggregates, followed by low-temperature "sintering" under high pressure.

Extensive studies were undertaken in a diamond anvil cell on pressure sintering and toughening of materials, which are optically transparent in the 8-14 μm range. These studies concentrated primarily on ZnS and examined the following processing variables: a) powder source; b) compaction pressure (to 4 GPa); c) sintering pressure (to 500 MPa) and temperature (to 500°C); d) transformation toughening additives; and e) temperature excursions. Chemically vapor deposited (CVD) samples of ZnS from Raytheon Corporation were used as a standard of comparison. Results to date are very interesting. As in ordinary sintering, pressure sintering results are dependent on powder source. One powder produced fracture toughness values ~ 50 % superior to the standard, while another source gave only about a 20 % improvement. The hardness of both samples is directly proportional to the initial compaction pressure. In contrast to conventional sintering, where temperature excursions are insignificant unless they are very large or involve phase changes, temperature excursions greatly affect compacts formed by pressure sintering, negating the above-mentioned improvements. Pressure sintering, therefore, most likely involves a mechanism which is different from classical sintering.

Work was initiated to fabricate larger samples in collaboration with the Temperature and Pressure Division (522). A compact, prepared in one of their large presses, had a fracture toughness which varied from 0.73 to 1.53 MPa.m½ with position in the sample. The K_{IC} of the standard ZnS is about 1.0 MPa.m½. Further improvements in K_{IC} are expected as the pressure induced processing procedures are optimized.

Mechanical Failure of Piezoelectric Components

G. S. White, S. W. Freiman, D. C. Cranmer, and A. M. Wilson[1]

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Experiments were conducted on cyclically loaded lead zirconate titanate (PZT) to clarify the mechanisms leading to mechanical failure. The work is directed toward three goals: 1) determining cyclic fatigue mechanisms in electrically stressed PZT 2) delineating the effects of the electric field itself on crack extension, and 3) determining possible contributions of the environment to crack growth. Indentation techniques are used to produce surface cracks which grow under an electric-field generated load. This approach permits us to monitor directly the crack interactions with pores and grains in the material. Preliminary results indicate that cracks tend to grow from pore to pore in the material rather than in straight lines. This result suggests that one possible mechanism driving crack growth is increased strain generated by enhanced electric fields around the pores. Preliminary data obtained on other piezoelectric ceramics also tends to support the concept of direct effects of electric field induced strain on crack extension.

Transformation toughening is a well-known and effective method for enhancing the fracture toughness of ceramic materials. Transformation toughening by the retention of high-pressure metastable phases is a concept that originated at NIST. Necessary criteria for such toughening require the toughening agent to exist metastably at ambient pressures and temperatures and to have a rapid, reversible, pressure-induced, phase transformation.

This new approach to toughening is currently being applied to toughen materials optically transparent in the 8-14 μm range. NiS/ZnS compacts were made by sintering under pressure to determine whether transformation toughening occurs. The fracture toughness as measured by an indentation technique increased by 100 % at 33 % NiS. Infrared transmission is problematical, probably depending strongly on stoichiometry and particle size. The two polymorphic forms of NiS, and their toughening effect are being investigated.

Studies of Residual Strain and Crystallite Size by X-Ray Diffraction

W. Wong-Ng, Y. Zhang[1], C. R. Hubbard, S. W. Freiman and J. M. Stewart[1]

[1]Guest Scientist, University of Maryland

Potential applications of the high T_c ceramics, $Ba_2RCu_3O_{7-x}$, where R are the lanthanide elements, depend a great deal on their electrical and mechanical properties. A thorough knowledge of the microstructure of these materials, in both their ceramic as well as powder forms, is of importance in order to understand and control the variation of their physical and mechanical properties with processing parameters.

Significant differences in the x-ray diffraction line widths have been observed for two orthorhombic barium yttrium cuprate powders with compositions of $Ba_2YCu_3O_{7.0}$ and $Ba_2YCu_3O_{6.8}$. The former was annealed in oxygen and the latter in air. It was found that the x-ray diffraction peaks of the air-annealed sample are ≈35% broader than those of the oxygen annealed sample. Since the coherent diffracting domain length (crystallite size), residual microstrains, and chemical inhomogeneity might all affect the superconducting and mechanical properties of these materials, x-ray diffraction line profile analysis using the Warren Averbach and Hall Williamson methods has been carried out to study these profile differences. A significant anisotropy in the crystallite size and residual strain for the air-annealed sample was observed relative to that for the oxygen-annealed material in which size and strain broadening were negligible.

Thermal Wave Measurements in Brittle Materials

G. S. White, H. P. F. Frederikse[1], and Xuan Tong Ying[2]

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Thermal Diffusivity of Diamond Films

Thermal diffusivity, α, measurements have been made on diamond films produced at NBS and at General Electric. The mirage technique has the capability to determine α in different directions; therefore, non-uniformities and directional dependence of the specimen's thermal characteristics can be detected. The value of α in the GE specimen was found to be about 3 cm^2/s along the sides but only 0.7 cm^2/s along a band passing through the center of the specimen. Subsequent discussions with scientists from GE confirmed that the Si substrate on which the diamond had grown was incompletely etched away along a band in the center of the specimen. The substrate material was not visible to the eye, but its thermal diffusivity value, 0.7 cm^2/s, was easily detected in the mirage experiment.

OPTICAL MATERIALS

Albert Feldman

The objective of the Optical Materials Group is to provide data, measurement methods, standards and reference materials, concepts, evaluated data, and other technical information on the fundamental aspects of processing, structure, properties and performance of optical and optoelectronic materials for industry, government agencies, universities, and other scientific organizations. The program supports generic technologies in crystalline, glassy, and thin film inorganic optical materials in order to foster their safe, efficient and economical use. Research in the group addresses the science base underlying new advanced optical materials technologies together with associated measurement methodology.

The principal area of optical materials research being covered is thin optical films, which addresses the processing/structure relationships of diamond and other ceramic coating materials and how they affect properties, optical performance, and optoelectronic performance as related to optical coatings, light emitting sources, detectors, and integrated optics.

Representative Accomplishments

- A new hot-filament CVD diamond deposition facility has been constructed. It allows us to observe the deposition, to vary the substrate/filament distance, and to employ different filament configurations. A significant accomplishment is the minimization of filament sagging resulting in much longer filament life.

- Diamond films have been deposited on Si wafers, Si highly doped with B, Ni, Si_3N_4, SiC, SiO_2, and mullite and on different crystallographic surfaces of Si. Mismatch of the thermal expansion leads to film crazing on SiO_2 substrates. Morphology appears to be relatively insensitive to the substrate material and orientation; however, films on Si_3N_4 have finer grains, and films on SiC appear to grow faster. Deposition on Ni was unsuccessful. Deposition on Si doped with B showed regions of continuous film growth and regions of particle growth.

- Substrate temperature (600-850°C) during deposition causes large variations in film morphology; the cleanest diamond surfaces occur at nominal substrate temperatures between 700 and 750°C. The cathodo- and photo-luminescence spectra also show significant variation indicating that defect center identities and concentrations are dependent on the substrate temperature during deposition. These defect centers can be correlated with defects centers observed in bulk synthetic and natural diamond.

- The thermal conductivities of plasma sprayed barrier coatings of chromia, alumina, and zirconia have been measured as a function of specimen temperature by means of photothermal radiometry as part of the NDE program.

- Thermal diffusivity measurements have been made on a diamond plate provided by General Electric and on a film deposited by us on mullite. The values obtained are less than those for bulk diamond but are greater than that of copper and silver.

- A. Feldman is serving on the National Materials Advisory Board Committee on Superhard Material examining the technological significance of materials such as diamond, diamond-like carbon (also called DLC), cubic boron-nitride, and SiC, and which is to recommend research priorities for exploiting these materials.

Diamond Film Research

Diamond Film Growth and Structural Characterization

E. N. Farabaugh and A. Feldman

A new hot-filament CVD diamond deposition facility has been constructed which has significant improvements over our first generation facility. (Our first facility was upgraded by the installation of flow controllers which allow us to vary the gas composition.) The new apparatus, shown schematically in figure 1, allows us to visually observe the deposition. The substrate holder contains a heater and has provision for movement relative to the filament. The filament holder allows for different filament configurations. A means was devised to support the filament thus minimizing filament sagging and resulting in much longer filament lifetimes. Filament lifetimes of 500 hrs. have been achieved. This new configuration also allows us to change specimens more easily without accidentally breaking the filament. All of the deposition described below were carried out in our first apparatus.

Diamond films have been deposited on a variety of substrates: different crystallographic surfaces of single crystal Si wafers; Si doped with B; Ni; Si_3N_4; SiC; SiO_2; and, mullite. Except for the Si doped with B, all of the substrates were prepared by rubbing with diamond paste and cleaned prior to deposition in order to obtain continuous film growth. Mismatch of the thermal expansion of the film and the substrate is important; for example, crazing of the film is observed when deposited on SiO_2 because the film contains a large tensile stress due to the higher thermal expansion of diamond. Morphology appears to be relatively insensitive to the substrate material and orientation; however, films on Si_3N_4 have finer grains, and films on SiC show larger grains and appear to grow faster. Deposition on Ni was unsuccessful.

In our previous depositions on Si, we found it necessary to pretreat the substrate surface with diamond paste, as discussed above, in order to obtain continuous films. It had been reported that B acts to nucleate diamond. We therefore wanted to investigate whether continuous films could be deposited on Si wafers that were heavily doped with B without the diamond paste pretreatment. Deposition on Si doped with B showed both regions of continuous film growth and regions of particle growth suggesting that B might facilitate diamond nucleation.

The effect of substrate temperature on diamond film morphology was examined. Films were deposited on pretreated Si substrates at nominal substrate temperatures of 600, 650, 700, 750, 800, and 850°C. The other film deposition

parameters were: gas composition, 0.5% methane/99.5% hydrogen; gas pressure, $5x10^3$ Pa; gas flow rate, 52 sccm; filament temperature, ≈1800°C. Large variations in film morphology were observed (see figure 2). At 600°C, grains with a cube-like habit seem to predominate. At 650°C the microstructure is less well defined with triangular facets beginning to develop and mix with the cube-like habit. At 700°C the triangular faces predominate and the cube-like faces are absent. Growth spirals become evident on some of the faces. At 750°C the film surface displays well defined triangular faces, the crystal grains are well defined, and the growth spirals are more distinct. At 800°C the crystal grains are less well defined with secondary nucleation occurring as evidenced by the appearance of small grains growing between the larger grains. The growth spirals appear to have evolved into steps and ledges. At 850°C the secondary nucleation is much more pronounced with a greater loss of definition of the microstructure. The cleanest diamond surfaces occur at substrate temperatures between 700 and 750°C. Luminescence spectra, discussed below, have been obtained on these same films.

Future work includes: effect of deposition parameters on growth rate and diamond perfection; effect of doping on film growth rate and morphology; dependence of shift of diamond Raman line on particle morphology (icosahedral vs. cubo-octahedral); deposition apparatus using microwave assisted CVD will be constructed. In addition films will be provided to support thermal conductivity measurements, luminescence measurements, infrared transmission measurements, and tribology measurements.

Optical and Optoelectronic Properties of CVD-grown Diamond Films and Particles

L. H. Robins, L. Cook*, E. N. Farabaugh, A. Feldman, and E. Etz**

*Electronic Materials Group
**Gas and Particulate Science Division/Center for Analytical Chemistry

The goals of this project are to identify and develop experimental techniques for characterizing the properties of diamond films that are relevant to projected applications in optical and optoelectronic devices, and to gain a better understanding of the relationship between CVD process parameters and the properties of the as-deposited films. Recent work has focussed on the influence of imperfections in the diamond lattice, including both native defects and chemical impurities.

Luminescence, the optical emission arising from electronic recombination at defect and impurity levels within the bandgap, is the principal technique currently being used. Two methods of producing luminescence are being pursued: cathodoluminescence (CL), in which a high-energy (1-30 keV) electron beam is the excitation source; and, photoluminescence (PL), in which photons (visible or ultraviolet light) are the excitation source.

A CL experiment has been set up in a scanning electron microscope. By using the imaging capability of the scanning electron optics, the spatial distribution of luminescent defects can be mapped, complementing the information about electronic structure provided by luminescence spectroscopy. Several interesting results have already emerged from this experiment. By comparing the CL spectra in our diamond films to spectra reported in the

literature for bulk natural and synthetic diamonds, we have tentatively identified defects associated with nitrogen impurity atoms, interstitials, atomic vacancies, and dislocation lines. In a series of films grown at different deposition temperatures, the nitrogen-related CL was most intense in films grown at low temperature, the dislocation-related CL dominated at intermediate temperatures, and the atomic vacancy CL was most intense at the highest temperature. Variations in the intensity of these CL bands appear to be correlated with changes in film morphology. CL imaging of single-crystal particles suggests that the concentration of luminescent defects is high on (100) crystal planes and low on (111) planes; secondary electron imaging showed that, at least in large isolated particles, the [100] planes have smooth surfaces while the [111] planes show growth steps.

PL excited by an argon ion laser has been studied in a Raman microprobe system. The initial results of the laser PL have shown that there are correlations between CL and PL spectra in films grown under the same conditions. In particular, the atomic vacancy related luminescence band was observed by both CL and PL in a film grown at high temperature, but was not observed by either method in films grown at lower temperatures. A broad, featureless spectrum at energies higher than the vacancy band has also been seen in laser PL; preliminary results suggest that the featureless spectrum is associated with polycrystalline films rather than single-crystal particles.

We plan to extend our experimental capabilities for PL and CL as techniques for characterizing defects in diamond. In the CL system, spectrally resolved imaging will be used to compare the spatial distributions of different types of luminescent defects. Possible linear polarization effects in the images will also be investigated. The spectral range of the CL detection system will be extended further into the ultraviolet, beyond the energy of the diamond bandgap, to allow the detection of near-band-edge as well as deep-level luminescence. In the PL experiment, a variable-temperature liquid-helium cryostat will be used to measure the temperature dependence of luminescence intensities and linewidths. Spectral lines of the ion laser, as well as tunable arc-lamp and flash-lamp light sources, will be used to investigate the dependence of PL on excitation photon energy. Related characterization techniques such as photoconductivity spectroscopy will also be started.

The coupling between film deposition and optical characterization activities in the Optical Materials Group is being strengthened. For example, luminescence is being used to compare the defects present in single-crystal diamond particles and continuous polycrystalline films. The influence of various deposition parameters on the optically active defects will be investigated in greater detail. One parameter that may be investigated is the addition of chemical dopants intended to produce electrically and optically active donor or acceptor levels; luminescence is expected to be a valuable technique for characterizing such impurity levels.

Photothermal Radiometry for Monitoring of Ceramic Film Quality

H. Frederikse, X. T. Ying*, A. Feldman, and E. N. Farabaugh

*Guest Scientist from Fudan University, Shanghai, PRC

Ceramic films. The purpose of this project is to inspect the thermal behavior and mechanical integrity of non-metallic coatings using the propagation of thermal waves. Such coatings play an important role in many technological areas: optical components, engines and combusters, corrosion protection, electronic devices, etc. Thermal wave techniques have gained considerable attention and popularity during the last 10-12 years. Both thin and thick layers, from a few microns to several millimeters, can be probed conveniently by thermal waves because the thermal diffusivity length can be adjusted to these depths by varying the modulation frequency. Several detection schemes can be used to determine the temperature variations in time or in space; a number of these techniques do not require contact with the material being probed and hence lend themselves well for Non-Destructive Evaluation.

We have investigated the heat resistance of a number of oxides coatings at temperatures up to 900°C. The coatings, deposited by plasma spraying to a thickness of 50-100 μm, were chromia, zirconia, and alumina; the substrates were stainless steel plates in all cases. The previous year we had developed Photo Thermal Radiometry (PTR) as a noncontact method to monitor the thermal quality of ceramic coatings at room temperature.

The experimental set up is similar to that described in last year's Annual Report. The only difference is that the sample is positioned inside a horizontal cylindrical furnace, about 6-8 cm from the opening at one end. Measurements were made at six temperatures between 20 and 900°C. Two infrared detectors were employed over this temperature range: a liquid nitrogen cooled InSb detector for temperatures up to 500°C and a Ge photodiode for temperatures between 500 and 900°C. The detector was needed because the InSb detector saturates above 500°C due to a large background thermal signal. Even in the range of 200-500°C small apertures had to be inserted to limit the amount of radiation falling on the sensitive InSb area. At the highest temperatures, the Ge photodiode also required aperturing.

At each temperature, the magnitude of the signal, $|S|$, and the relative phase, $\Delta\phi$, were measured as a function of the modulation frequency which was varied from 9-333 Hz. Analysis of the $\Delta\phi$-vs-$\sqrt{f}$ plot yielded the thermal diffusivity α and the thermal conductivity κ of the coatings. The values of α and κ are about a factor two smaller than the Handbook data for bulk ceramic specimens and much smaller than the single crystal values. This is not surprising considering the high degree of disorder and the relatively low density of plasma sprayed coatings. Another indication of large thermal scatter is the temperature dependence; α and κ show a nearly constant behavior rather than the predicted 1/T dependence.

Thermal Properties of Diamond. In the last few months we have turned our attention to the thermal properties of diamond films. One of the properties of great importance is the high thermal conductivity of diamond. Consequently it is important to determine this property both as a measure of diamond film quality and as a specimen parameter for a particular use. In recent months we

have studied several Thermal Wave Techniques in order to determine the most suitable method for diamond coatings. Results have been obtained on a 1/2 mm thick film (obtained from G.E. Laboratories). In this case, PTR was the preferred method. Other promising approaches are a longitudinal method - propagation of the heat wave along a film of diamond deposited on a narrow strip of thermally insulating ceramic - and the optical beam deflection technique (mirage effect). Preliminary measurements of thermal conductivity indicate values less than that of the best diamond but greater than that of copper. In addition, optical beam deflection measurements indicated thermal inhomogeneity.

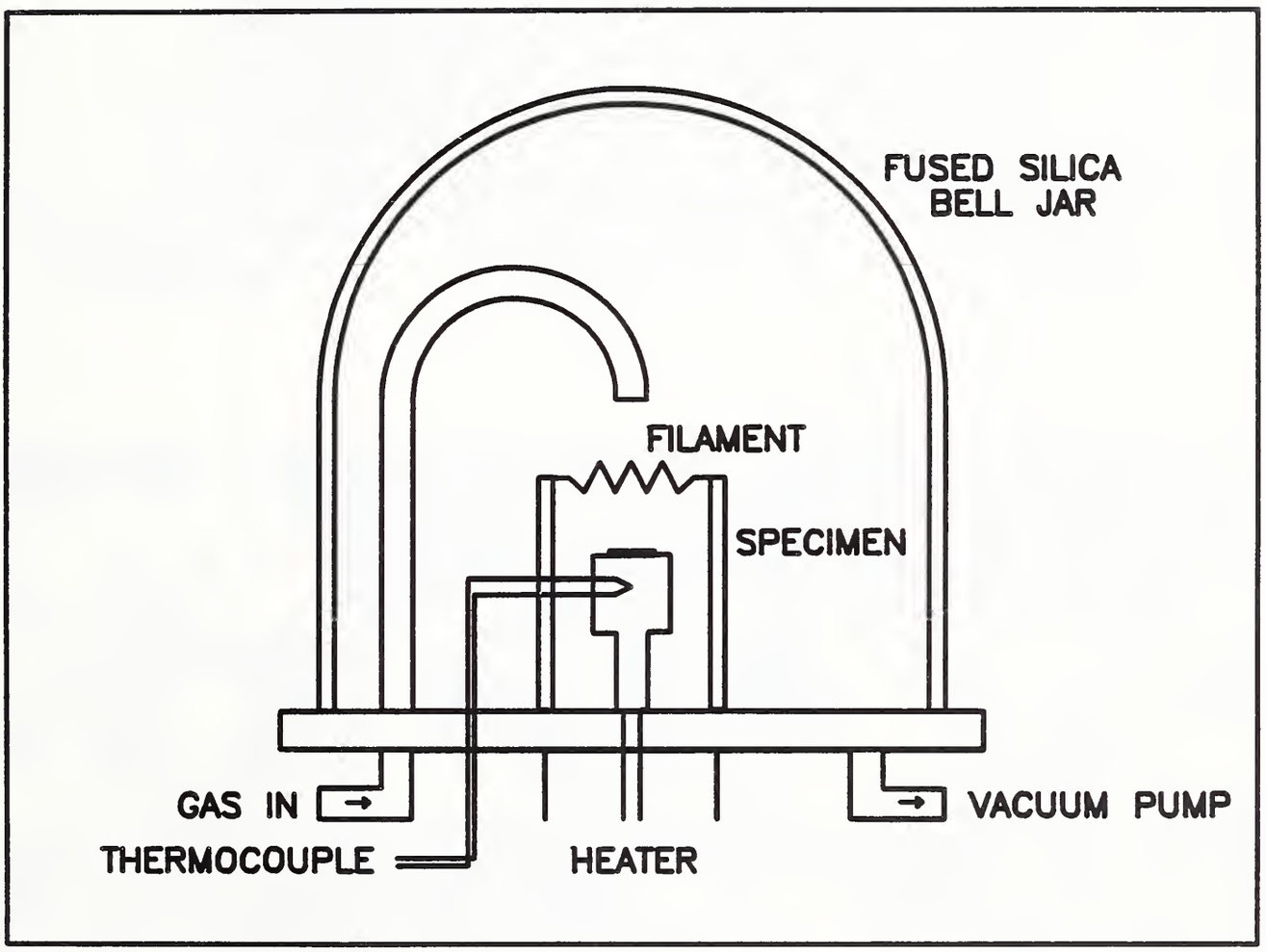

Figure 1. Schematic diagram of redesigned hot filament chemical vapor deposition apparatus for depositing diamond films.

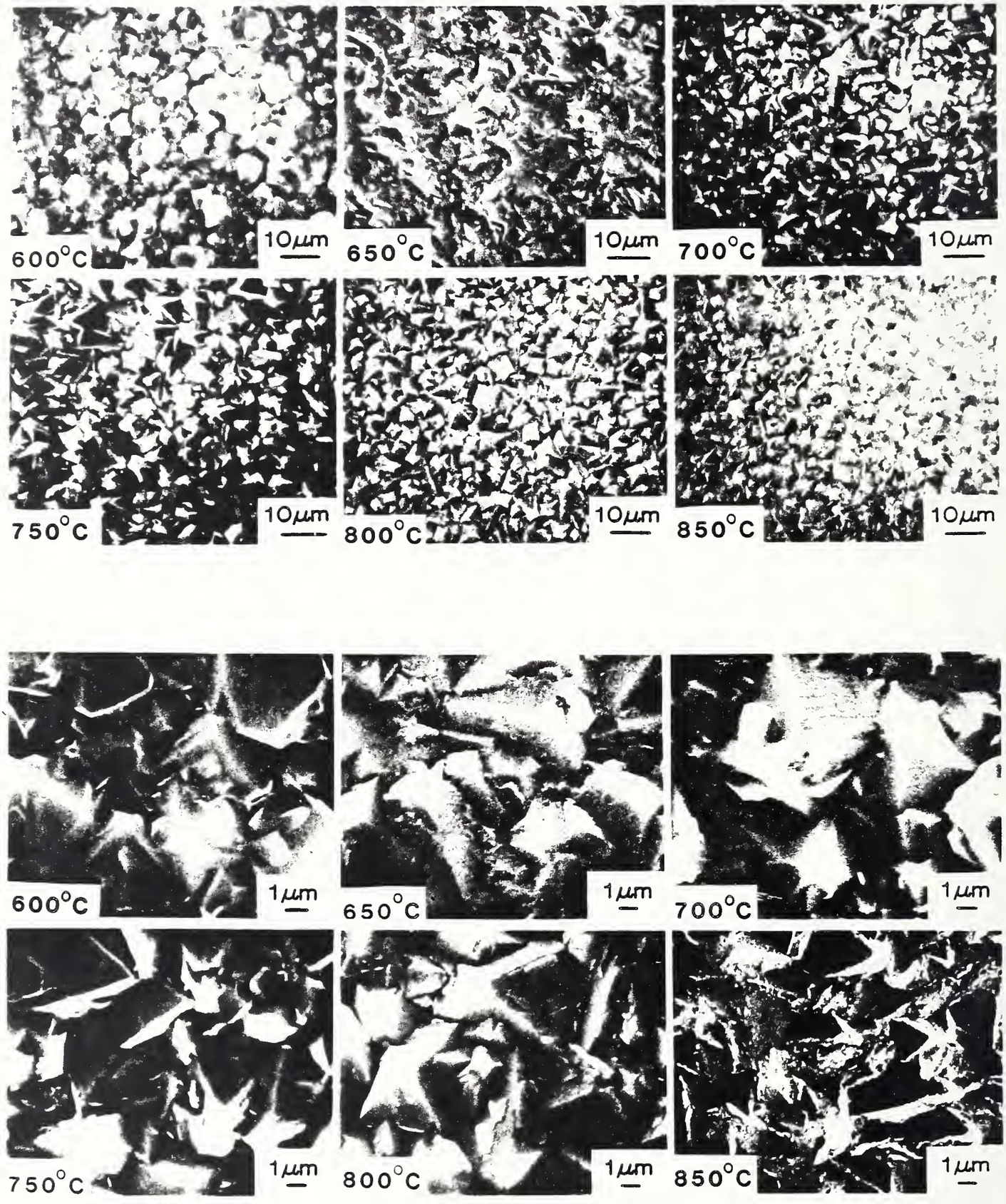

Figure 2. Scanning electron micrographs of the surface morphologies of diamond films prepared at different substrate temperatures. Two levels of magnification are shown.

SYNCHROTRON RADIATION ANALYSIS

Masao Kuriyama

New materials with enormous practical interest are now being produced in industry by far more sophisticated processing methods than utilized a decade ago. These materials are made with control of their buildup designed at the atomic level. Success with such materials primarily requires the knowledge of new ways to arrange the atoms in order to achieve the desired properties. But such knowledge, while important and necessary, is insufficient by itself. The structure of all materials, when formed, is non uniform locally over regions of the order of a micrometer. Heterogeneity occurring as grain boundaries, phase interfaces, interacting dislocations, local compositional variations, regionally homogeneous strains (plastic deformation), and inhomogeneous strains, etc., often alters the performance of materials designed for sophisticated and demanding applications. Thus, successful fabrication of such materials by atomic design or ultra-molecular engineering of structures depends entirely on structural details and their influence on properties.

The Synchrotron Radiation Group's objective is to develop and use new measurement technology for the characterization of such advanced materials and better starting materials for traditional materials particularly by applying recent advances of synchrotron radiation diffraction imaging techniques. This effort aims at the fundamental understanding of the genesis of imperfections and the processing mechanisms of advanced materials, in particular, modern ceramic materials. This fundamental knowledge will directly assist U.S. industrial scientists and engineers to make high quality advanced microcircuits and electrooptic communications devices competitive in the world market. In this support of intelligent processing, the group's current activity emphasizes efforts to improve generic measurement technology and to provide basic data that will lead to the production of advanced materials with superior properties for devices of higher quality and improved reliability, in collaboration with U.S. industrial scientists.

Representative Accomplishments

- Discovery of novel microstructural features in undoped semi-insulating LEC gallium arsenide by monochromatic synchrotron diffraction imaging, and explanation of this new phenomenon in terms of antiphase platelets (or interfaces).

- Proposal of a unified theory of defect generation based on the antiphase structure in undoped semi-insulating LEC gallium arsenide; this provides an understanding of the crystal growth mechanism.

- Establishment of a new analysis method for polycrystalline materials by imaging individual particles in synchrotron radiation diffractometry, and its application to alumina and silicon particles.

- o Completion of a new experimental station, A2, at NIST/IMSE beam line for EXAFS, standing wave, and total reflection analysis of interfaces in collaboration with CEEE.

- o Development and implementation of collaborative research programs with industrial and governmental laboratories, such as Westinghouse, Grumman, Rockwell International (Science Center), EG&G, U. S. Army Materials Technology Lab, and business firms interested in crystal growth of liquid encapsulated Czochralski grown gallium arsenide and temperature-gradient freeze-Bridgman grown gallium arsenide, and cadmium telluride.

- o Application of the x-ray image magnification technique to electronic device materials in diffraction imaging, reaching submicron resolution.

New Analysis Method of Polycrystalline Materials by Imaging Individual Particles in Diffraction

D. R. Black, R. Spal and M. Kuriyama

The determination of particle size, orientation, strain, and distribution normally requires elaborate analyses of x-ray diffraction data obtained from line profiles or small angle scattering (SAXS) profiles. These analyses are dependent entirely on mathematical models which are chosen by investigators. With a highly parallel (a few arc-second divergence) beam prepared from synchrotron radiation, dependence on these models is no longer necessary. Diffraction lines actually consist of numerous small spots, although they are grouped to form a ring, historically called "Debye-Scherrer" ring. The individual spots are, in fact, diffracted from individual grains and particles, as shown in Figure 4a. From samples provided by other groups in the Ceramics Division, diffraction images have been obtained with 10 μm spatial resolution. The relative orientation of individual particles has been determined, as shown in Figure 4b. The beam was 2 arc-seconds wide in the vertical direction and 30 arc-seconds in the horizontal direction, and had a 1 mm X 0.2 mm cross section. These conditions can be adjusted for each measurement as required. The acquisition of the total profile for all particles in one diffraction line can be achieved within 20 minutes. The relative orientation of particles can be recorded within 5 minutes by rotating the sample while a detector is at a fixed position. In the demonstration experiments on a silicon standard sample and an alumina disk using 8.048 KeV radiation, particles of slightly less than 10 μm can clearly be separated. This resolution can be improved as experiments progress. Within each particle, one can see fine structure, namely, crystal imperfections and subgrain boundaries. The diffraction profile of a single particle, typically called its rocking curve, can be obtained within a minute to give an estimate of the magnitude of inhomogenous strains. The next objective is to determine accurately the magnitude of homogeneous strains in individual particles, that is, the determination of residual strains. The information obtained from this new type of model-independent measurement has proven to be useful for the characterization of green state materials and sintered materials. Diamond

films, superconducting pellets, and powder of superconducting materials are being investigated in the current beam time at X23A3.

Spatial Resolution in X-Ray Image Magnification of Diffraction Images

R. C. Dobbyn, R. Spal and M. Kuriyama

There have been many advances in obtaining direct images and diffraction images in real-time. An important question has been what is the limit of spatial resolution? Is it limited by diffraction effects of samples and/or x-ray optical elements that prepare the beam and images? An x-ray image magnifier of 30 X to 40 X was used to obtain diffraction images from electronic device features on gallium arsenide. The device was set in the (400) symmetrical diffraction condition in the surface reflection (Bragg) geometry. The magnifier was aligned in the non-dispersive geometry with 9.3 KeV radiation. As shown in Figure 5a and 5b, the details of the device down to approximately 3/10 of a micrometer can clearly be visible, although diffraction effects due to crystalline imperfections are evident along with the device image. The present result indicates that the resolution has not been limited by diffraction effects, and the increase of magnification factors will be useful to achieve real-time imaging with submicron resolution, along with efforts to develop high sensitivity 2D detectors. For the evaluation of devices, diffraction images demonstrate the uniqueness in identifying the role of crystalline imperfection in relation to individual device areas.

Diffraction Imaging for Process Control in Commercial Crystal Growth

B. Steiner, M. Kuriyama, R. C. Dobbyn and H. E. Burdette

The uniqueness of the NIST/IMSE Synchrotron Radiation Beam line, X-23A3 at National Synchrotron Light Source, is based on unconventional parallel monochromatic beam optics combined with the distinctive advantage of the small source size of the storage ring. Diffraction imaging at this unique facility is leading to an understanding of various defects and strain fields and of their genesis and interactions during growth and subsequent device fabrication. This capability has now been put in full use with industrial scientists for the production of better semiconductors and optoelectronic materials. In collaboration with EG&G, Grumman, Rockwell International (Science Center), Westinghouse, and other firms, the group has been investigating undoped and indium doped LEC gallium arsenide, temperature-gradient freeze-Bridgman gallium arsenide, cadmium telluride, mercury iodide and other epitaxial layers.

Figure 3. Enlarged portion of a transmission (400) diffraction image through a 0.7 mm thick undoped gallium arsenide single crystal, taken at 10 KeV on the NIST Materials Science Beam Line at NSLS. Typical cellular structure is accompanied by streaking images running diagonally in the [100] direction.

Figure 4a. Diffraction lines, magnified 2.5 times, from α-Al_2O_3, indicating individual particles undergoing diffraction, taken at 8.048 KeV with a parallel (2 arc-seconds) monochromatic synchrotron radiation beam. Film was perpendicular to the (113) line. The film-sample distance is 5 cm.

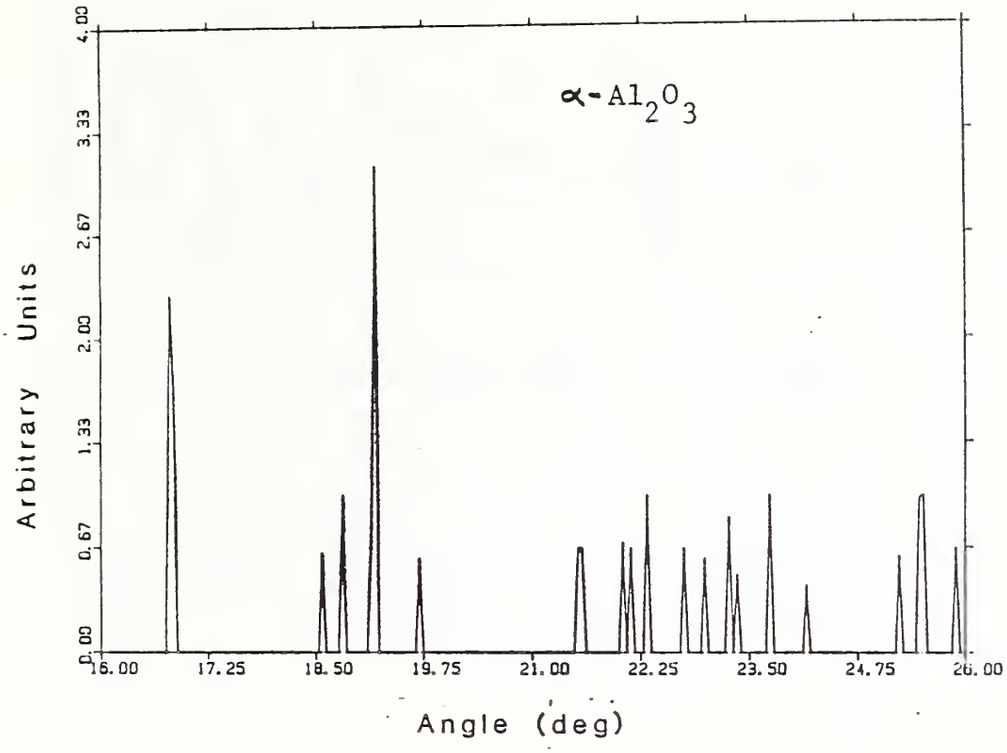

Figure 4b. The relative angular orientation of individual particles is shown as the sample is rotated. The detector is set to receive the (113) diffraction line of αAl_2O_3.

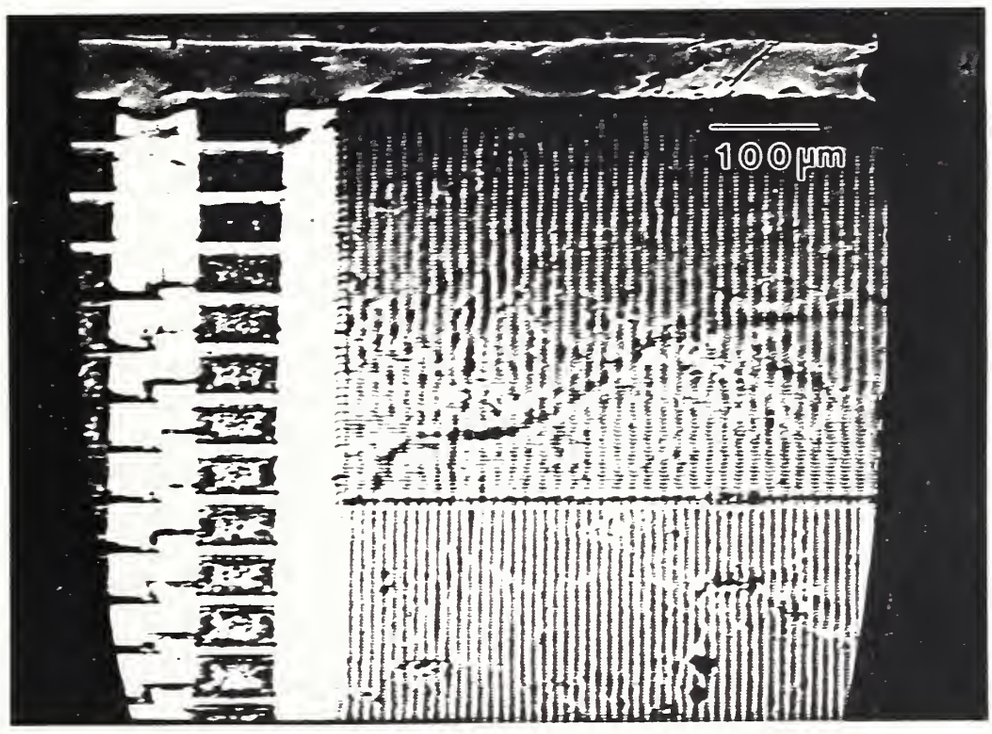

Figure 5a. (400) diffraction image in the surface reflection geometry taken from a device on a gallium arsenide (100) substrate at 9.3 KeV, using an x-ray image magnifier, 30 X.

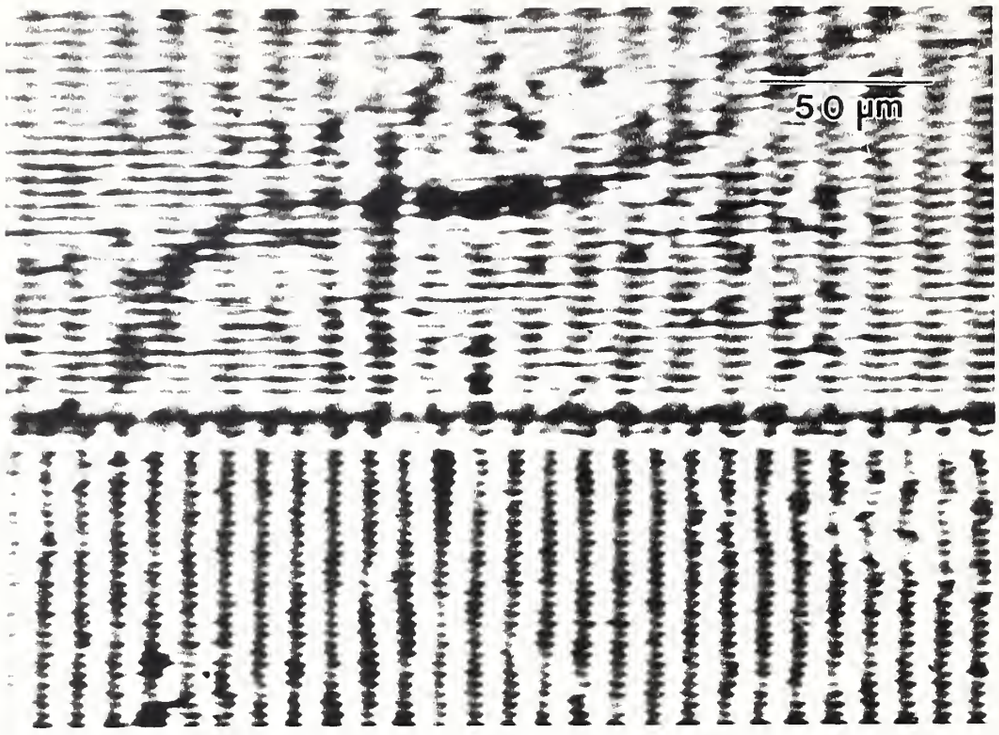

Figure 5b. Enlarged portion of the device of Figure 3a, showing details of approximately 0.3 μm.

Discovery of Pervasive Antiphase Boundaries in Liquid Encapsulated Czochralski-Grown Semi-insulating Undoped Gallium Arsenide

M. Kuriyama, B. Steiner, and R. C. Dobbyn

Novel, pervasive, streak-like features restricted to the direction of the scattering vector have been observed in diffraction images of monochromatic synchrotron radiation (8-10 KeV) transmitted through LEC-grown (liquid encapsulated Czochralski) semi-insulating undoped gallium arsenide (Figure 3). The appearance of such features is not predicted by commonly accepted dynamical diffraction imaging theory, but can be interpreted by dynamical theory that had been generalized to include scattering by imperfect crystals. As a result, these observations have been shown to be caused by the disruption of diffraction by very thin {110} boundaries characterized by lattice coherence but incorporating a phase (atomic) shift. Of the various possible crystal defects, only antiphase boundaries are consistent with these observations as well as with the other aspects of the new high resolution diffraction images: cellular structure, linear and very low-angle subgrain boundaries in <110> directions, surface stripes in a <110> direction, and systematic differences in the acceptance angle for images involving various diffraction vectors. Some of the individual features had been observed at lower resolution, indicating that the crystals in this study are typical of undoped LEC gallium arsenide. However, a unified interpretation had not been achieved. The observation of pervasive antiphase regions suggests that approaches to greater crystal perfection, which is required for commercial exploitation of gallium arsenide crystals for high speed information processing, must be fundamentally reconsidered. The new observations have been carried out on the NIST/IMSE materials science beam lines (X23A) at the National Synchrotron Light Source.

RESEARCH STAFF

Powder Synthesis and Characterization

Cline, James P.	o High-temperature x-ray diffraction o Microstructural effects in x-ray diffraction o Standard reference materials
Dragoo, Alan L.	o Powder characterization o Ceramic process characterization o X-ray characterization o Chemical synthesis of ceramic powders
Faltynek, Robert A.	o Organometallic synthesis of ceramic precursors o FTIR characterization of powders o Spectrophotometry
Hegemann, Bruce E.	o Time-resolved micro-Raman spectroscopy o Micro-FTIR spectroscopy o Laser-induced fluorescence spectroscopy
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Long, Gabrielle G.	o Small angle neutron scattering o Small angle x-ray scattering o Surface EXAFS
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Pei, Patrick	o Chemical instrumental analysis o Separation of complex organic mixtures o Characterization of lubricants and lubricant products o Trace organic compound identification
Ritter, Joseph J.	o Ceramic powders from organometallic precursors o Ceramic powders from solution precipitation reactions
Wallace, Jay S.	o Processing-microstructure-property relationships o Forming, compaction and sintering o Processing of high T_c ceramic superconductors o Processing of structural ceramics

Wang, Pu Sen	o Solid state NMR o Nuclear magnetic imaging of materials o Surface characterization by x-ray photoelectron and Auger spectroscopy

Mechanical Properties

Blackburn, Douglas H.	o Glass properties o Melting of glasses
Chuang, Tze-jer	o Ceramics o Diffusional crack growth o Finite element analysis o Creep theory
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Cranmer, David C.	o Ceramics and glasses o Ceramic matrix composites o Viscosity
Hockey, Bernard J.	o Ceramics o Scanning and transmission electron microscopy o Interfaces o Microstructure
Horn, Roger G.	o Surface forces o Tribology o Colloidal science
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Lawn, Brian R.	o Microstructure/strength relations o Fracture mechanics o Contact phenomena o Surface forces in fracture
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Roberts, D. Ellis	o Mechanical Properties
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Tribology

Duvall, William W.	o Wear test analysis
Hegemann, Bruce E.	o Time-resolved micro-Raman spectroscopy o Micro-FTIR spectroscopy o Laser-induced fluorescence spectroscopy
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Peterson, Marshall B.	o Wear of materials o Solid film lubricants o Mechanical behavior

Ruff, Arthur W.	o Wear of materials o Microstructure effects o Mechanical behavior
Strakna, Timothy J.	o Wear test analysis o Self lubricating components
Whitenton, Eric P.	o Electronics o Computer science o Surface measurement

Electronic Materials

Balmer, Mari Lou	o Mechanical Property Testing o Fiber processing
Blendell, John	o Ceramic processing and clean-room processing o Sintering and diffusion controlled processes o Processing high T_c ceramic superconductors o Activation chemical analysis
Block, Stanley	o Ceramic processing and high-pressure sintering o Pressure-induced transformation toughening o High-pressure physical properties & structures o High-pressure X-ray diffraction and spectroscopy
Chiang, C. K.	o Electronic ceramics o Superconductivity
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White, Grady S.	o Ceramics and glass o Nondestructive evaluation o Subcritical crack growth
Wong-Ng, Winnie	o X-ray analysis o X-ray standards

<u>Optical Materials</u>

Farabaugh, Edward	o Thin film deposition and analysis o X-ray diffraction analysis o Scanning electron microscopy o Surface analysis o Diamond films
Feldman, Alberto	o Optical films o Guided waves o EXAFS o Diamond films
Frederikse, Hans P. R.	o Thin film thermal wave analysis

Robins, Lawrence H.	o Photoluminescence spectroscopy o Cathodoluminescence spectroscopy o Photoconductivity o Diamond films

Synchrotron Radiation Analysis

Black, David R.	o Inelastic x-ray scattering o Energy dispersive diffraction o Fluorescence and absorption
Burdette, Harold E.	o X-ray optics engineering o Crystal growth o Instrumentation
Dobbyn, Ronald C.	o X-ray imaging o X-ray optics o Microradiography
Kuriyama, Masao	o Scattering physics o Condensed matter physics o Crystallography
Spal, Richard D.	o X-ray optics o X-ray image detectors o Condensed matter physics
Steiner, Bruce W.	o X-ray diffraction imaging o Optoelectronic materials o Crystal growth

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OUTPUTS AND INTERACTIONS

SELECTED TECHNICAL PUBLICATIONS

Powder Synthesis and Characterization

Faltynek, R. A. Lanthanide Coordination Chemistry: Spectroscopic Properties. Submitted to J. Coord. Chem.

Long, G. G.; Fischer, D. A.; Kruger, J.; Black, D. R.; Tanaka, D. K. and Danko, G. A. Surface-EXAFS Experiments at Atmospheric Pressure by Means of a Photocathode Proportional Counter with Monolayer Sensitivity. Physical Review B. Accepted for publication.

Long, G. G. and Kruger, J. "Surface X-ray Absorption Spectroscopy, EXAFS and NEXAFS for the in-situ and ex-situ Study of Electrodes," Chapter in Techniques for the Characterization of Electrodes and Electrochemical Processes. In press.

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Synchrotron Radiation Analysis

Kuriyama, M. Synchrotron Diffraction Imaging for the Characterization of Advanced Electronic and Optoelectronic Materials Proceedings of the International Conference and Exhibition on Optoelectronics (OPT '88 Hyogo, Japan) (submitted).

Kuriyama, M.; Steiner, B.; Dobbyn, R. C.; Laor, U. Streaking Images that Appear Only in the Plane of Diffraction in Undoped GaAs Single Crystals: Diffraction Imaging (Topography) by Monochromatic Synchrotron Radiation J. Physical Review B (accepted for publication).

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Steiner, B.; Kuriyama, Dobbyn, R. C.; Laor, U.; Larson, D.; Brown, M. Structural Anomalies in Undoped Gallium ARsenide Indicated in High Resolution Diffraction Imaging with Monochromatic Synchrotron Radiation Journal of Applied Physics (accepted for publication).

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American Ceramics Society
- Glass Division
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  - Committee on Glass Standards Classification and Nomenclature
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    - S. M. Wiederhorn, Subchairman
- Basic Science Division
  - Editorial Committee
    - B. R. Lawn, Chairman
  - Program Committee
    - E. R. Fuller, Jr., Chairman
- Communication of the American Ceramic Society
  - E. R. Fuller, Jr., Contributing Editor

American National Standards Institute (ANSI)
- Committee 43.1--Safety Standards for X-ray Diffraction and Fluorescence Analysis Equipment
  - S. Block, Chairman

American Physical Society Editorial Board
- Review of Scientific Instruments
  - P. K. Schenck

ASM International
- Energy Division
  - S. J. Dapkunas, Vice Chairman
- Journal of Engineering Materials
  - S. J. Dapkunas, Associate Editor

American Society for Testing and Materials
- C14: Glass and Glass Product
  - M. J. Cellarosi, Chairman
- C14.01: Nomenclature of Glass and Glass Products
  - M. J. Cellarosi, Chairman
- D2: Petroleum Products and Lubricants
- D2.09G: Response of Base Oils to Oxidation Inhibitors
  - J. M. Perez, Chairman
  - C. S. Ku, Secretary
- E29.01: Advanced Ceramics, Organizational Meeting
  - M. J. Cellarosi
- E49.01.02 Computerization of Materials Property Data
  - C. R. Hubbard, Chairman
- F1: Electronics
- F1:02: Lasers
  - A. Feldman, Subcommittee Editor
- G2: Erosion and Wear
- G2.2.02: Solid Particle Erosion

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G2.4.04: Pin-on-Disk
A. W. Ruff, Chairman

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Subcommittee on Wear
S. Jahanmir, U. S. Representative

INDUSTRIAL AND ACADEMIC INTERACTIONS

The Ceramics Division actively participates with Industry, Academia and other Government Laboratories in research programs of mutual interest. The following examples are illustrations.

INDUSTRIAL

1. ISCAR Ceramics, Inc. (Dr. Joseph Barta)

   A research associate from ISCAR Ceramics is working with Division personnel on the processing (blending and hot pressing) of silicon carbide whisker-reinforced alumina composites. Processing conditions are correlated with both microstructural and mechanical properties.

2. Norton Company (Dr. P. Tewari)

   An FTIR study of aqueous slurries and surface treatments of Si_3N_4 and SiC is in progress.

3. Naval Research Laboratory (D. Schrodt, B. Bender)

   The project is on the thermochemical treatment of polymer-derived SiC fibers and the degradation mechanisms of these fibers during high-temperature heat treatments.

4. Oak Ridge National Laboratory (Dr. T. M. Besmann)

   The project is on the microstructural and structural characterization of ceramic matrix composites produced by chemical vapor infiltration (CVI). Mechanical properties are correlated with microstructure and processing.

5. 3M, Inc. (M. S. Leitheriser)

   This is a collaborative project to examine the surface chemistry of ceramic powders.

6. Advanced Composite Materials Corporation (Dr. James F. Rhodes)

   The project is to characterize the microstructures of silicon carbide whisker-reinforced alumina composites. Mechanical properties (fracture toughness and creep behavior) are correlated with microstructural properties and processing conditions.

7. E.I. DuPont De Nemours and Company (Drs. David Roach, P. Morris, F. Tabbe, and R. French)

   Research is being conducted for the DuPont Co. to evaluate the static fatigue behavior of polycrystalline aluminum oxide fibers intended for reinforcement of other ceramic materials. In this project, the strength, toughness and resistance of these fibers to environmentally induced fracture will be evaluated at room temperature. The NIST clean room is being used in joint research projects addressing production of barium titanate and sintering of ultra high purity alumina.

8. Southwest Research Institute (Dr. R. Page)

   The project is to conduct SANS beam broadening experiments to follow pore evolution during early and intermediate stages of alumina sintering.

9. Boeing Company

   An activity has begun with Boeing Company, Seattle, WA, to examine the wear characteristics of SiC-coated carbon composites at high temperatures. Specimens have been prepared, and have been examined so far in the high temperature microindenter system. A significant temperature dependence of microhardness was found which should assist in interpreting the wear data to be obtained.

10. Gas Research Institute and Pennsylvania State University (Dr. R. Tressler)

    The Division is leading an effort with GRI and PSU to develop a materials property computerized database targeted for gas-fueled heat exchangers and recouperators as well as conducting research addressing the tribological properties of materials for gas-fired applications.

11. Cummins Engine Co. (Dr. D. Steuhower)

    A simple bench test method to evaluate diesel engine oil performance was developed in cooperation with Cummins Engine Co. Validation of the method was performed using samples from Detroit Diesel Allison Division, GMC and Caterpillar, Inc.

12. John Deere and Company (Dr. P. Swanson)

    This program is concerned with investigating problems connected with the measurement of galling damage and the development of tests to evaluate alloys used in agricultural and industrial equipment where severe wear is a serious problem.

13. Battelle Columbus Laboratories (Dr. W. Glaeser)

A joint activity is underway to prepare a wear atlas from selected literature and research findings at Battelle Columbus Laboratories and NIST. Battelle and NIST are evaluating 250 publications in wear and friction to select authoritative findings that relate wear and friction with materials properties and surface morphology. The findings will be published as an atlas under a cooperative effort that also includes the West German Bundesanstalt fur Materialprufung.

14. VAMAS Standardization

An international round-robin to develop test procedures for determining the stress corrosion susceptibility of advanced ceramic materials are conducted. Approximately 20 laboratories in 6 countries are participating in the interlaboratory testing program. A second cooperative program is underway to evalute the tribology of structural ceramics.

15. Max Planck Institute, Stuttgart, Federal Republic of Germany

Collaborative research with the processing group of Max Planck Institute on the clean-room processing of advanced ceramic material is in progress. The influence of clean-room processing on chemical and phase composition of ceramic superconductors in the barium-yttrium-copper-oxide system and in similar systems with lanthanide (rare earth) substitutions for yttrium has been examined.

16. AT&T Bell Labs (Dr. P. Gallagher)

This is a joint research on the phase relations in superconducting ceramics.

17. Electric Power Research Institute (Mr. W. Bakker)

EPRI is funding a program in the Electronic Materials Group to develop more economical superconducting ceramics for conductor applications.

18. Applied Physics Laboratory (Dr. Moorjani)

This is to study the laser-ablated thin films of both the BiSrCaCuO and BiPbSrCaCuO high T_c superconductor systems. Initial results indicate an improvement in superconductivity in the thin films when compared to this property in the target from which they are derived.

19. AVX Corporation (Dr. Bharet Rawal)

The joint effort is to understand the mechanical properties of multilayer ceramic capacitors. AVX is preparing specimens of differing composition and properties. These are subsequently tested at NIST.

20. W. R. Grace (Dr. L. Dolhert)

This research addresses sintering properties of barium-yttrium-copper-oxide superconductor materials which have been prepared by chemical routes and milled to different size fractions.

21. Applied Physics Laboratory (Dr. K. Moorjani)

This is an investigation of the processing conditions and superconducting properties of Bi-Sr-Ca-Cu-O materials. Emphasis has been on fabricating thin films using a laser ablation technique and measuring the properties of the resulting films.

22. Raytheon Corporation

A joint activity has been initiated to examine the toughness of CVD and HIPed zinc sulfide materials by a microindentation technique.

23. Clarkson University

This is a consortia program to study electrooptic material crystal growth.

24. Accumetrix Corporation (Dr. D. Greenspan)

This is a program to study the thermal and adhesive properties of plasma sprayed ceramic films. The films are prepared at Accumetrix and their properties were measured at NIST by means of photothermal radiometry.

25. Naval Surface Weapons Center (Dr. P. Miller)

This research characterizes the influence of pressure on the decomposition kinetics of energetic materials by a combination of FTIR and x-ray diffraction techniques.

UNIVERSITIES

1. University of Minnesota (Dr. D. Pui)

This is a collaborative project on the aerodynamic sizing of fine ceramic powders and on computer fitting of standard particle size distribution functions to particle size distribution data.

2. Florida State University (Dr. B. Moudgil)

   This is a project on SANS characterization of the structure of agglomerates in dense slurries.

3. Rutgers University (Dr. R. Gerhardt)

   This is a collaboration on the characterization by SANS of microporous silica as a function of thermal processing.

4. Lehigh University (Prof. M. Harmer)

   Joint research on the effect of microstructure on the fracture resistance of ceramic materials. The materials under study will be manufactured at Lehigh University and will be characterized and tested at the National Institute of Standards and Technology.

5. University of Michigan (Dr. T. Y. Tien)

   This is joint research on the creep and creep rupture behavior of SiAlON composites at high temperature. These materials were manufactured at the University of Michigan and characterized both microstructurally and mechanically at NIST.

6. Drexel University (Dr. M. Koczak)

   This is a joint program with Dr. M. J. Koczak of Drexel University on the fracture behavior of ceramic matrix composites.

7. Northwestern University (Prof. H. Cheng)

   Joint research involves lubrication modeling. The research focuses on the microelastohydrodynamic theories under wearing conditions. This is the first attempt at combining surface chemistry with surface mechanics to create a predictive wear model.

9. University of Illinois (Dr. S. W. Lee)

   The project centers on an investigation of the fundamental mechanisms of friction, wear, and surface damage in tribological applications of advanced ceramics.

10. University of Maryland (Profs. J. Dally, and J. Stewart)

    Two projects are underway; one a joint research project on wear models of ceramics; and, the other on the determination of residual stresses in ceramics by x-ray techniques.

11. University of Pennsylvania (Prof. P. Davies)

    This is a collaborative project on the properties and structure of microwave dielectrics and high T_c superconductors.

STANDARD REFERENCE MATERIALS

The Division provided science, industries, and government a central source of well-characterized materials certified for chemical composition of physical or chemical properties. These materials are issued with a certificate and are used to calibrate instruments, to evaluate analytical methods, or to produce scientific data which can be referred to a common base.

DESCRIPTION	SRM NUMBER
Alumina Elasticity	718
Alumina Glass Anneal Point	714
Alumina Glass Anneal Point	715
Alumina Melting Point	742
Aluminum Magnetic Susceptibility	763-1
Aluminum Magnetic Susceptibility	763-2
Aluminum Magnetic Susceptibility	763-3
Barium Glass Anneal Point	713
Borosilicate Glass Composition	93(A)
Borosilicate Glass Thermal Expansion	731L1
Borosilicate Glass Thermal Expansion	731L2
Borosilicate Glass Thermal Expansion	731L3
Cadmium Vapor Pressure	746
Chlorine in Base Oil	1818
Container Glass Composition	621
Container Glass Leaching	622
Container Glass Leaching	623
Copper Thermal Expansion	736L1
Fused Silica Thermal Expansion	739L1
Fused Silica Thermal Expansion	739L2
Fused Silica Thermal Expansion	739L3
Glass Analytical Standard	1835
Glass Dielectric Constant	774
Glass Electrical Resist	624
Glass Fluorescence Source	477
Glass Liquidus Temperature	773
Glass Refractive Index	1820
Glass Sand (High Iron)	81A
Glass Sand (Low Iron)	165A
Glass Stress Optical Coefficient	708
Glass Stress Optical Coefficient	709
Glass Viscosity Standard Renewal	717
Gold Vapor Pressure	745
High Boron Glass Viscosity	717
Intensity XRD Set	674
Lead Barium Glass Composition	89
Lead Glass Anneal Point	712
Lead Glass Viscosity	711
Line Profile	660

Liquids Refractive Index	1823
Low Boron Glass Composition	92
Lube Oil Oxidation Test Kit	1817
Lube Oxidation Catalysts	8500
Lubricant Oxidation Research Test Kit	8500a
MNF_2 Magnetic Susceptibility	766-1
Mica X-Ray Diffraction	675
Neutral Glass Anneal Point	716
Nickel Magnetic Susceptibility	772
Opal Glass Composition	91
Palladium Magnetic Susceptibility	765-1
Palladium Magnetic Susceptibility	765-2
Palladium Magnetic Susceptibility	765-3
Platinum Magnetic Susceptibility	764-1
Platinum Magnetic Susceptibility	764-2
Platinum Magnetic Susceptibility	764-3
Refractive Index Glass	1822
Respirable Cristobalite	1879
Respirable Quartz	1878
Ruby EPR Absorption	2601
Sapphire Thermal Expansion	732
Silicon X-Ray Diffraction	640(b)
Silver Vapor Pressure	748
Soda Lime Flat Glass Composition	S620
Soda Lime Float Composition	1830
Soda Lime Glass Viscosity	710
Soda Lime Sheet Composition	1831
Sulfur in Base Oil	1819
Toluene 5 ML	211C
Tungsten Thermal Expansion	737

APPENDIX

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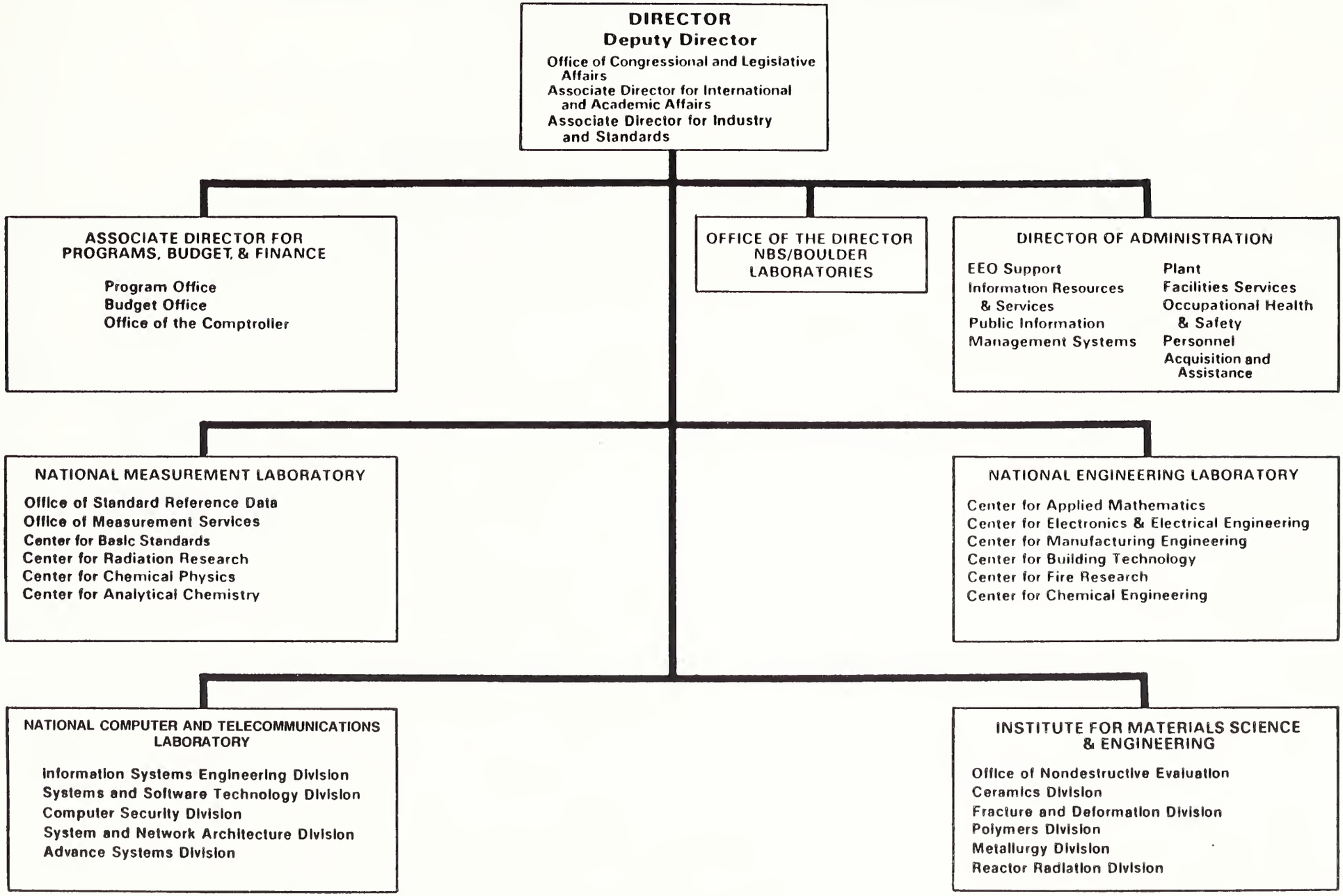

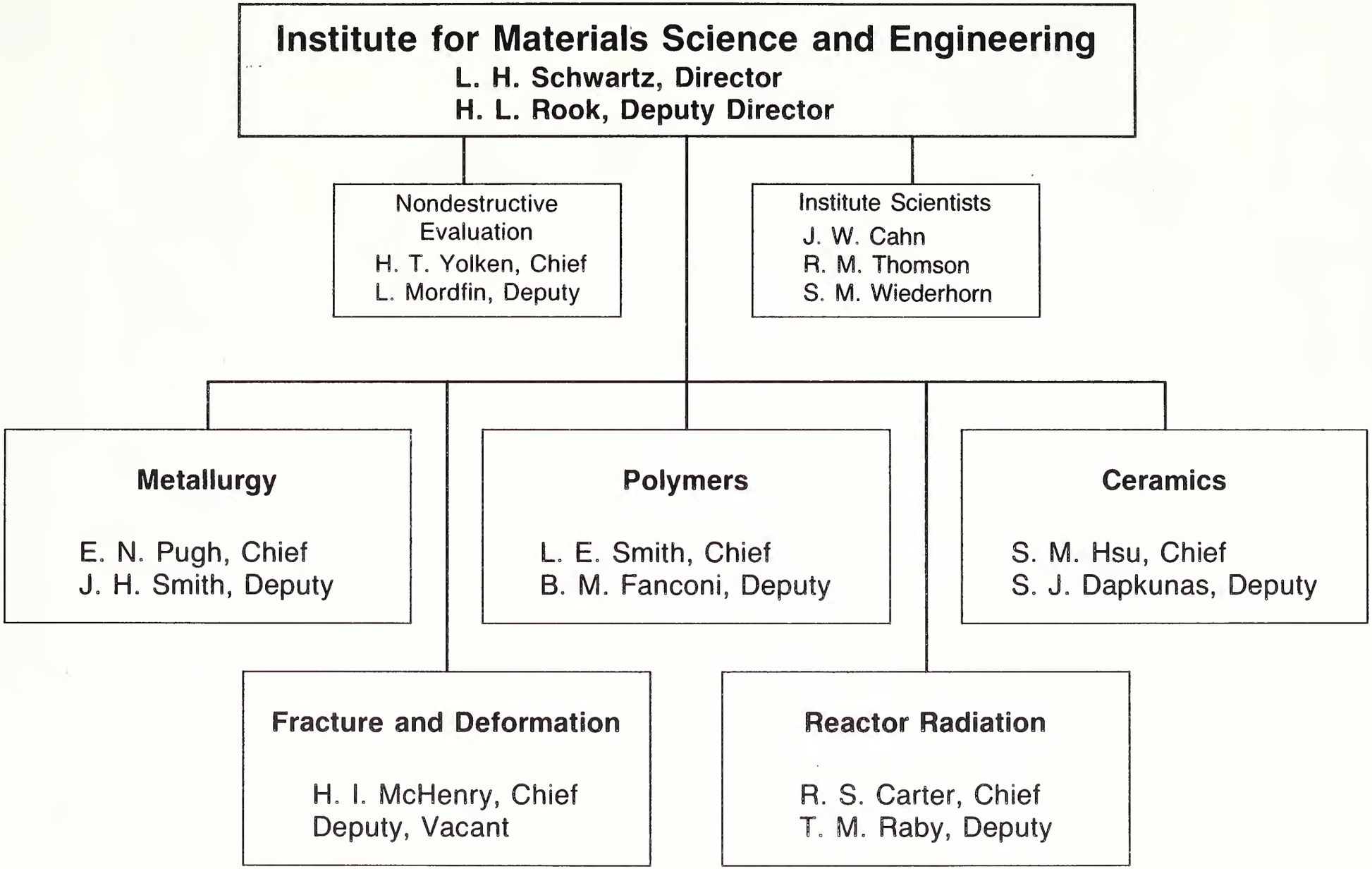
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11. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)*

Current programs of the Ceramics Division are reviewed.

12. KEY WORDS *(Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)*

Advanced Ceramics; Data Bases; Electronic Ceramics; Mechanical Properties; Optical Materials; Powder Processing/Characterization; Tribology; Superconductors; Synchrotron Radiation

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