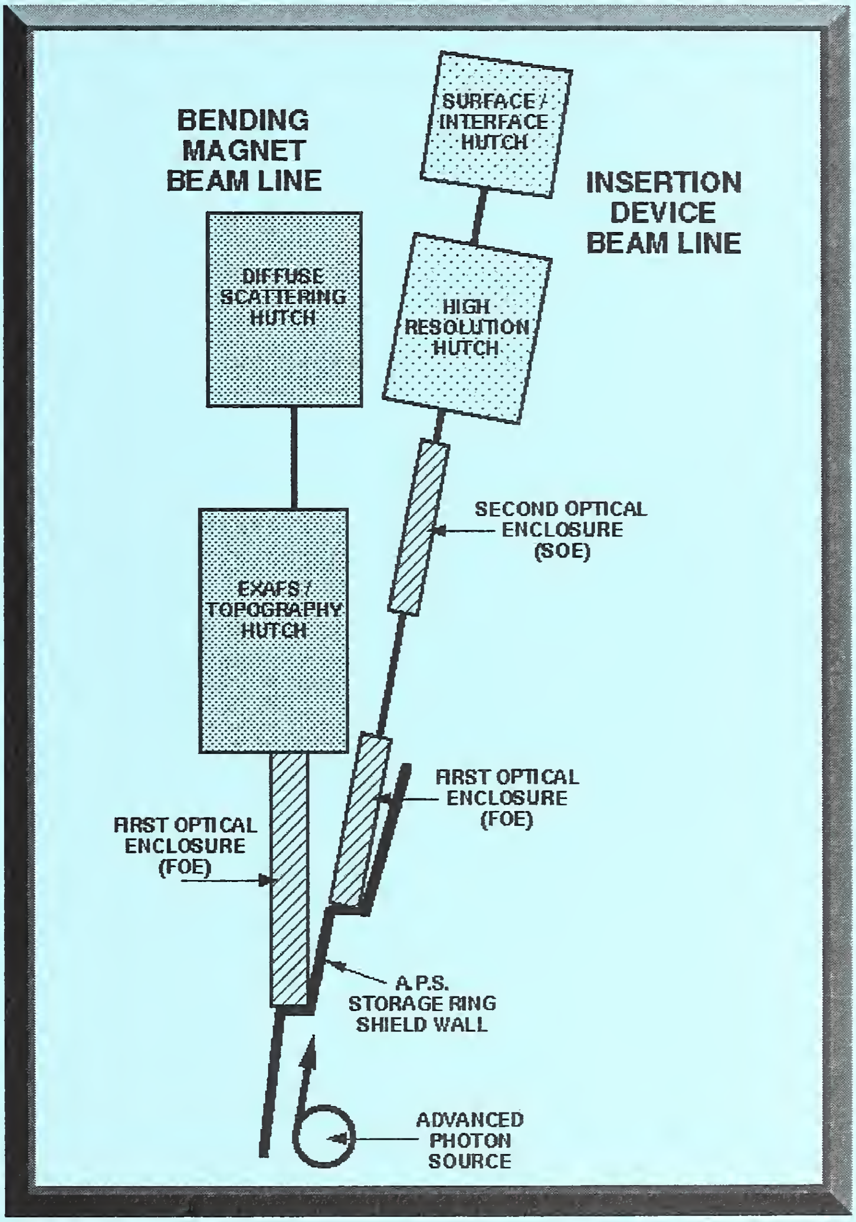
MSEL
Materials Science and Engineering Laboratory

# CERAMICS






NISTIR 5962
U.S. Department of Commerce
Technology Administration
National Institute of Standards
and Technology

# Technical Activities 1996

Ceramics

Floor plan of the UNI-CAT beam line on Sector 33 of the Advanced Photon Source at Argonne National Laboratory. MSEL is a 30% partner in the construction and operation of UNI-CAT. On the insertion device line, there are two enclosures of the optics (for filters, mirrors, and crystal monochromators) and two experimental stations: a high-resolution diffraction station and a surface/interface diffraction station. On the bending magnet line, there is one optical enclosure and two more experimental stations: a EXAFS/x-ray topography station and a diffuse scattering station.

MSEL

Materials Science and Engineering Laboratory

# CERAMICS

S.W. Freiman, Chief
S.J. Dapkunas, Deputy

NISTIR 5962
U.S. Department of Commerce
Technology Administration
National Institute of Standards
and Technology

# Technical Activities 1996

**U.S. DEPARTMENT OF COMMERCE**
**Michael Kantor, Secretary**
**TECHNOLOGY ADMINISTRATION**
**Mary L. Good, Under Secretary for Technology**
**NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY**
**Arati Prabhakar, Director**

# TABLE OF CONTENTS

# EXECUTIVE SUMMARY

The 1996 NIST Ceramics Division Report is organized in the form of programs, emphasizing a desire to develop more extensive collaborations among both Division and Materials Science and Engineering Laboratory personnel, and to conduct focussed activities on a scale that can lead to greater benefits for the U.S. advanced ceramics community. At the same time, we continue to maintain a Division management structure in the form of scientific-discipline-based Groups.

The technical programs of the Division are made up of projects whose primary goal is the understanding of materials phenomena essential to the development of measurement techniques and standards. The participation of U.S. industry in all phases of the research has been strongly encouraged, as typified by the consortium on Machining of Ceramics. Standard Reference Materials and Standard Reference Data remain important outputs of the Ceramics Division efforts.

We continue to monitor the direction of U.S. industrial interests in ceramic materials. Based on these observations as well as other inputs from industry and academia, a shift in emphasis within the programs of the Ceramics Division has been effected over the last few years from materials and processes relevant to structural applications to those of primary importance for electrical, thermal, and optical functions, and, in turn, to expanded research in ceramic coatings and films.

A significant change in staff occurred during the past year. Subhas Malghan, the former Leader of the Powder Characterization and Processing Group, left the Division to take another position at NIST. He has been replaced by Dr. George Onoda who was previously at Alfred University, and who has an international reputation in the area of ceramic processing.

The Ceramics Division had the following significant accomplishments during FY 1996.

- Determination of the primary crystallization field of the BiSCCO 2212 ($T_c$ = 90 K) superconductor in air and in the presence of silver impurities has been completed. These data can be used to create "processing maps" for the superconducting phases, thereby assisting wire developers in synthesizing higher quality materials.

- An improved cutting fluid chemistry was developed, and has been tested in a plant trial in the machining of cemented tungsten carbide cutting tool inserts. Use of the new cutting fluid resulted in the reduction of the diamond wheel dressing cycle from one per 30 inserts to one per 500.

- A consortium of six orthopaedic joint manufacturers was formed with NIST, including the Polymers and Ceramics Division of MSEL, to develop rapid, economic wear test methods for biomaterials. The consortium will support measurement method development in order to promote faster materials introduction and improved wear control.

- An experimental determination of the phase diagram for the $SrO:TiO_2:Nb_2O_5$ system has been completed. Of particular interest in this system are compounds in equilibrium with $SrTiO_3$, a microwave ceramic requiring second-phase compensation of its large positive temperature coefficient of permittivity. Twelve hitherto unreported ternary compounds have been confirmed, some of which show potentially useful microwave properties.

- Standard Reference Material (SRM) 1982, Zirconia Thermal Spray Powder - Particle Size Distribution, was produced in cooperation with fourteen companies representing various segments of the thermal spray community. This SRM will be used in the thermal barrier coating industry where particle size distribution is an important process control parameter.

- Working with five industrial partners, NIST researchers demonstrated the capability for non-destructive, ultrasonic measurements for characterization and control of aqueous slurries of silicon used in processing reaction bonded silicon nitride. As a consequence, collaborators are investigating slurry chemistry variations to increase process control.

- An object-oriented finite element code (OOF) has been developed to help materials scientists calculate macroscopic properties from microstructural images. Material properties are assigned to all parts of an image; finite element calculations are then performed using appropriate boundary conditions. This code is available as public domain software on the World Wide Web.

- Version 2.0 of the High $T_c$ Superconductor Database was published in a software package that runs on personal computers. This Database provides a full range of structural, thermal, and mechanical property information in addition to superconducting properties for more than 150 chemical families.

- The use of small-angle neutron scattering has enabled NIST researchers to unravel the orientation dependence of cracks and pores in plasma spray coatings, and to relate these to fabrication and processing parameters.

- Diffraction imaging carried out on the NIST beamline at the National Synchrotron Light Source has led to the first direct observation of photorefractive gratings placed within oxide crystals enabling them to be used for information storage. The observation of these gratings allows the influence of crystal defects on the storage process to be determined.

- In collaboration with a major engine manufacturer, failure mechanism maps were constructed from creep and creep rupture data on two candidate silicon nitride materials. These maps are being used by the company in their design of auxiliary power turbines.

Stephen W. Freiman
Chief, Ceramics Division

# TECHNICAL ACTIVITIES

# CERAMIC COATINGS

# CERAMIC COATINGS

The Ceramic Coatings Program is a measurement and characterization effort which addresses the processing reproducibility and performance prediction issues associated with, primarily, thermal-spray deposited ceramic coatings. The program focuses on plasma-spray-deposited ceramic thermal barrier coatings used in aircraft gas turbines and expected to be used in land-based turbines and diesel engines. Sales in the thermal-spray industry are currently valued at over one billion dollars annually, a significant portion of which is ceramic thermal-barrier coatings. Collaborations have been established with industrial organizations including Pratt and Whitney, General Electric, Caterpillar, METCO, MetTech and Zircoa as well as the Thermal Spray Laboratory at the State University of New York at Stoney Brook and the Thermal Spray Laboratory at Sandia National Laboratory. The program includes collaboration with the National Aerospace Laboratory and the National Mechanical Engineering Laboratory, both in Japan, to examine functionally gradient materials.

Participants in the NIST program are located in the Ceramics, Materials Reliability and Reactor Radiation Divisions of the Materials Science and Engineering Laboratory as well as the Chemical Science and Technology Laboratory.

The approach taken in the plasma-spray (PS) research has been to build on the analytical capabilities at NIST and the material processing capabilities of collaborators. The program has the following elements:

- development of techniques for characterization of physical and chemical properties of stabilized zirconia feedstock to provide data for increased processing reproducibility as well as data required for production of a standard reference material suitable for calibration of light-scattering size distribution instruments used in industry for analysis of PS powder;
- development of scattering techniques to determine the quantity, size and orientation of porosity and microcracks in PS ceramic coatings suitable for use in modeling the thermomechanical behavior of these materials;
- development of methods to measure chemical, elastic modulus, and thermal properties on a scale suitable for use in microstructural models of behavior;
- development of techniques to model thermomechanical behavior of thermal-barrier coatings to enable more reliable performance prediction; and
- development of techniques for accurate measurement of the thermal conductivity of PS coatings, by use of the guarded hot-plate technique suitable for incorporation in ASTM standards and by the pulsed laser heating technique, to provide a method for comparison with routine industrial techniques.

- development and refinement of more sensitive methods for accurate analysis of oxide phases and residual stresses which affect performance and durability of coatings.

Research on chemical mapping of powders and microstructures is conducted in the Microanalysis Division of the Chemical Science and Technology Laboratory. Thermal property research is conducted in the Materials Reliability and Metallurgy divisions and the Reactor Radiation Division participates in both the powder analysis and scattering projects. A strong attribute of the PS coatings research is the use of common materials for which complementary data can provide a more complete understanding of processing-microstructure-property relationships.

**PROGRAM TITLE:** Ceramic Coatings

**PROJECT TITLE:** Characterization of Thermal Spray Zirconia Powders

**Principal Investigators:** Stanley J. Dapkunas, Patrick Pei, James F. Kelly, Judith Stalik (Reactor Radiation Division) and Eric Steel (Chemical Science and Technology Laboratory)

**Technical Objective:**

This research is conducted in cooperation with the thermal spray industry, universities and government laboratories. Feedstock powders are an important determinant of the final microstructure, and hence properties, of thermal barrier coatings. Important powder characteristics include particle size distribution, chemistry, phase content, flow and thermal properties.

Collaborative research has emphasized NIST powder characterization and plasma spray deposition by others with joint analysis to relate powder properties to process parameters, microstructure and performance. Earlier research with Pratt & Whitney addressed the role of organic binders in zirconia feedstock on the thermal shock behavior of coatings. Recent research has been conducted in cooperation with a broad range of powder producers, plasma spray equipment and analytical instrument manufacturers, and coatings producers. This research culminated in the development of SRM 1982 for the calibration of particle size distribution measurement instruments.

The program attempts to develop a comprehensive understanding of the interrelationshpis between powder, deposition behavior and microstructure/properties. This is accomplished by conducting a broad range of characterizations on a given powder or deposit. In this vein, additional research in collaboration with the Sandia National Laboratory has utilized the same powder (SRM 1982) to determine the role of size fractions on behavior in the plasma spray process. Parameters studied at Sandia included particle temperature and velocity distributions and well as spacial distributions in the plasma plume. Research is underway at NIST to characterize these coating deposits for microstructural and chemical inhomogeneities as well as elastic modulus.

**Technical Description:**

This research has been conducted in cooperation with the thermal spray industry. The research includes the development of techniques to determine the binder content of powder and to relate the effect of that constituent on thermal shock behavior as well as the development of particle size distribution Standard Reference Material for the calibration of light scattering instruments used in the industry. The availability of this SRM allows improved process control and deposition efficiency.

**External Collaboration:**

Technical collaboration with organizations representing engine manufacturers, material manufacturers, spray equipment and instrument suppliers includes: Pratt & Whitney, General Electric, Caterpillar, Praxair, Metco, Zircoa, TAFA, Metech, H. C. Stark, Leeds and Northrup, Horiba, Sandia National Laboratory, and the State University of New York at Stony Brook.

**Planned Outcome:**

The planned outcome of this research is the development of analytical methods which will enable manufacturers to improve process and material specifications.

**Accomplishments**:

- An empirical relationship between the binder content of spray dried zirconia and thermal shock behavior of coatings was established.

- SRM 1982, Plasma Spray Zirconia-Particle Size Distribution was completed.

- Collaborative research with Sandia National Laboratory was conducted under the auspices of a NIST/SNL memorandum of understanding (MOU) and the behavior of SRM 1982 feedstock in a plasma plume was determined as a function of size cut.

**Impact:**

Pratt & Whitney modified their spray dried zirconia feedstock binder content specification to improve coating performance as a result of this collaborative project.

**Publications:**

Characterization and Processing of Spray-Dried Zirconia Powders for Plasma Spray Application, P. Pei, S. G. Malghan, S. j. Dapkunas, and P. H. Zajchowski, Journal of Thermal Spray Technology, Volume 5 (3) September 1996, 343-351.

Analysis of Zirconia Powder for Thermal Spraying: Reference Material for Particle Size Distribution Measurement, P. Pei, J. Kelly, S. Malghan and S. Dapkunas, Proceedings of the National Thermal Spray Conference, October, 1996, "Thermal Spray: Practical Solutions for Engineering Problems", C. C. Berndt (Ed), ASM International, Ohio, USA, p263-273.

**PROGRAM TITLE:** Ceramic Coatings

**PROJECT TITLE:** Mechanical Property Evaluation and Test Development

**Principal Investigators:** Douglas T. Smith and Jay Wallace

**Technical Objectives:**

1. To use instrumented indentation to quantify hardness, Young's modulus, porosity and microcrack density in ceramic coatings, both to characterize as-prepared coatings and to quantify damage evolution.

2. To collect experimental indentation data (load-displacement curves) and correlate them with analytical and numerical modeling of the indentation process, in order to better understand deformation mechanisms beneath indenters, particularly in film-substrate and multilayer systems.

3. To study the microstructural damage done during the indentation of brittle coatings and bulk material and, when possible, to correlate that damage with other material properties such as machinability and wear resistance that depend on microfracture processes.

4. To organize workshops and symposia that will bring the instrumented indentation community towards consensus on recommended test and analysis procedures, and to participate in indentation round robins.

**Technical Description:**

The program uses two instrumented indenters (one a commercial nanoindenter and one a NIST-modified microhardness machine) to probe the mechanical properties of bulk materials and thin films. Taken together, the two machines permit indentation studies at peak indentation loads ranging from 50 μN to 40 N, using Vickers, Berkovich and spherical diamond and WC-Co indenter tips. The resulting experimental load-displacement curves are analyzed to yield the hardness and Young's modulus of the material probed, as well as the energy absorbed in the indentation process.

The focus of the program is on the development of the *technique* of instrumented indentation, rather than the application of the technique to particular material systems. Although data are taken on specific materials of technological interest (*e.g.*, thermal barrier and wear-resistant coatings, dental restoration materials), primary interest is in model experimental systems and in the modeling of the indentation process, particularly for layered systems. International workshops, symposia, and round robin standards testing are organized and executed in an effort to guide the instrumented indentation community toward greater standardization in data analysis, and to expand the range of mechanical property characterization possible with the technique.

**External Collaborations:**

1. National Physical Laboratory, U.K. and Tokyo University: Design and execution of VAMAS instrumented indentation round robin testing of model film-substrate systems.

2. Federal Institute for Materials Research and Testing (BAM), Berlin: Development of reference coatings using indentation and spectroscopic ellipsometry.

3. Praxair Surface Technologies: Characterization of TiN and CrN coatings developed as replacements for chrome plating in wear applications.

4. Department of Material Science and Bioengineering, AIST, MITI, Japan: Study of functionally graded materials prepared by plasma arc sintering.

5. Kansas State University and Naval Research Laboratory: Mechanical properties studies of group III nitride thin films (AlN, BAlN, InN) for electronic and optoelectronic applications.

6. Johns Hopkins University: Mechanical properties studies of nanocrystalline iron films.

**Planned Outcomes:**

Reliable mechanical property data at small length scales will aid designers of thin-film and multilayer structures while the use of instrumented indentation to introduce and quantify microcrack damage may lead to the use of the technique to predict wear resistance and fracture toughness easily.

The standardization of the analysis of instrumented indentation data will lay the groundwork for a reliable, quantitative description of the mechanical properties of coatings, thin films and surface treatments. It is expected to have a significant impact in the coatings industry because it will, for the first time, give both producers and consumers of coatings a set of well-defined mechanical properties that can form the basis for comparison of coatings and other surface treatments.

Recommended guidelines for instrumented indentation testing and analysis procedures will help researchers with different indentation systems at different laboratories compare results effectively.

**Accomplishments:**

In collaboration with the National Physical Laboratory in England and Tokyo University, a new VAMAS Technical Working Area has been started (TWA 22: Mechanical Properties of Thin Coatings), and the first project has begun (Hardness and Modulus Measurement Using Depth Sensing Indentation). Sets of film/substrate specimens are being prepared for distribution in December, 1996.

Extensive measurements have been made of the mechanical properties of several zirconia air-plasma-sprayed thermal barrier coatings. Elastic properties are seen to be anisotropic, in agreement with neutron scattering results. The coatings are also seen to be stiffer after heat treatment, a result that also is consistent with neutron scattering results showing that microcrack density drops after annealing.

One symposium on mechanical property testing for coatings was held as part of the International Conference on Metallurgical Coatings and Thin Films, April, 1996, in San Diego. Another is currently being organized for April, 1997.

**Publications:**

D.T. Smith, "Conference Report: International Workshop on Instrumented Indentation." *J. Res. Natl. Inst. Stand. Technol.* **101**, 77 (1996).

"Conference Proceedings: International Workshop on Instrumented Indentation." D.T. Smith, Ed., NIST Special Publication 896 (1996).

J.H. Edgar, C.A. Carosella, C.R. Eddy and D.T. Smith, "Effect of Beam Voltage on the Properties of Aluminum Nitride Prepared by Ion-Beam-Assisted Deposition," *J. Mater. Science: Electronic Materials* 7, 247-253 (1996).

J.B. Savader, M.R. Scanlon, R.C. Cammarata, D.T. Smith and C. Hayzelden, "Nanoindentation Study of Sputtered Nanocrystalline Iron." Accepted by *Scripta Mater.*

J.H. Edgar, D.T. Smith, C.R. Eddy, C.A. Carosella and B.D. Sartwell, "C-Boron-Aluminum Nitride Alloys Prepared by Ion-Beam-Assisted Deposition." Accepted by *J. Mater. Science: Electronic Materials.*

J.H. Edgar, C.H. Wei, D.T. Smith, T.J. Kistenmacher and W.A. Bryden, "Hardness, Elastic Modulus and Structure of Indium Nitride Thin Films on AlN-Nucleated (00.1) Sapphire Substrates." Submitted to *J. Applied Phys.*

**PROGRAM TITLE:** Ceramic Coatings

**PROJECT TITLE:** Modeling of Coating Microstructure and Failure

**Principal Investigator:** Edwin R. Fuller, Jr., W. Craig Carter, and Andrew Roosen

**Technical Objectives:**

This research is designed to assist industry in developing new paradigms for elucidating micro-mechanical behavior, fracture, deformation, damage, and other nonlinear phenomena, in real and simulated microstructures of ceramic coatings A technique for obtaining average linear response from a particular microstructure is envisioned. Predictions of response for simulated and digital representations of actual microstructures with subsequent comparison to measured properties are a primary goal. Efficient storage and microstructural representation techniques will be developed. The goal is the development of a set of tools which all materials scientists can and will want to use.

**Technical Description:**

This research models the mechanics and physics of the heterogeneous microstructure of ceramic coatings at the mesoscopic level and develops computationally efficient algorithms and computational codes for simulating the micro-mechanical behavior of these materials. New methods are developed to simulate concurrent physical phenomena in realistic coating microstructures. Surface and sub-surface damage of thermal barrier coating systems produced by contact loading is quantified using the finite element method. Additionally, the project seeks to develop computationally efficient algorithms for simulations of the microstructural development in these materials.

**External Collaborations:**

Chuanshu Ji and Robert Derr, Dept. of Statistics, University of North Carolina, Chapel Hill, NC are collaborating with E. R. Fuller on the development of mathematical methods of modeling microstructures.

**Planned Outcome:**

A new paradigm for materials calculations is foreseen through the development of the computational tools which will forge this paradigm shift. The tools could be further developed by third parties and potentially lead to new commercial ventures associated with software repackaging. Finally, inexpensive means by which industry may test and design new coating microstructures are envisaged.

A two-dimensional or three-dimensional finite element model is expected to be developed which is capable of predicting the damage zone underneath the indenter as a function of loading history including loading and unloading. Effects of indenter geometry, coating/substrate materials elastic/plastic properties, damage characteristics as well as film thickness on the damage state are expected to be investigated.

**Accomplishments:**

An object-oriented finite element code (OOF) has been developed, and several case studies involving coating microstructures have been performed. OOF is really two different programs (*ppm2oof* and *oof*) which are designed to help materials scientists calculate macroscopic properties from images (pictures) of microstructures. The *ppm2oof* code operates on ppm (Portable Pixel Map) graphics files, assigning material properties to various microstructural features in a graphical image of a microstructure. The goal is to assign material properties to all parts of the image and then write a file which the program, *oof*, uses as an input. The *oof* code performs finite element calculations on the processed image, applying appropriate boundary conditions, temperature changes, and distortions. *ppm2oof* and *oof* are public domain codes, which were written at NIST by Steve Langer of the Applied and Computational Mathematics Division ( ITL), Craig Carter, and Andy Roosen.

Using OOF, averaged elastic behavior of thermal barrier coatings was calculated on a microstructural basis from digitized images and compared with experimental measurements. The computational simulations were performed on random regions from a micrograph of polished sections of a zirconia plasma sprayed coating. Both plan and section views were considered. Elastic properties were treated as orthotopic in the plane. Experimental measurements were performed via Hertzian indentation with a spherical indenter on an instrumented micro-hardness machine. The specimen area sampled for both the simulations and the experiments was approximately 0.01 $mm^2$. Other studies examined the influence of observed porosity fluctuations on the elastic behavior.

Codes were developed in collaboration with Prof. Chuanshu Ji and Robert Derr of the University of North Carolina, Chapel Hill, to generate computer simulated microstructures of plasma sprayed coatings. Currently, statistical aspects of these simulated microstructures are being investigated, but we anticipate using these virtual microstructures as input into OOF to elucidate the influence of various microstructural features on coating properties and performance.

**Publications:**

The important output derived from this project is the computer code: OOF (Object-Oriented Finite Elements), which is currently available for alpha-testing. The binary code can be downloaded from the NIST Center for Theoretical and Computational Materials Science (CTCMS) software archives on the Internet. A short description and links to the archives are located at Internet address: http://www.ctcms.nist.gov/~wcraig/oof.html. Although OOF currently runs only on SGI workstations, work is underway for porting the code to other Unix platforms.

**PROGRAM TITLE:** Ceramic Coatings

**PROJECT TITLE:** Processing/Microstructure Relationships in Plasma-Sprayed Coatings

**Principal Investigators:** Gabrielle G. Long, Andrew J. Allen, and Jan Ilavsky

**Technical Objectives:**

The object of this research is to develop techniques for the analysis of microstructure of plasma sprayed coatings. As is the case for many materials, the microstructure of plasma-sprayed ceramic deposits governs their properties. In an effort to study how the plasma-sprayed microstructure is formed, we have been studying the anisotropic small-angle neutron scattering by these materials. Neutron scattering techniques offer an opportunity for quantitative and nondestructive microstructure characterization. In the case of these coatings, there are two void systems - interlamellar pores (parallel to the substrate) and intralamellar cracks (perpendicular to the substrate) - which can each be separately and quantitatively characterized.

**Technical Description:**

Several spray and postprocessing parameters have been studied during the development and testing of this technique. The difference in the microstructure of plasma sprayed alumina and zirconia (actually yttria-stabilized zirconia, YSZ) deposits was found to be an important issue in explaining the formation of intralamellar cracks. Crack surfaces in alumina deposits are a significantly larger fraction of the total void surface area (~50%) than in YSZ deposits (~10%), probably as result of the greater brittleness of alumina.

**External Collaborators:** Christopher Berndt and Herb Herman, SUNY/Stoney Brook, and Alan Goland, Brookhaven National Laboratory are collaborating with the Ceramics Division on the processing-microstructural relationships utilizing small angle neutron scattering as the primary characterization technique.

**Accomplishments:**

The influence of the spraying method was studied by examining samples sprayed by water-stabilized plasma (WSP) and by gas-stabilized plasma (GSP). The differences in the microstructures formed by means of these two processes are due to the temperatures and speeds of impacting particles. For alumina, the WSP spraying (high-power, higher temperature and lower impact speed) resulted in a larger proportion of cracks in the void system, the surfaces of which were about 80% of the total surface area in the microstructure. This indicates that interlamellar contact in WSP deposits is better and therefore cooling stresses, which cannot be relaxed by sliding of splats, result in cracking. For YSZ the differences in the microstructures produced by WSP and GSP were less pronounced, and the crack surface area fraction was between 10% and 20% of the void surface area for all samples.

The influence of the spray angle between the axis of the plasma torch and the substrate is important because there can be only limited control of this parameter for complex substrate shapes. Alumina deposits sprayed by means of WSP showed a strong dependence of the crack system, as well as total porosity, on the spray angle. The microstructure of the interlamellar pore system, on the other hand, showed no dependence on the spray angle. YSZ deposits, sprayed by GSP, displayed negligible dependence on the spray angle. The different relationship between the two void systems and the spray angle is a new result which indicates that spraying complex shapes with YSZ may be relatively simple, while spraying the same shapes with alumina may be significantly more challenging.

A new, unexpected, result was obtained in the latest experiments on the microstructural changes in YSZ deposits during annealing. YSZ deposits are commonly used as thermal-barrier coatings (TBCs), where they are exposed to temperatures 1100 °C - 1400 °C. The changes in the microstructure of TBCs as a function of temperature are complex and depend on the whole coating/bond coat/substrate assembly as well as on the environment and heating and cooling conditions. We tested free-standing samples of YSZ deposits to study the behavior of the ceramic layer only. Such data are pertinent for modeling of properties and lifetime predictions. Different kinetics in the two void systems were found. The interlamellar crack system was sintered away at relatively low temperatures (below 1100 °C) whereas changes in the intralamellar pore system occurred slowly at higher temperatures. At about 1100 °C the microstructure contained only intralamellar pores and was more anisotropic than in the as-sprayed condition. The anisotropy was retained even up to 1400 °C and the total surface area of these voids slowly decreased with temperature and time.

Studies such as these are expected to have a beneficial impact on structure optimization for coatings used in jet-, diesel-, and gas-engine and turbine applications. Improved microstructures can be expected to lead to increased fuel efficiency and increased coating lifetime.

**Publications:**

J. Ilavsky, A. J. Allen, G. G. Long, S. Krueger, H. Herman, C. C. Berndt, and A. N. Goland, "Anisotropy of the Surfaces of Pores in Plasma Sprayed Alumina Deposits", pp. 483-488 in *Thermal Spraying - Current Status and Future Trends*, Proceedings of the 14th International Thermal Spray Conference (Kobe, Japan, May 1995), Edited by A. Ohmori, High Temperature Society of Japan, Osaka, Japan, 1995.

G. G. Long, A. J. Allen and J. Ilavsky, Multiple small-angle neutron scattering (MSANS) and Ultra-small-angle X-ray scattering (USAXS): Application to Anisotropic Microstructures, presented at the March Meeting of the American Physical Society, March 1995. Abstract published in the Bulletin of the American Physical Society (March meeting) **40** (1), pg. 476 (paper J 28 5).

A. J. Allen, N. F. Berk, S. Krueger, G. G. Long, H. Kerch, and J. Ilavsky, "New Developments in Multiple Small-Angle Neutron Scattering Studies of Advanced Ceramics", MRS Symp. Proc. Vol. **376**, *Neutron Scattering in Materials Science, II*, (MRS, Pittsburgh, PA, 1995).

J. Ilavsky, A. J. Allen, G. G. Long, S. Krueger, C. C. Berndt, H. Herman, "Influence of the Spray Angle on the Pore and Crack Microstructure of Plasma Sprayed Deposits," *Journal of the American Ceramic Society*, in press.

J. Ilavsky, G. G. Long, A. J. Allen, H. Herman, C. C. Berndt, "The Effect of Spray Distance and Chemistry on Pore and Crack Development in Plasma-Sprayed Ceramic Deposits", NTSC'96.

J. Ilavsky, A. J. Allen, G. G. Long, H. Herman, and C. C. Berndt, "Characterization of the Closed Porosity in Plasma-Sprayed Alumina", submitted to *J. Mater. Sci.*

# CERAMIC MACHINING

# CERAMIC MACHINING

The Ceramic Machining Program was established in response to a comprehensive survey of the U. S. advanced ceramics industry indicating that the high cost of machining and at times uncertain reliability associated with machining damage are primary impediments to the widespread use of these materials. This program is designed to address generic industry needs related to measurement methods and standards in order to assist industry in the development of machining technology for the manufacture of reliable and cost-effective components made from advanced ceramics. The specific projects include: (1) effects of grinding on strength, surface roughness, and wear; (2) influences of finishing methods on strength and contact fatigue; (3) ceramics machinability database; (4) intelligent machining of ceramics; (5) chemical and chemomechanical effects of grinding fluids; and (6) abrasive finishing and wear of dental ceramics.

Current activities include those ceramics intended for structural applications, such as silicon nitride, and the ceramics used for dental restorations, such as machinable glass-ceramics. The first three projects are conducted jointly with the twenty-member Ceramic Machining Consortium with input from the Precision Engineering Division, the Statistical Engineering Division, and the Standard Reference Data Program. The consortium members, representing a broad spectrum of industry consisting of materials producers, machine tool builders, suppliers of expendables (such as grinding wheels and fluids), and end-users, participate by providing materials, testing, advice, and other in-kind contributions. The consortium members also provide input to the other three projects and assist NIST in formulating the scope of the research projects. The close working relationship developed between industry, academic institutions, and NIST not only ensures the relevance of the research projects but also promotes an efficient and timely transfer of research information to industry for implementation.

**PROGRAM TITLE:** Ceramic Machining

**PROJECT TITLE:** Ceramic Machining Consortium

**Principal Investigators:** Said Jahanmir, Lewis K. Ives, and Mario Cellarosi

**Technical Objectives:**

Advanced ceramics are being increasingly used in automotive, aerospace, and manufacturing applications due to their excellent wear and corrosion resistance. Examples include cutting tools, valves, bearings, and seals. Although these materials have attractive mechanical and chemical properties for such applications, the high cost associated with machining and sometimes an uncertain reliability due to machining damage have prevented their wide-spread use. During the past decade there has been a strong push toward net-shape processing of ceramics, for example by injection molding, but the tolerances and surface finish necessary for most precision components still requires considerable machining and finishing. The goal of this project is to assist industry in the development of machining technology for the manufacture of reliable and cost-effective components made from advanced ceramics. This project provides measurement methods and data to assess the influence of damage produced by high-rate machining on properties and performance of ceramics.

**Technical Description:**

Specific tasks during the reporting period consisted of the following: (1) Effects of Grinding on Strength and Wear of Silicon Nitride, (2) Influence of Finishing Methods on Surface Contact Fatigue of Silicon Nitride, (3) Ceramic Machinability Database, and (4) Standard Test Method for Assessment of the Effects of Machining Damage on Strength. These tasks were carried out jointly with the members of the Ceramic Machining Consortium. The consortium members provide in-kind contributions consisting of ceramic materials, diamond grinding wheels, sample preparation, testing, and input to the project direction.

**External Collaborations:**

Industrial and academic organizations participate in this project by joining the Ceramic Machining Consortium and signing a CRADA for joint research on specific research tasks. The following is a list of organizations that were members of the Consortium during the last year: Ceradyne, Inc.; Cercom, Inc.; Cincinnati Milacron, Inc.; Eaton Corporation; Ford Motor Company; General Electric Company; General Motors Corporation; Georgia Institute of Technology; Kansas State University; Landis / Western Atlas; Lehigh University; Norton Company; Stevens Institute of Technology; Technology Assessment and Transfer, Inc.; Torrington Company; University of Delaware; University of Maryland; University of Massachusetts; University of Rochester; and West Advanced Ceramics, Inc.

**Planned Outcome:**

Four major outcomes are expected from this program: (1) recommendations for selection of optimum grinding parameters to be used for specific silicon nitride ceramics, (2) guidelines on finishing methods to obtain damage-free nano-precision surfaces on bearing grade silicon nitride ceramics, (3) a PC-based database containing data and information on machinability of advanced ceramics, and (4) a recommended test procedure for the assessment of the effects of machining damage on strength.

**Accomplishments:**

The experimental phase of the task, to evaluate the effect of grinding on the strength of selected silicon nitride materials, was completed. The data from this study, which were generated in conjunction with members of the Ceramic Machining Consortium, were analyzed with the assistance of the NIST Statistical Engineering Division. The results clearly show the effects on fracture strength of batch-to-batch material variations, test repeatability, interlaboratory reproducibility, and machining conditions for three different silicon nitrides being considered for commercial applications by the consortium members. A comprehensive study of this type conducted by several laboratories/participants, which relies on statistical design of experiments, has not been performed before. The results showed no distinguishable change in fracture strength with different grinding conditions for the samples ground parallel to the tensile direction of the flexure test bars. Samples ground transverse to the tensile direction showed a substantial decrease in strength. Among the grinding parameters studied, wheel grit size had the greatest influence on strength. The strength of samples was lower when a wheel with coarse diamond grit was used for grinding. In addition to the effects on strength, wear tests on ground samples indicated an increased wear rate as the severity of grinding was increased, suggesting a deleterious effect of grinding-induced damage on wear.

In connection with the investigation of the influence of machining damage on rolling contact fatigue, test samples of a hot-isostatically pressed silicon nitride were prepared and distributed to the participating Consortium members. Three finishing methods: chemomechanical polishing, conventional bearing superfinishing, and magneto-rheological finishing are being used on the samples. An important requirement in this experiment is that sufficient material be removed during final finishing to eliminate all damage introduced by prior preparation steps. To evaluate the extent of this prior damage, flexure bars were made from one pre-finished blank. The flexure tests on these bars indicated that subsurface damage (i.e., microcracks) extended to about 50 μm below the surface. Based on this information, the participants have been instructed to remove at least 75 μm from the surface by their finishing method.

During the past year the database effort was focused on collecting data from the open literature. Based on the availability of information and the requirements for certain types of parameters, a minimum set of required information was determined. A Lotus spreadsheet data file was designed and constructed which included fifty-five fields of information applicable to ceramic grinding including; material identification and properties, grinding parameters and conditions, process outputs and results, and references and comments. After evaluating several hundred publications, about forty references were selected that met minimum requirements. More than four hundred data records were extracted from the papers and were entered into the spread sheet. The data were then examined and entries were corrected for errors; also inconsistent and/or duplicate data were removed. The next step in this project is to design a database structure and search strategy using a commercial database management software. All the evaluated data collected from the literature and those obtained at NIST will be added to the final version of the Ceramic Machinability Database.

Discussions have been initiated with the Advanced Ceramics Committee (C28) of ASTM regarding the need for a standard test procedure for the assessment of the effects of machining on strength of advanced ceramics. The test procedures that have been developed as a part of this project at NIST will be offered to ASTM for evaluation and potential standardization by ASTM.

The twelve companies that have signed CRADA's to join the Ceramic Machining Consortium and to participate in joint research, have direct access to the information generated in this project. The results are being used by the member companies to develop new ceramic materials, grinding wheels, and grinding fluids, and to optimize the manufacturing operations to develop cost-effective machining methods.

**Publications:**

The results of this research project are discussed with the industrial and academic partners on a semi-annual basis. In addition to these interactions, the NIST staff were invited to participate in more than a dozen conferences and technical workshops devoted to ceramic machining.

Technical Papers:

H. H. K. Xu, L. Wei, and S. Jahanmir, "Influence of Grain Size on Grinding Response of Alumina," J. Am. Ceram. Soc., 79 (1996) 1307-1313

H. H. K. Xu and S. Jahanmir, "Transitions in the Mechanism of Material Removal in Abrasive Wear of Alumina," Wear, 192 (1996) 228-232.

H. S. Ahn, L. Wei, and S. Jahanmir, "Non-Destructive Detection of Damage Produced by a Sharp Indenter in Ceramics," J. Eng. Materials and Technology, 118 (1996) 402-409.

T. J. Strakna, S. Jahanmir, R. L. Allor, and K. V. Kumar, "Influence of Grinding Direction on Fracture Strength of Silicon Nitride," J. Eng. Materials and Technology, 118 (1996) 335-342.

H. H. Xu, S. Jahanmir, and L. K. Ives, "Material Removal and Damage Formation Mechanisms in Grinding of Silicon Nitride," J. of Materials Research, 11 (1996) 1717-1724.

L. K. Ives, S. Jahanmir, L. M. Gill, and J. J. Filliben, "Effect of Grinding on Strength of a Sintered Reaction Bonded Silicon Nitride," Proceedings of the Second International Conference on Machining of Advanced Materials, Aachen, Germany, September 1996.

S. Jahanmir, "Ceramic Machining Research in the United States," Proceedings of the Second International Conference on Machining of Advanced Materials, Aachen, Germany, September 1996.

H. H. K. Xu, S. Jahanmir, and L. K. Ives, "Mechanisms of Material Removal in Abrasive Machining of Ceramics," Proceedings of the Second International Conference on Machining of Advanced Materials, Aachen, Germany, September 1996.

R. L. Allor and S. Jahanmir, "Current Problems and Future Directions for Ceramic Machining," Ceramic Bulletin, 75 (1996) 40-43.

H. H. K. Xu, S. Jahanmir, and L. K. Ives, Effects of Workpiece Properties on Material Removal Process and Damage Tolerance in Ceramic Grinding," Proceedings of Precision Grinding of Brittle Materials, Am. Soc. of Precision Eng., June 1996, Annapolis MD, 52-56.

T. J. Strakna, S. Jahanmir, R. Allor, and K. Kumar, "Effect of Grinding Strength of Silicon Nitride," Technical Papers of the North American Manufacturing Research Institution, (1995) 85-90, Society of Manufacturing Engineers, Dearborn, MI, Technical Paper No. MR95-138.

S. Jahanmir and L. K. Ives, "Machining of Advanced Ceramics," Tribology International, 28 (1995) 415-420.

H. H. K. Xu, N. P. Padture, and S. Jahanmir, "Effect of Microstructure on Material Removal Mechanisms and Damage Tolerance in Abrasive Machining of Silicon Carbide," J. Am.Ceram. Soc., 78 (1995) 2443-2448.

H. H. K. Xu, L. Wei, and S. Jahanmir, "Grinding Force and Microcrack Density in Abrasive Machining of Silicon Nitride," J. Mat. Res., 10 (1995) 3204-3209.

H. H. Xu, S. Jahanmir, and L. K. Ives, "Short-Crack Toughness and Abrasive Machining of Silicon Nitride," J. Am. Ceram. Soc, (1996).

Patent:

"Method of Fabricating Articles," U.S. Patent No.5,507,962.

**PROGRAM TITLE** Ceramic Machining

**PROJECT TITLE:** Chemical Effects of Machining

**Principal Investigators:** Stephen M. Hsu and Richard Gates

**Technical Objective:**

The goal is to develop a low cost machining technology using surface chemistry to enhance the machining rate and improve the surface quality of machined parts. Using conventional machining tools, the overall cost of machining ceramics should be lowered significantly.

**Technical Description:**

The project surveys a wide variety of chemical substances using a small bench top diamond cutter and an instrumented surface grinder. Test methods were developed to evaluate different substances in terms of the materials removal rates, surface finish, and amount of diamond worn during ceramic machining.

**External Collaboration:**

Russ Uphoster, Kennametal Inc., is cooperating in the industrial evaluation of chemically assisted machining of tungsten carbide.

**Planned Outcome:**

The viability of using chemistry to enhance machining rate, reduce surface defects while avoiding using modern ultra-stiff machining tools will make U.S. machining industry more competitive in the world market place. Ceramics, in particular, have long been prohibited from wide application due to high cost of fabrication. Availability of this technology will lower the cost substantially as evidenced by the plant trial.

**Accomplishments:**

Several substances were identified that can substantially increase the silicon nitride machining rate. These substances are environmentally friendly and non-toxic. A patent was disclosed. We are working closely with Kennemetal Corp. and in March 1996, a plant trial was conducted at a Kennemetal plant machining cemented tungsten carbide inserts. The plant trial was successfully concluded on August 23, 1996 after machining 170,000 inserts. The main benefit of the chemistry was to reduce the dressing cycle required to machine the parts to specifications. The maximum dressing cycle interval was increased from one dressing per 30 pieces machined to one dressing per 500 pieces machined.

Patents

U.S. Patent 5,447,466 Chemically Assisted Process for the Machining of Ceramics was granted on Aug. 15, 1995.

A process to assist machining of ceramics using chemicals, patent disclosure filed in NIST in Oct. 1996.

**Publications:**

Wang, J. and Hsu, S. M., "Chemically Assisted Machining of Ceramics," J. of Tribology, 116, 423-429, 1994.

Hsu, C. J., Wang, J. C., and Hsu, S. M., "Chemically Assisted Machining of $Si_3N_4$," Advances in Science and Technology 9, High Performance Materials in Engine Technology, P. Vincenzini, Editor, Techna, 1995.

Ying, T. N. and Hsu, S. M., "Chemical Effects in Ceramic Grinding," Proceedings of the JST International Tribology Conference, Vol. 3, p. 1725-1730, Jap. Soc. of Trib., Tokyo, Japan, 1966.

**PROGRAM TITLE:** Ceramic Machining

**PROJECT TITLE:** Intelligent Machining of Ceramics

**Principal Investigators:** Said Jahanmir and Tze-jer Chuang

**Technical Objective:**

The current practice of grinding, as applied to ceramics, is labor-intensive and operator-dependant. Since grinding can introduce surface and subsurface damage in the form of microcracks, residual stresses and phase changes (in some ceramics), operators take a conservative approach, using a "slow" grinding process, which further increases the cost of ceramic components. The objective of this project is to develop measurement methods and models needed for a sensor-based intelligent grinding process that can be used to optimize the machining process, such that ceramic components can be machined at a high rate without detrimental machining-induced damage.

**Technical Description:**

Grinding, by definition, is a process where removal of material takes place at individual contacts made between the abrasive particles in the grinding wheel and the workpiece. As the wheel engages the workpiece at a predetermined depth of cut (or down feed) each contact point experiences a set of normal and tangential forces. Summation of all the forces associated with the individual contact points gives the overall macroscopic grinding forces that can be measured by an appropriately configured force transducer. The specific activities in this project consist of the following: (1) mechanics-based model for prediction of surface and subsurface grinding damage, (2) in-process measurement of wheel topography, (3) measurement of grinding forces and correlation with wheel topography, (4) stochastic model for damage formation in grinding, and (5) prediction of fracture strength of ground samples.

**External Collaborations:**

This research is coordinated with the present activities of the NIST Ceramic Machining Consortium.

**Planned Outcome:**

The expected outcome from this project is a methodology for intelligent grinding of ceramics, consisting of sensors for monitoring the wheel topography and grinding forces, a damage formation model for grinding with wheel topography and grinding forces as inputs, and a strategy for on-line modification of grinding parameters to avoid subsurface damage and attendant low strength.

**Accomplishments:**

A two-dimensional finite element model was constructed to model the forces produced between the grinding wheel and the workpiece in addition to the deformation field and stresses produced in the workpiece. The input parameters for the model included both material properties and grinding parameters. For a given set of input parameters, the model predicts the vertical and horizontal forces imposed by the grinding wheel. The deformation and the stress fields created in the workpiece were calculated. The results indicated that, for a sintered reaction bonded silicon nitride, the high shear stresses in the cutting zone could control the mode of failure and result in the formation of microcracks and removal of material by a microfracture process. The forces on the workpiece computed from the finite element model were equivalent to the measured grinding forces.

**PROGRAM TITLE:** Ceramic Machining

**PROJECT TITLE:** Machining of Dental Materials

**Principal Investigator:** Said Jahanmir

**Technical Objective:**

The purpose of this research is to assess the influence of machining damage on strength and wear of dental ceramics.

**Technical Description:**

The use of ceramics for dental restorations has been on a rapid rise in recent years due to their desirable aesthetics and durability. The conventional approach for preparing a ceramic restoration, for example a crown, consists of first taking an impression of the clinically prepared tooth (or teeth), followed by preparation of a mold for casting. The cast crown is then shaped by a finishing process, which involves grinding and polishing, prior to fixation into the patients oral cavity. As a final step, the dentist finishes the contacting surfaces with a dental handpiece to ensure a good fit. This sequence of events is time consuming and expensive. In a recently developed procedure, the dental restorations are prepared by a machining process using a computer aided design and machine technique, which is a well developed method in manufacturing. Application of machining to ceramics, however, requires data and information on machinability as well as on the effects of machining on strength, wear resistance, and contact fatigue of ceramics. Most premature clinical failures have been observed to result either from processing defects in the material, damage produced by machining, or from wear.

Abrasive machining by means of grinding with diamond particles is a process routinely used in dental laboratories for shaping of ceramic restorations and in dental clinics for tooth preparation and finishing of ceramic restorations. The surface and subsurface damage produced by the cutting action of diamond particles can be detrimental to the strength and clinical performance (e.g., wear) of restorations. The specific tasks during this reporting period consisted of the following: (1) Influence of Microstructure on Mechanical Properties and Abrasive Machining, (2) Relationship Between Microstructure and Wear Resistance, and (3) Machining Damage in Enamel Associated with Clinical Tooth Preparation.

The subsurface damage in tooth enamel due to tooth preparation with diamond burs was also evaluated using a recently-developed technique for subsurface damage evaluation. The specimens were prepared by sectioning human third molars and cementing together highly polished sections. These "bonded-interface" specimens were machined, then separated, and the polished surfaces examined using both light microscopy and scanning electron microscopy. Tooth preparation was carried out with respect to two enamel rod orientations. Four clinical diamond burrs (coarse, medium, fine, and superfine) were used sequentially in a dental handpiece. Tooth preparation with the coarse diamond burr produced relatively large median-type cracks in enamel. Finishing with fine diamond burrs was effective in crack removal. In order to investigate the influence of machining parameters on the extent of damage in a more controlled manner, four grinding wheels each containing a different diamond particle size were used in a surface grinder at three different depths of cut. Crack lengths were significantly smaller for finer than coarse diamond abrasive particles, while variations in depth of cut did not influence crack size. It is concluded that relatively large subsurface cracks can be produced during clinical tooth preparation and cracks can be longer in certain orientations.

The overall program in which this project is a participant is unique as it brings together a diverse group of scientists and engineers with backgrounds in materials science, tribology, mechanical engineering, physics, chemistry, and dentistry. This diverse group meets once a month to exchange information and plan future research activities. These meetings are highly beneficial for cross-fertilization of ideas and transfer of information between the different disciplines. The team members have been participating in workshops and conferences related to their respective fields of expertise as well as those outside their field for information exchange with their colleagues. In addition, the three international companies that provide materials for research receive the data and information generated in this program for their internal use in microstructural design of dental ceramics.

**External Collaborations:**

This project is an integral part of a larger program funded at the University of Medicine and Dentistry of New Jersey by the National Institute of Dental Research to evaluate the relationship between the microstructure of dental ceramics and their machinability and mechanical properties. NIST Ceramics Division (S. Jahanmir) and MSEL (B. Lawn) are participating in this program together with the University of Maryland at College Park (Departments of Mechanical Engineering and Materials Science), the University of Maryland at Baltimore (Department of Restorative Dentistry), and the Naval Dental School (Department of Prosthodontics). In addition to the academic collaborators, four industrial companies participate in this program by providing ceramic materials and special cutting tools. The companies include: Corning, Inc.; Vita Zhanfabrik; Career, and Technology Assessment and Transfer, Inc.

**Planned Outcomes:**

This project will provide (1) recommendations for microstructural design of dental ceramics for best overall performance, and (2) guidelines for proper selection of machining parameters for use in abrasive finishing processes by dental technicians and dentists.

**Accomplishments:**

During this year, our studies were focused on mica-containing glass ceramics used in dental restorative applications for crowns, bridges, and inlays. These materials contain internally nucleated and crystallized mica platelet in a glass matrix having a composition approaching a trisilicic fluorophlogopite. The influence of microstructure on the abrasive machining and indentation response for the glass-ceramics was characterized. Wear experiments were conducted at a low sliding speed with distilled water lubrication using a pin-on-disk tribometer. The test parameters (e.g., load, speed, sliding distance, etc.) were selected to simulate typical oral conditions. Examinations of the wear scars on the samples and of the wear debris using a scanning electron microscope indicated that wear of these materials was dominated by a microfracture mechanism initiated either along the cleavage planes or the weak mica-glass interfaces. As the size of the mica platelet increased, wear rate also increased. Coarser microstructures exhibited a sudden transition in wear as the load was increased. The results suggested that wear of these machinable glass-ceramics was microstructure-dependent. Since there exists a trade-off between machinability and wear performance, the microstructure (i.e., the size of the mica platelet) must be optimized to obtain restorations with a high machinability rating and at the same time a suitably high wear resistance.

**Publications:**

In addition to the following technical papers, the NIST staff and Guest Researchers contributed more than ten technical presentations and poster sessions at various conferences and workshops.

H. H. Xu, D. Smith, and S. Jahanmir, "Microstructural Effects in Machining of Dental Glass-Ceramics," 5th World Biomaterials Congress, Toronto, Ontario, May 1996.

H. H. K. Xu and S. Jahanmir, "Scratching and Grinding of a Machinable Glass-Ceramic with Weak Interfaces and Rising T-Curve," J. Am. Ceram. Soc., 78 (1995) 497-500.

S. Jahanmir and X. Dong, "Wear Mechanisms of a Dental Glass Ceramic," Wear, 181-183 (1995) 821-825.

H. H. Xu, D. Smith, and S. Jahanmir, "Influence of Microstructure on Indentation and Machining of Dental Glass-Ceramics," Journal Materials Research, 11(1996) 2325-2337.

H. H. Xu, J. R. Kelly, S. Jahanmir, V. P. Thompson, and E. D. Rekow, "Enamel Subsurface Damage due to Diamond Teeth-Preparation," Journal of Dental Research, in review.

V. S. Nagarajan and S. Jahanmir, "Relationship Between Microstructure and Wear of Mica-Containing Glass-Ceramics," Wear, 200 (1996).

H. H. Xu, D. T. Smith, S. Jahanmir, E. Romberg, J. R. Kelly, V. P. Thompson, and E. D. Rekow, "Indentation Damage and Mechanical Properties of Human Enamel," Journal of Dental Research, in review.

# CERAMIC PROCESSING

# CERAMIC PROCESSING

Ceramic products are primarily produced by powder processing, where raw material powders are mixed with forming additives and shaped by various means into green bodies, which are then fired to the final, hardened state. The processing costs can vary greatly depending on the reproducibility and reliability of the process operation. One key to reliable and rapid development of new products is having good test methods to analyze the material at its various stages of processing. Unfortunately, no satisfactory measurement infrastructure yet exists within the ceramic industry, and as a result, much processing relies largely on art.

The program on ceramic processing focuses on measurement methods of generic value to all ceramic companies. Measurement needs, procedures and reliability must all be considered. The value of the measurement to the optimization of processing operations must also be assessed.

All subsequent operations depend on characteristics of the raw materials. Measurement of the physical and chemical properties of powders is therefore an important component of the program. The reliability of various measurement techniques is being assessed in a cooperative international program under the direction of the International Energy Agency and its subtasks on ceramic powder characterization which is being coordinated at NIST in the ceramic processing program. In addition, several SRMs are advancing to completion that are needed to calibrate the measurement instruments in use.

A second component within the program focuses on the properties of powders in aqueous media. A consortium effort has just been completed on electroacoustic measurements on powder suspensions, which provides information on the electrical interactions between particles and on the size distribution of particle flow units. Work to support an ATP program in aqueous injection molding and gel casting has also been completed, where new insights on the influence of organic and inorganic additives that cause or modify gelation and dispersion have been gained.

A modified mission has evolved and planning has been underway on establishing a new, large consortium among researchers at NIST, other federal laboratories, universities, and ceramic companies. The mission of this consortium will be to strengthen the measurement infrastructure in ceramic processing at an enhanced rate by organizing cooperative work among top researchers throughout the country. Teams will be formed to address specific issues concerning the reliability and reproducibility of commonly used instruments, and the development of new methods. A better understanding the relationship of measured properties on the behavior of materials at different stages of processing will result from these generic and nonproprietary studies. Now that the basic concept for the consortium has been formulated and discussed with many external researchers, efforts will continue toward establishing the consortium formally and effectively under the leadership of the ceramic processing program personnel at NIST.

**PROGRAM TITLE:** Ceramic Processing

**PROJECT TITLE:** Advanced Ceramic Processing

**Principal Investigator(s):** Pu-sen Wang, Vincent A. Hackley, and Subhas G. Malghan

**Technical Objectives:**

This project was designed to provide new insights on the physical and chemical interactions that take place in two innovative ceramic processing methods, namely aqueous injection molding and gel casting. The focus is on how water interacts in these processes during the formation of a green body and measurement methods that can reveal useful information.

**Technical Description:**

In collaboration with four ceramic companies, we investigated the application of solid state nuclear magnetic resonance (NMR) imaging to determine the state of water in green bodies and the spatial distribution of water. The bodies consist of ceramic powder, water, agar, and gels of water and agar. Water can exist in a free state (as in pure water), in bound states with agar or with the surface of the ceramic particles, and the distribution of all of the components in the body may not be uniform. NMR imaging has the ability to assess these states and distributions.

**External Collaborations:**

Collaborators include ATP awardees and members of the Intelligent Processing of Ceramics Consortium: these are Allied Signal Ceramic Components, Allied Signal Research Laboratories, Ceramatec and the Eaton Corporation.

**Planned Outcomes:**

Planned outcomes are the identification of the existing states of water and their spatial distribution in wet bodies produced from aqueous injection molding and gel casting. The results are expected to help the industrial collaborators identify processing problems so that they can be corrected, and to demonstrate the unique ability of NMR imaging to provide new insights on the chemical reactions and the inhomogeneities that occur during processing.

**Accomplishments:**

It was clearly demonstrated that the different states of water in green bodies can be identified.Two types of protons with distinct relaxation times were observed from the agar powder,O-H and C-H. The $^{1}H$ $T_2$ from water molecules in the gel was found to be shorter than that for pure water due to the proton spin exchange between free water and a small fraction of water interacting with polysaccharide networks. The relaxation rate was found to be directly proportional to the agarose concentration in the gels because of increasing exchange rate. When the gel was blended with an alumina powder, the free water was absorbed by the alumina powder surfaces and lost its molecular motion, existing in a bound state with an extremely short relaxation time.

The distribution of water in its various states were mapped adequately by $T_2$- weighted imaging. Three dimensional $T_2$- weighted mapping of $LiAlSiO_4/SiO_2$/agarose green gel compacts indicated an overall homogeneous distribution of water throughout the samples.

**Publications:**

Pu Sen Wang, " $^1H$ NMR Characterization of Aqueous Injection Molded Ceramics: Physical States of Water Molecules by Spin Relaxation and Water Distribution in Green Compacts by $T_2$-Weighted Imaging," submitted to J. American Ceramic Society.

Pu Sen Wang,"NMR Characterization of Silicon Nitride: Slurry Homogeneity by $T_2$- Weighted Proton Imaging," Submitted to J. Materials Science.

**PROGRAM TITLE:** Ceramics Processing

**PROJECT TITLE:** Development of Powder Characterization Procedures

**Principal Investigators:** Subhas G. Malghan and Lin-Sien Lum

**Technical Objectives:**

The objectives of this project conducted in cooperation with DOE and IEA are: (1)improvement of the precision of measurement of primary properties (physical, bulk chemistry and surface chemistry) of ceramic powders through tightening of previously developed procedures, (2) evaluation of the methods for measurement of the secondary properties (such as pH of slurries, rheology, green density and porosity of green ceramics) of ceramic powders.

**Technical Descriptions:**

The structural ceramics industry needs a set of commonly accepted procedures for measurement of powder properties. A series of programs was established for the development of pre-standards procedures for characterization of ceramic powders. The activities are conducted under the auspices of the International Energy Agency under the Annex II agreement. The current project, Subtask 8, has thirty-five laboratory participants in six countries (Belgium, Germany, Japan, Norway, Sweden and the U.S.) involved in an interlaboratory study of the characterization of powders.

**External Collaborations:**

This program is conducted in cooperation with industrial and academic research laboratories who participate in the round robin evaluation to determine the limits of applicability of several powder parameter measurement techniques. These include:

*United States*
Golden Technologies, Inc, Allied-Signal, Inc., W.R. Grace and Company, St. Gobain/Norton Industrial Ceramics Corporation, AlSiMag Technical Ceramics, Dow Chemical Company,

*Federal Republic of Germany*
Technische Hochschule Darmstadt, Fraunhofer-Institut für Keramische, VAW AG; Feuerfest-Prüflabor FPL, Robert Bosch
Hermsdorfer Institut für Technische Keramik, H.C. Starck,
Fraunhofer-Institut für Silicatforschung, BAM,

*Sweden*
Swedish Ceramic Institute; Institute for Surface Chemistry, PERMASCAND AB

*Japan*
JFCC, Nagaoka University of Technology, NGK Insulators, Ltd., Osaka National Research Institute, Asahi Glass Co., National Industrial Research Institute of Nagoya, NGK Spark Plug Co., Toshiba Corporation, Showa Denko K.K., Sumitomo Electric Industries,UBE Industries, Denki Kagaku Kogyo Co., Kyocera Corporation,

*Norway*
SINTEF, The Norwegian Institute of Technology

*Belgium*
VITO

**Planned Outcomes:**

Outcomes expected are: (1) further development of the initial procedures by the standards setting bodies in the individual countries,(2) refinement and further development of the measurement methods for the secondary properties, (3) development of standard reference materials using procedures from this subtask, and (4) international cooperation in the development of powder characterization procedures which will allow uniform, consistent analytical standards.

**Accomplishments:**

An international project on ceramic powder characterization has been recently completed. Countries participating in the joint project were Belgium, Sweden, Germany, Japan, and the United States. NIST served as the project coordinator. The project (Subtask 8) was conducted under the auspices of the International Energy Agency's (IEA) Implementation Agreement for a Programme of Research Development of High Temperature Materials for Automotive Engines, with the U.S. Department of Energy as the operating agent. The objective of the project was to evaluate the reliability and reproducibility of measurement methods for primary and secondary properties of six industrially-important ceramic powders, and involved round robin testing in industrial and government laboratories in the various countries. Primary properties are defined as direct measurements on powders, e.g. particle size distribution, specific surface area, density, chemical composition, and phase analysis. Secondary properties are those determined for powders suspended in water and include surface chemistry, rheology, sedimentation, flow and compaction of granules, and the bulk density and porosity of compacts. All studies of primary properties have been completed; the results are being used to develop international standards and SRM's. Studies of secondary properties will be continued in a subsequent project which is now being initiated (Subtask 10).

**PROGRAM TITLE:** Ceramic Processing

**PROJECT TITLE:** Electroacoustic Characterization of Slurries

**Principal Investigators:** Vincent A. Hackley and Raymond Mountain, (Physics Laboratory)

**Technical Objectives:**

This project was carried out as a Consortium on Intelligent Processing of Ceramic Powders, involving five companies. Its purpose was (1) to utilize non-destructive ultrasonic techniques for characterizing particle size and charge in aqueous ceramic powder slurries, (2) to improve this measurement science and computational tools, and (3) to compliment these results with adsorption isotherm data and rheological data so as to understand better the significance of the ultrasonic measurements to processing phenomena.

**Technical Description:**

The studies were carried out on aqueous slurries of silicon containing dispersants and binders used to manufacture reaction bonded silicon nitride (RBSN). The measurement techniques employed were electroacoustic analysis, rheology, and surface area analysis. New or improved methodology was developed for data analysis.

**External Collaborations:**

Industrial collaborators during the past year have included Cercom Inc., Eaton Corp., Golden Technologies, and Kerr-McGee Corp. In addition, we have worked closely with instrument manufacturer Matec Applied Sciences to develop electroacoustic spectroscopy for ceramic powder applications.

**Planned Outcomes:**

Two primary outcomes are expected to result from this research: (1) development of the necessary methodology to apply ultrasonic analysis for control of liquid-media-based powder processing, and (2) improvement of the understanding of component interactions during aqueous processing of complex, highly concentrated slurries.

**Accomplishments:**

New and improved information regarding the aqueous suspension behavior of metallic silicon powders and their interaction with other slip constituents. This has had a direct impact on processing formulations for aqueous RBSN used by at least one consortium member, and led others to test or incorporate various technical results into their own applications. NIST testing and evaluation has provided feedback to the instrument manufacturers which resulted in system improvements. NIST measurements have provided necessary information regarding the application of ultrasonic methods to characterize ceramic powders, which is currently being employed for the analysis of materials used by consortium participants.

Specific studies included adsorption isotherm and electroacoustic analysis of silicon/dispersant/binder systems, rheological investigations of concentrated silicon powder slips and the effects of various dispersant/binder systems, rheological investigations of concentrated multicomponent slips, surface chemical investigation of slip aging and the interaction of secondary powders (sintering and nitriding agents), the development of a computational tool for evaluating the effects of variations in the particle size distribution on the electroacoustic spectral analysis of dilute and moderately concentrated suspensions, the establishment of measurement and data analysis methodology for evaluating truncated log-normal particle size distributions based on the application of acoustic attenuation spectroscopy.

**Publications:**

Hackley, V.A. and Malghan, S.G. "Electroacoustic Characterization of Particle Size and Zeta Potential in Moderately Concentrated Suspensions", in *Ceramic Transactions*, Volume 56, Advanced Synthesis and Processing of Composites and Advanced Ceramics (American Ceramic Society, Westerville, OH, 1995) p 283.

Hackley, V.A. and Malghan, S.G. "Modification of Silicon Nitride Slip Properties by Poly(acrylic acid)", in *Ceramic Transactions*, Volume 62, Science, Technology and Commercialization of Powder Synthesis and Shape Forming Processes (American Ceramic Society, Westerville, OH, 1996) p 117.

Hackley, V.A. "*Ultrasonic characterization of particle size and charge in ceramic powder suspensions*," in the Proceedings of the 5th World Congress of Chemical Engineering, Vol. VI, *2nd International Particle Technology Forum* (American Institute of Chemical Engineers, NY, 1996) p 557.

Hackley, V.A., Malghan, S.G., "Colloidal Processing of Silicon Nitride with Poly(acrylic acid). I. Adsorption and Electrostatic Interactions", submitted to *J. Am. Ceram. Soc.* (1996).

Hackley, V.A., Paik, U., Kim, B. and Malghan, S.G., "Aqueous Processing of Sintered Reaction-Bonded Silicon Nitride. I. Dispersion Properties of Silicon Powder", submitted to *J. Am. Ceram. Soc.* (1996).

Dukhin, A.S., Goetz, P.J. and Hackley, V.A., "Modified Log-Normal Particle Size Distribution in Acoustic Spectroscopy", submitted to *Colloids Surf. A* (1996).

**PROGRAM TITLE:** Ceramic Processing

**PROJECT TITLE:** Fundamentals of Interface Development

**Principal Investigators:** John Blendell and Mark Vaudin

**Technical Objectives:**

The objective of this research is to understand the effect of interfacial energy anisotropy on the microstructure evolution of ceramics. The microstructural features of concern are the pore location, the distribution of liquid phases and the crystallographic texture.

**Technical Description:**

The driving force for the consolidation and densification of ceramic powders during sintering is the difference between the energy of the free surfaces which are eliminated and the energy of the grain boundaries which form. While the modeling of microstructure development during sintering of ceramics has generally assumed that all interfacial energies are isotropic, measurements of the interfacial energies have shown that most materials are anisotropic. Anisotropy of these interfacial energies will lead to differences in the local rate of densification, shape of pores and the location of pores (either attached to or separated from grain boundaries). When pore separation occurs, shrinkage of the pores effectively stops and a limiting density is reached. Large differences in mobility of specific grain boundaries can result in a highly textured microstructure consisting of elongated grains. If a liquid phase is present, not all grain boundaries will be wetted depending on the local energy balance.

It is well known that the composition of a surface can change the magnitude and anisotropy of the interfacial energy, but direct measurements are limited. Previously we measured the shape of small internal cavities in sapphire, but this process is time consuming and it is difficult to change the composition. We have developed a technique which uses, Atomic Force Microscopy (AFM) to measure the surface faceting of an individual grain in a polycrystalline material. This allows us to examine a wide range of grain orientations and has the advantage that the composition is easily modified. Initial results on $Al_2O_3$ have been used to develop and quantify the technique. Future experiments will examine the specific effects of doping. In addition, a recently developed model for the wetting of grain boundaries, which includes the effect of anisotropy, can be used to predict the resultant microstructure in liquid phase sintered ceramics. This model can then be used to modify the microstructure through changes in composition.

Another area where the interface properties can have a large influence is in epitaxial growth of thin films. The morphology of a film is often dominated by the substrate morphology and orientation. We plan to use the newly developed AFM technique to measure the substrate morphology. This will then be related to the deposited film morphology and correlated with the properties of the film.

**Planned Outcomes:**

The AFM technique will allow materials developers to use the anisotropy of materials to enhance/improve the properties in specific orientations, and to use changes in anisotropy (via doping) to control microstructure. Development of measurement techniques for easily determining the surface energy anisotropy is also anticipated.

**Accomplishments:**

We have determined the equilibrium (Wulff) shape of $Al_2O_3$ in air. The resultant shape was compared with the shapes predicted from theoretical calculations of the surface energy and large discrepancies were found.

The conditions for wetting of low angle grain boundaries in $Al_2O_3$ by anorthite glass have been measured. It was shown that not only is the degree of grain boundary misorientation important, but the normal to the boundary plane also controls the wetting.

A technique for measuring individual grain orientations from surface facetting using AFM measurements has been developed. This technique uses the observed faceting and the Wulff shape to determine the orientation and is being calibrated using orientations determined by electron backscatter patterns of the same grains.

**Publications:**

"The Equilibrium Shape of Internal Cavaties in Sapphire," J-H. Choi, D-Y. Kim, B.J. Hockey, S.M. Wiederhorn, C.A. Handwerker, J.E. Blendell, W.C. Carter and A.R. Roosen, to be published in J. Amer. Ceram. Soc., 1996-7.

"A System for Measuring Surface Facet Orientations from Atomic Force Microscope Data," J.G. Hagedorn, H.E. Rushmeier, J.E. Blendell, M.D. Vaudin, Proceedings Visualization '96, pp. 397-400, October 1996.

**PROGRAM TITLE:** Ceramic Processing

**PROJECT TITLE:** Low Temperature Fabrication of Silicon Nitride

**Principal Investigators:** Eduardo J. Gonzalez, Bernard J. Hockey, and Gaspar Piermarini

**Technical Objectives:**

This program was designed to assist industry in the development of processing technology for the production of nanostructured ceramics possessing mechanical properties superior to those commonly found in conventional ceramic materials.

**Technical Description:**

Available nanosize powders such as amorphous $Si_3N_4$ and $\gamma$-$Al_2O_3$, were compacted in a piston cylinder die to pressures as high as 2.8 GPa and in a diamond anvil pressure cell for pressures up to 6 GPa. The resulting transparent green bodies of these materials were then pressureless sintered at a variety of temperatures. The microstructures of these materials were evaluated by careful SEM and TEM microscopy. Since the microstructures that develop from the sintering of nanosize powders are typically different from conventional ceramics, basic mechanical properties such as hardness were evaluated and compared those of conventionally prepared ceramics.

**External Collaborations:**

Nanosize powders of amorphous $Si_3N_4$ are specially prepared for us by Richard Buss of Sandia Laboratory. Dr. Buss uses a pulsed plasma reactor under low vacuum pressure to produce the powders from carefully controlled mixtures of silane and ammonia gases. In addition, owing to the extreme reactivity of nanosize particles with air, the amorphous $Si_3N_4$ powders are provided to us in inert environments to minimize surface oxidation.

**Accomplishments:**

We have demonstrated that the compaction pressure on nanosize $\gamma$-$Al_2O_3$ powder has an enhancing effect on: 1) the green body density, and 2) the $\gamma$-to-$\alpha$ transformation rate and temperature of transformation. Samples compacted to 1 GPa and sintered at temperatures below 1300 °C yielded consistently lower bulk densities than the samples pressed to 2.5 GPa and sintered at the same temperatures. The density of both samples approached the same value ($\approx$3.2 g $cm^{-3}$) for sintering at temperatures near 1300 °C. For these samples, full density, 3.98 g $cm^{-3}$, was never attained even for higher sintering temperatures (maximum value, $\approx$3.80 g $cm^{-3}$). In contrast to these results, samples compacted to 3 GPa were sintered to almost full density (estimated from porosity in the microstructure) at 1150 °C in one hour. In addition, these samples maintained a small grain size. These results demonstrate that high pressure compaction alone can create a sufficient number of nucleation sites to inhibit the formation of the vermicular structure which normally follows the

$\gamma$-to$\alpha$ transformation of $Al_2O_3$. The results also indicate that average grain size can be reduced further, perhaps by applying even higher pressures to the nanosize powder during compaction.

To process nanosize powders at extreme conditions of pressure and temperature, a new cubic zirconia anvil high pressure cell was designed and built to replace the diamond anvil cell which is limited to temperatures of 800 °C because of oxidation of the diamond anvils. Because high temperatures also affect the mechanical properties of the components of the pressure cell, heating these metal parts to extreme temperatures must be avoided in order to maintain the applied pressure. Consequently, it was necessary to develop a new heating technique which uses only the gasket confining the nanosize powder under pressure as the resistance heater, thereby minimizing heat dissipation to the pressure cell components. Preliminary experiments with this new system indicated that sample temperatures as high as 1200 °C can be achieved routinely, while maintaining the integrity of the pressure cell metal components.

**Publications:**

1. E. Gonzalez, G. J. Piermarini and B. Hockey, "Processing Nanosize $\gamma$ $Al_2O_3$ Powder by High Pressure Compaction," J. Am. Ceram. Soc. submitted.

2. T. P. Russell and G. J. Piermarini, "A High Pressure Optical Cell Utilizing Single Crystal Cubic Zirconia Anvil Windows," J. Phys. Chem. submitted.

**PROGRAM TITLE:** Ceramic Processing

**PROJECT TITLE:** Particle Size Distribution Standards

**Principal Investigator:** James F. Kelly

**Technical Objectives:**

The primary objective of this work is to develop and certify glass/ceramic powders as particle size distribution standards. A necessary adjunct to this certification is the development of sampling protocols and size measurement procedures.

**Technical Description:**

The initial work in the development of these standard reference materials is the selection of a powder material with the desired chemical and physical characteristics. These characteristics include size, shape, durability, and reactivity. Industrial sources of powders are identified, test powders are evaluated, and production specifications are developed in cooperation with the powder manufacturer. Procedures have been developed for splitting and bottling of the powder to achieve the necessary level of sample to sample homogeneity. The instrumental techniques utilized for the particle size measurements include optical and scanning electron microscopy, laser diffraction, sieving, sedimentation and electrical zone sensing. The primary techniques are the microscopies because of the direct calibration with NIST line standards.

**Planned Outcomes:**

Development is underway for the certification of SRM's 1018b and 1019b which will extend the upper range of available size distributions to the mm range.

**Accomplishments:**

The work for SRM's 1018b and 1019b continues, with a significant portion of the work having been completed this year. In recently developed SRM's, namely SRM's 1003b, 1004a, 1017b, and 1982 covering particle size ranges from 15 μm to 400 μm are now available to industrial laboratories and test facilities. Several thousand units of these materials have been produced and certified for size distribution and homogeneity. Approximately 500 units per year of these size distribution standards are purchase by industry for use in their quality control test programs.

# ELECTRONIC AND PHOTONIC MATERIALS

# ELECTRONIC AND PHOTONIC MATERIALS

The Electronic and Photonic Materials Program endeavors to provide the electronics and opto-electronics communities with improved characterization tools and data to evaluate advanced material systems, both in bulk and in thin film structures. A major component of this effort is the development of new characterization tools for thin films. These tools include *in situ* deposition characterization techniques, enhanced processing models, and better understanding of measurement techniques and of film property/processing relationships. Increasingly stringent demands placed upon films for electronic and opto-electronic applications, e.g., decreasing size, increased purity, improved interface properties, increased production rates, and tighter control of properties, place correspondingly stringent demands on film processing control, models relating processing parameters to film properties, and film characterization techniques. However, through lack of basic understanding of interrelationships between processing conditions and final film properties, most film processing is currently done on an empirical basis. The range of activities in the Electronic and Photonic Materials Program is designed to address these issues, both in specific, short term industrial needs as well as in the development of a materials science knowledge base required for application of ceramic films to future electronic and photonic applications. These issues are being addressed with a two-prong approach.

The first approach, using pulsed laser deposition, focuses on *in situ* control of and improved models for processing conditions. This effort involves designing measurement techniques to monitor film deposition without disturbing final film properties and enhancing previously available theoretical models to describe the time and spatial behavior of plasmas used to deposit films. Special emphasis has been given, during the past year, to exporting these techniques to industrial environments and relating the *in situ* measurements to film properties of interest.

The second approach features film property determination. In this regard, measurement procedures intended to determine optical, thermal, and microstructural film material properties are being evaluated and improved. Simultaneously, using metallo-organic chemical vapor deposition (MOCVD), relationships between processing parameters, e.g., temperature, substrate, etc., and properties such as microstructure and $2^{nd}$ harmonic generation are being investigated for photonic applications. Finally, in collaboration with both companies and universities, defect sites in films intended for blue/green emitters and receivers are being identified and mapped using a combination of optical techniques.

Issues being addressed by the Electronic and Photonics Program concerning bulk systems include generation of new phase diagrams needed by the high temperature superconductor industry and the microwave communications industry. Phase diagrams for both of these applications provide basic structural maps which allow companies to pinpoint compositions of greatest potential benefit. Another investigation of bulk materials for the electronics industry involves the mapping of defects in the crystal structure of $LiNbO_3$ . This research, which uses synchrotron radiation, provides industry with a new tool for evaluating the quality of single crystals.

**PROGRAM TITLE:** Electronic and Photonic Materials

**PROJECT TITLE:** Defect Studies in Photonic Materials

**Principal Investigators:** Bruce Steiner and Lawrence Robins

**Technical Objective:**

The objective of this project is to utilize unique high sensitivity measurement facilities to characterize materials for optical devices (such as light emitting diodes and fiber optic gyroscopes), optical computing, optical communications, and optical information processing.

**Technical Description:**

One principal approach to this objective is by using the NIST Materials Science and Engineering Beamline X23A3 high resolution synchrotron x-radiation diffraction imaging at the National Synchrotron Light Source at Brookhaven National Laboratory. This is used in conjunction with multiple *in situ* laser fields. Other principal techniques employed are cathodoluminescence electron microscopy and optical microscopy.

The various imaging procedures lead to the identification of crystal defects, their association with fabrication factors, and their influence on device performance. The objective is the control of those defects that are found to be the most important in influencing device performance and production yield.

Single crystals receiving primary attention this past year include strontium barium niobate, barium titanate, lithium niobate, and zinc selenide. Layered crystals include a variety of III-V systems and related materials such as aluminum gallium nitride films.

**External Collaborations:**

Collaborative studies are conducted with several companies and universities to utilize NIST analytical capabilities in characterizing the structure of photonic materials and relating those structures to material processing conditions and properties. These companies include: Rockwell Science Center, Deltronic Crystal Industries, Litton Guidance and Control Systems, Johns Hopkins University, Optex, and Eagle-Picher.

**Planned Outcomes:**

Two primary outcomes are planned: diffraction imaging will be used to make *in situ* observation of interactions between fixed photorefractive gratings (for high capacity optical information storage) and specific crystal defects; and, the influence of specific native defects in lithium niobate crystals on the satisfactory formation of wave guides for fiber optic gyroscope components and the associated improvement in the yield of these devices will be determined.

**Accomplishments:**

We have observed directly for the first time a fixed photorefractive grating. This was prepared in strontium barium niobate on the West Coast and shipped to Brookhaven for observation by high resolution diffraction imaging. We have also succeeded in observing directly for the first time *in situ* the fixing, reversal, and repeated fixing of a photorefractive grating, in barium titanate. This experiment also was carried out at Brookhaven.

We have observed the progressive breakup of the single crystal structure of lithium niobate in such a way as to interfere with the subsequent imposition of waveguides on the surfaces of wafers. Moreover, waveguide formation has been shown to be affected not only by the very low angle subgrain boundaries that arise but also by other processing steps. As a result, satisfactory control of the various fabrication stages is gradually being achieved.

Two types of defect structure have been found in aluminum-gallium-nitride films and associated with energy shifts in the cathodoluminescent spectra. The spatial distribution of defects in a zinc selenide crystal also has been mapped.

**Impacts:**

The observation of subgrain growth in lithium niobate has led successfully to the modification of growth procedures in such a way as to reduce the formation of subgrains and thus has enabled the more reliable manufacture of waveguides. Also the observation of surface texture in lithium niobate as part of the waveguide fabrication process has led to greater attention to this part of the processing.

**Publications:**

G. Fogarty, B. Steiner, M. Cronin-Golomb, U. Laor, M. A. Garret, J. Martin, and R. Uhrin, High Resolution X-Ray Diffraction Imaging of Anti-Parallel Ferroelectric Domains in Photorefractive Barium Titanate and Strontium Barium Niobate, JOSA **B** in press (1996).

Bruce Steiner, L.E. Levine, Margaret Brown, and David Larson, Residual Disorder in Low Pressure, Low Thermal Gradient Liquid Encapsulated Czochralski Gallium Arsenide Observed in High Resolution Synchrotron Diffraction Imaging, J. Crystal Growth in press (1996).

Ravindra B. Lal, Ashok K. Batra, Bruce Steiner, and Uri Laor, High Resolution Monochromatic Synchrotron Radiation Diffraction Imaging of Triglycine Sulfate (TGS) Crystals, Proc ISAF 10 (1996).

**PROGRAM TITLE:** Electronic and Photonic Materials

**PROJECT TITLE:** Development of Tests for Thermal Properties

**Principle Investigators:** Eduardo J. Gonzalez, Grady S. White, and Joseph Ritter

**Technical Objective:**

One objective of the thermal properties characterization project is to develop and exploit the photothermal deflection technique as an analytical tool for measuring the thermal diffusivity of different materials, with a special emphasis on electronic materials in thin film form. This research work is also attempting to identify those microstructural features that affect thermal transport in bulk samples and thin films.

**Technical Description:**

Thermal diffusivity measurements have been carried out using the photothermal deflection technique. The principle of this technique consists in periodically heating the surface of the sample with an intensity modulated laser, and measuring the phase and magnitude of the photothermal signal in the heated region. Using this technique, we have studied the effects of microstructure on heat transfer properties. This was accomplished by systematically isolating different specific features of the microstructure in a number of specimens. The microstructural features of interest are: (1) fine scale porosity, (2) well dispersed precipitates of another phase of thermal properties different from the matrix material, (3) grain size and grain boundary effects, (4) interfaces, and (5) crystallographic texture. The effects of fine scale porosity ($< 0.5$ μm in diameter) have been studied in samples of $\alpha$-$Al_2O_3$. Samples with increasing amounts of homogeneously disperse porosity were made by sintering $\gamma$-$Al_2O_3$ nanosize powder. $\gamma$-$Al_2O_3$ powder was used because the microstructure that results from the transformation and sintering is characterized by a well dispersed, small sized porosity. A series of these samples has also been used to study the effects of grain size. The scattering effects of small precipitates in a matrix have been addressed by producing crystalline films of $ZrO_2$ with small precipitates of amorphous $Al_2O_3$. These films have been prepared by a continuous dip-coating method developed at NIST. Crystallographic texture effects on thermal diffusivity have been studied on samples of $Bi_2Te_3$ with different degrees of texture. These samples were prepared by hot-pressing and hot-forging experiments. Finally, the effects of interfaces have been studied in metal/ceramic multilayer films.

**External Collaborations:**

In cooperation with Toshiba, Dow Chemical, Electronics and Electrical Engineering Laboratory of NIST, and Materials Modification Inc., we are conducting thermal diffusivity measurements to evaluate the effects of structure and chemistry on the properties of aluminum nitride.

**Planned Outcomes:**

This research program is expected to develop the basic scientific background necessary to understand the effects of the microstructure on thermal properties of bulk and thin film materials.

**Accomplishments:**

It was demonstrated that the photothermal deflection technique can measure changes in thermal diffusivity in bulk specimens resulting from porosity, crystallographic texture, and crystallization events. For example, results have indicated that very fine porosity (< 0.5 μm in diameter) distributed uniformly in a sample can scatter heat more effectively than coarse porosity. We have recorded thermal diffusivity values ranging from 0.037 $cm^2s^{-1}$ to 0.14 $cm^2s^{-1}$, for samples with 38% volume fraction porosity and fully dense, respectively. The effects of fine scale porosity are such that the thermal diffusivity of the sample with 38% porosity is three times lower than what is predicted by the available theoretical models. We also demonstrated the effects of crystallographic texture on heat transfer in samples of $Bi_2Te_3$. We recorded differences in thermal diffusivity greater than 35% between samples with no texture and textured specimens.

Since the photothermal deflection technique can have a high spatial resolution, we studied films with relative ease. For instance, we studied the crystallization sequence of alumina films on substrates. The thermal diffusivity in these specimens changes from 0.0035 $cm^2s^{-1}$ for an amorphous film to 0.023 $cm^2s^{-1}$ for a crystalline film with a complex microstructure.

**Publication:**

L. Wei, M. Vaudin, C. S. Hwang, and G. White, "Heat Conduction in Silicon Thin Films: Effect of Microstructure," J. Mater. Res., **10** [8], 1889-1896 (1995).

**PROGRAM TITLE:** Electronic and Photonic Materials

**PROJECT TITLE:** Ferroelectric Oxide Thin Films

**Principal Investigators:** Debra Kaiser and Lawrence Rotter

**Technical Objective:**

The objectives are to identify and address key materials issues vital to the advancement of ferroelectric oxide thin film devices for electronics and optoelectronics industries and to develop appropriate measurement methodology as needed to study these issues.

**Technical Description:**

This project involves a study of the complex relationships between thin film deposition, microstructure, optical properties and electro-optical properties of barium titanate thin films deposited by metallo-organic chemical vapor deposition (MOCVD). Techniques that are being employed in the studies include x-ray diffraction, wavelength dispersive x-ray spectrometry, transmission electron microscopy, atomic force microscopy, Raman spectroscopy, second harmonic generation, spectrophotometry, prism coupling, and polarimetry.

**External Collaboration:**

In collaboration with NZ Applied Technologies we are examining the relationship between MOCVD processing conditions and electro-optic properties.

**Planned Outcome:**

The microstructural characterization and electro-optical measurement techniques needed to understand the processing/structure/property relationships of importance for electronic and optoelectronic applications will be established.

**Accomplishments:**

Barium strontium titanium oxide thin films of various compositions were deposited by MOCVD on (100) MgO substrates at differing growth conditions. The conventional $\Theta$-$2\Theta$ x-ray diffraction patterns from films that had molar ratios (Ba+Sr)/Ti that were significantly different from one showed only the presence of crystalline $Ba_{1-x}Sr_xTiO_3$ ($x = 0.058$). The second phase material in these films gave no discernible x-ray diffraction peaks and was likely to be amorphous. The orientation of the $Ba_{1-x}Sr_xTiO_3$ grains in the films (all *a*-axis normal to the substrate surface, all *c*-axis normal to the substrate surface, or a mix of the two) was found to be strongly dependent upon film composition.

Films with duplex $Ba_{1-x}Sr_xTiO_3$/amorphous structures may be of interest for ferroelectric dynamic access memories.

Our studies have shown that conventional Θ-2Θ x-ray diffraction measurements alone do not provide sufficient evidence that a film contains only $Ba_{1-x}Sr_xTiO_3$. Measurements of film composition indicate the presence of phases of different stoichiometry than $Ba_{1-x}Sr_xTiO_3$ (i.e., (Ba+Sr)/Ti not equal to one). Techniques that have been used to detect the presence of amorphous phases are transmission electron microscopy, Raman spectroscopy and glancing angle x-ray diffraction. The detectability limits of amorphous material for the latter two techniques are being investigated.

Second harmonic generation (SHG) experiments showed that the second harmonic signal from some as-grown $BaTiO_3$ thin films is unrelated to the crystallographic orientation of the films. More recent SHG measurements were made using a second harmonic signal above the bandgap of $BaTiO_3$, allowing for a comparison of the mean value of the SHG coefficient averaged through the depth of the film to the values in approximately 15 nm thick regions at the film-air and film-substrate interfaces. These measurements demonstrated that the observed SHG coefficients are strong functions of depth in the film. We suggest that the observed SHG is due to a polarization normal to the plane of the surface which varies with depth in the film; this polarization is likely due to charged defects in the film. Sufficiently large internal fields resulting from charged defects might induce "self-poling" of the films during cooling through the Curie temperature, thereby eliminating the need for a poling process in the fabrication of electro-optic film devices.

**Publications:**

"Effect of Film Composition on the Orientation of $Ba_{1-x}Sr_xTiO_3$ in Thin Films Prepared by MOCVD," D. L. Kaiser, M. D. Vaudin and J. A. Armstrong, submitted to J. Crystal Growth.

**PROGRAM TITLE:** Electronic and Photonic Materials

**PROJECT TITLE:** Phase Equilibria Studies of Dielectric Oxides for Wireless Communications

**Principal Investigator:** Terrell A. Vanderah

**Technical Objective:**

Phase equilibria diagrams for complex titanate-based dielectric oxides of interest as filters, oscillators, and circulators for microwave communications systems will be experimentally determined.

**Technical Description:**

Dielectric ceramics are used to fabricate a variety of components in cellular communications circuits that store, filter, and/or transfer electromagnetic energy with minimal loss (e.g., resonators, bandpass filters, circulators). The required properties for the ceramic materials include high dielectric constant, minimal dielectric loss (which precludes the use of ferroelectric oxides), and essentially zero temperature dependence of dielectric properties. Knowledge of phase equilibria relations is important owing to the additive nature of dielectric properties; e.g. practically all ceramic components are processed as mixtures to achieve compensation and a net overall zero temperature coefficient. Thus, identification and characterization of phases in equilibrium with the dielectric ceramic are essential in order to process ceramic components that meet current standards of tightly controlled dielectric constant (±0.25%), low dielectric loss, and temperature coefficients near zero (±4 ppm/°C). The approach taken by the phase equilibria group emphasizes experimental determination of previously unknown ternary (or higher) oxide systems containing one or more components or compounds that exhibit useful properties as dielectric ceramics for microwave communications. Technical efforts include synthesis, structural analysis, determination of phase relations, and characterization (via collaborative efforts) of dielectric properties.

**External Collaborations:**

Electromagnetic Fields and Technology Divisions, NIST, Boulder campus; Electrical Engineering Department, UCLA; AT&T Bell Labs; NRL; and Geology Department, University of Maryland

**Planned Outcome:**

Accurate, experimentally determined phase diagrams will be available that are of immediate interest to U.S. industry involved in the production of ceramics for wireless communications systems.

**Accomplishments:**

In November 1995, a Workshop on Materials and Measurements for Wireless Communications was held at NIST, Gaithersburg. The primary goal was to identify, document, and prioritize key R&D needs which, if addressed, would help U.S. businesses become more competitive in the global commercial wireless market. A secondary goal was to obtain an overview of R&D needs in order to focus in-house technical work at NIST. The workshop was attended by all the leading U.S. companies in the area of microwave ceramics. At the end of the workshop a list of R&D issues in the areas of materials and measurements was compiled interactively and mailed to industrial participants for ranking in order of urgency and importance. Fundamental materials issues, e.g., chemistry-structure-property relations were clearly ranked as the most important materials problems. Standard materials and measurement techniques were ranked as most important in the area of measurements.

Several phases found previously in the $BaO:Fe_2O_3:TiO_2$ system have been characterized. For the compounds $Ba_4Fe_2Ti_{10}O_{27}$ (4:1:10) and $Ba_3Fe_{10}TiO_{20}$ (3:5:1), crystal structures were determined by single-crystal X-ray and powder neutron diffraction, dielectric properties, and magnetic behavior. Neutron diffraction studies of 3:5:1 at room temperature revealed a magnetic lattice with reduced symmetry; an additional magnetic structure was observed at 13 K and below. Magnetic susceptibility measurements for this compound indicated complex magnetic behavior with transitions at 45 and 5 K; in contrast, 4:1:10 was essentially paramagnetic. Unusual structural features were found by high-resolution electron microscopy in one of a pair of ternary compounds, $Ba_4Fe_4Ti_3O_{16}$ (E-phase) and $Ba_{26}Fe_{20}Ti_{21}O_{98}$ (M-phase), near the hexagonal $BaTiO_3$- type solid solution in this system. The compounds were found to be structurally related and built from two types of structural blocks, one of which is related to the perovskite structure. Whereas the E-phase was found to have a well-ordered structure, the M-phase exhibited persistent and *regularly* occurring structural disorder as revealed by the presence of diffuse, continuous streaks. The permittivities of seven of the ternary compounds in the $BaO:Fe_2O_3:TiO_2$ system have been evaluated and range from 15 for $Ba_3Fe_{10}TiO_{20}$ to a high of 52 for $Ba_{44}Fe_6Ti_{106}O_{265}$, as compared to 15 for $BaFe_{12}O_{19}$ and 40 for the microwave ceramic $Ba_2Ti_9O_{20}$.

Experimental determination of the $SrO:TiO_2:Nb_2O_5$ system is nearing completion. Of particular interest in this system are the compounds found in equilibrium with $SrTiO_3$, a potentially useful microwave ceramic requiring second-phase compensation of its large positive temperature coefficient of permittivity. Fifteen ternary compounds have been confirmed in this system, three having been previously reported. Thirteen of these occur in three homologous series, two of which are perovskite slab structures, the third a rutile slab structure. A considerable solid solution exists for $Nb^{5+}$ substitution in the $SrTiO_3$ structure. The crystal structure of $Sr_6TiNb_4O_{18}$ was determined by single-crystal X-ray diffraction and consists of infinite perovskite-type slabs, five octahedral in thickness, extending parallel to $(111)_{perovskite}$. The cation coordination spheres in and bordering the gaps between the slabs were found to be highly distorted with bond valence sums indicative of residual chemical strain; these sites were found to be preferentially occupied by $Nb^{5+}$.

X-Ray powder diffraction reference patterns were prepared for $SrTi_3Nb_4O_{17}$, $SrTi_5Nb_4O_{21}$, $SrTi_7Nb_4O_{25}$, $SrTi_9Nb_4O_{29}$, $SrTi_{11}Nb_4O_{33}$, $SrTi_{13}Nb_4O_{37}$, and $SrTi_{15}Nb_4O_{41}$, which form a homologous series $SrM_{2n+1}O_{4n+5}$ (M = Ti,Nb; n = 3®9). This series is isostructural with the orthorhombic "chemically twinned rutile" series found previously in the $K_2O$-$TiO_2$-$Ta_2O_5$ and BaO-$TiO_2$-$Nb_2O_5$ systems. The structures are built of corner-sharing slabs of the rutile structure; successive members are generated by adding $2TiO_2$ to the slab thickness of the previous member. Preliminary screenings of permittivities and temperature coefficients for fourteen compounds in the SrO:$TiO_2$:$Nb_2O_5$ system indicated an interesting change in sign of the temperature dependence within one of the perovskite-slab homologous series.

**Impacts:**

The BaO:$Fe_2O_3$:$TiO_2$ phase diagram, documented in a pre-print, was immediately used by workers at Trans-Tech, Inc. to prepare large batches of all compounds found in equilibrium with the technically important ferrite $BaFe_{12}O_{19}$. These compounds may be used to modify the properties of $BaFe_{12}O_{19}$ ceramics, used as microwave circulators and isolators.

**Publications:**

"Magnetic Dielectric Oxides: Subsolidus Phase Relations in the BaO:$Fe_2O_3$:$TiO_2$ System," T.A. Vanderah, J.M. Loezos, and R.S. Roth; J. Solid State Chem. **121**, 38 (1996).

"Structural Features of "$Ba_4Fe_4Ti_3O_{16}$" and "$Ba_{26}Fe_{20}Ti_{21}O_{98}$" as Revealed by High Resolution Electron Microscopy," L.A. Bendersky, T.A. Vanderah, and R.S. Roth; J. Solid State Chem., in press.

"Preparation and Crystal Structure of $Sr_6TiNb_4O_{18}$," A.R. Drews, W. Wong-Ng, T.A. Vanderah, and R.S. Roth; J. Alloys Comp., in press.

"Crystal Structures and Properties of $Ba_4Fe_2Ti_{10}O_{27}$ and $Ba_3Fe_{10}TiO_{20}$," T.A. Vanderah, W. Wong-Ng, Q. Huang, R.S. Roth, R.G. Geyer, and R.B. Goldfarb; J. Phys. Chem. Solids, in press.

"Workshop on Materials and Measurements for Wireless Communications, A Conference Report," T.A. Vanderah, J. Res. NIST, in press.

"A Series of "Chemically Twinned Rutile" Oxides, $SrM_{2n+1}O_{4n+5}$ (M=Ti,Nb; n=3 to 9)", J.M. Loezos, T.A. Vanderah, A.R. Drews, and R.S. Roth; submitted to Powder Diffraction.

**PROGRAM TITLE:** Electronic and Photonic Materials

**PROJECT TITLE:** Prediction of Phase Diagrams with First-Principles Phase Diagram Calculations.

**Principal Investigators:** Benjamin P. Burton and Ryan P. McCormack

**Technical Objective:**

This research is designed to assist industry by elucidating the role of order-disorder phenomena in determining the phase relations and physical properties of certain technologically important ceramic materials. An additional technical objective is to benchmark various techniques for calculating the formation energies on which FPPD calculations are based.

**Technical Description:**

Typically, the ferroelectric, dielectric, magnetic, or transport properties of these materials are sensitive functions of the state of cation order. Therefore, First-Principles Phase Diagram (FPPD) calculations are used to predict cation ordering phenomena, and critical experiments are performed to test the predictions.

**External Collaborations:**

Jordi Sanchez and Carles Comas I Moras (Univ. Autonoma, Barcelona, Spain) on FPPD calculations of the NaCl-KCl, NaBr-KBr, and NaI-KI phase diagrams.

M. Asta (Sandia National Laboratory, Livermore) on techniques for fitting data on diffuse diffraction from short-range order to cluster expansion Hamiltonians.

Anna Roig (ICMAB, Univ. Autonoma, Barcelona, Spain) Mossbauer studies of magnetism, and iron in elevated valence states.

H. Stokes (BYU), and L. Boyer (NRL), application of the SSCAD model to calculate structure energies for FPPD calculations for oxide systems.

J.J. Hoyt (Washington State University), B.C. Chakoumakos and S.T. Misture (Oak Ridge National Laboratory), M. Asta, J.D. Althoff, and D.D. Johnson (Sandia National Laboratory, Livermore), joint experimental measurement and first-principles calculation of order-disorder phenomena in the Heusler alloy.

**PROGRAM TITLE**: Electronic and Photonic Materials

**PROJECT TITLE:** Characterization of Pulsed Laser Thin Film Deposition

**Principal Investigators:** John W. Hastie, David W. Bonnell, Albert J. Paul, and Peter K. Schenck,

**Technical Objective:**

The project seeks to develop molecular-level measurement capabilities needed (a) to monitor, *in situ* and in real-time, the processing of thin films using pulsed laser deposition (PLD) and (b) to provide basic data for development of process models. The measurement methods and process insight developed are intended to allow industry to utilize in-process monitoring for optimum control of the resultant thin film properties.

**Technical Description:**

The approach is to relate time-dependent process parameters and process models to final film properties, thereby reducing the need for time consuming empirical derivation of optimal processing conditions and extensive post processing analysis currently used in industry. Owing to the short time scale involved (ns to μs) and the chemical complexity of the deposition species (atoms, molecules, ions, clusters,...), several types of complementary measurement techniques are required to make real-time process measurements. The measurement approaches developed include: molecular beam sampling mass spectrometry, optical spectroscopy with optical multichannel analysis and optical imaging with charged-coupled device (CCD). The measurements are complemented by process models based on coupled fundamental processes including hydrodynamics, thermodynamics, and chemical kinetics. Using the combined real-time results of optical spectroscopy, optical imaging and molecular beam mass spectrometry molecular-level models are being developed and tested for the PLD process. Good progress has been made in understanding the laser interaction with the target and plume and also gas transport of the plume to the substrate. Models of the plume substrate interaction are currently under investigation.

**External Collaborations:**

To provide laser/material interaction measurement support, collaborations have been developed with the following individuals: T. J. Hsieh, Optex, Dr. B. Siu, Simpex Technologies, Dr. P. Ghosh, Indian Institute of Technology, Kanpur, India, Dr. M. Joseph, Indira Gandhi Institute, Kalpakkam, India, Dr. J. Drowart, Free University of Brussels.

**Planned Outcome:**

The outcome of this work will be the development of *in situ* characterization techniques and process models which will allow real-time analysis of the details of the deposition process during PLD and possibly for other deposition processes.

**Accomplishments:**

Control of undesirable particulates is a common problem in vapor phase thin film deposition processes. This problem remains a significant technical barrier to the commercial utilization of PLD. Using real-time optical imaging methods, we monitored particulate formation and transport to film substrates. These observations have led to the development of a novel particulate reduction approach, based on a pulsed gas jet, timed to coincide with the appearance of the particulates. This method is still being optimized but the feasibility has already been demonstrated for a substantial reduction in the number of particulates reaching the substrate using $BaTiO_3$ and graphite as test cases.

A collaboration with a small company, ATP awardee (Optex Communications), has demonstrated the feasibility of producing SrS-based optically active thin films with potential application as electron trapping optical storage, next generation compact discs. Optical spectroscopic techniques, developed at NIST for PLD process monitoring, have been demonstrated at the Optex deposition facility. The deposition facility at Optex utilizes magnetron sputtering in an $H_2S$ atmosphere. The optical emission spectra obtained showed features characteristic of each of the key components present, namely Ca, Sr, Eu, S and H. Hence, it should be possible to use these real time observations to monitor and control the film composition. Similar spectra were obtained on PLD plumes during complementary film depositions at NIST. Also, one of the PLD films tested for optical storage capability showed the presence of color centers necessary for the optical storage effect. The PLD films are more readily produced than in magnetron sputtering and do not require added $H_2S$.

**Publications:**

"Gasdynamic Effects in the Laser Sputtering of AlN. Part 1. Evidence for Phase Explosion," R. Kelly, A. Miotello, A. Mele, A. Giardini, H. Okabe, J. W. Hastie, and P. K. Schenck, J. Appl. Phys., in press, 1996.

"In Situ Monitoring by Mass Spectrometry of Laser Ablation Plumes Used in Thin Film Deposition," J. W. Hastie, A. J. Paul, D. W. Bonnell, and P. K. Schenck, in High-Temperature Synthesis of Materials, ACS pub., in press, 1996.

"Imaging and Gasdynamic Modeling of Pulsed Laser Film Deposition Plumes," P. K. Schenck, J. W. Hastie, A. J. Paul, and D. W. Bonnell, Opt. Eng. 35, 3199 (1996).

**PROGRAM TITLE:** Electronic and Photonic Materials

**PROJECT TITLE:** X-Ray Characterization of Photonic Materials

**Principal Investigator:** Charles Bouldin

**Technical Objective:**

The purpose of this work is to provide U.S. industry with advanced x-ray characterization methods for evaluating materials used in photonic materials.

**Technical Description:**

A number of technologically important photonic materials are prepared as thin films or nano-particles. These films often contain unknown minority phases or amorphous components that can adversely alter the desired film properties through scattering, degradation of transport properties or other mechanisms. Such unintended phases or amorphous materials are difficult to detect using materials characterization tools that are now in common usage. A combination of x-ray absorption fine structure measurements, conventional and "anomalous" x-ray diffraction measurements are used to study the phase composition of a thin film photonic materials.

**External Collaborations:**

Extended x-ray absorption fine structure (EXAFS) has been applied to various materials systems to determine variations in composition. This work has been done in collaboration with City University of New York, University of Washington, and Johns Hopkins University. In collaboration with Carnegie Mellon University and the Naval Research Laboratory, EXAFS has been used to investigate quantum dots.

**Accomplishments:**

An x-ray absorption study of CdSe nano-particles has shown that the surface properties of this material depend on the fabrication steps used in precipitating it from solution. Variation in the precursor compounds containing Cd and Se atoms leads to variable Cd atom surface structure containing remnants of the precursor compounds, while the Se surface environment is largely independent of the type of precursor materials. This study shows that Se atoms with dangling bonds exist at the surface of the nano-particles, and that, despite annealing, the nano-particles remain disordered, i.e., are not fully crystalline. Subsequent measurements of CdSe and ZnSe nano-particles capped with ZnS have shown that S atoms displace Se in the particles and that very few Se atoms are included in the capping layer. Replacement of Se atoms by S is nearly complete at the particle surfaces CdSe particles (which are exposed to the /Zn and S ions) and also occurs, at a lower rate in the interior of the particles. Displaced Se atoms are expelled from the particles and removed by binding into the surround liquid reagents.

**Publications:**

A.C. Carter, K. M. Kemner, M. I. Bell, C. E. Bouldin and J.C. Woicik, "Surface Structure of Cadmium Selenide Nanocrystallites," accepted by Physical Review B, in press.

Charles Bouldin, "The Crystallographic Phase Problem and Site-Selective Local Structure in YBCO," Proceedings of the First International Conference on Synchrotron Radiation in Materials Science.

# EVALUATED MATERIALS DATA

# EVALUATED MATERIALS DATA

The objective of the Evaluated Materials Data Program is to develop and facilitate the use of evaluated databases for the materials science and engineering communities. Both research- and application-directed organizations require readily available evaluated data to take advantage of the large volume of materials information developed on public and private sponsored programs. This information, particularly numeric data, is available in an ever increasing number of publications published worldwide. The necessity to consolidate and allow rapid comparison of properties for product design and process development underlies the database projects.

Evaluated databases are developed in cooperation with the NIST Standard Reference Data Program Office and, often, coordinated with the activities of other laboratories and scientific/technical societies. Research consists of the compilation and evaluation of numeric data as well as recently initiated efforts directed at more effective distribution and use of data. Database activities reflect laboratory programs with scientific capabilities required for appropriate data evaluation.

Database projects in MSEL include:

- Phase Diagrams for Ceramists (PDFC), conducted in cooperation with the American Ceramic Society;
- the Structural Ceramics Database (SCD), a compilation of evaluated mechanical and thermal data for nitrides, carbides, and oxides of interest to engineers and designers;
- a ceramic machinability database, coordinated with the Ceramic Machining Research Program (see Ceramic Machining Program overview);
- a high $T_c$ superconductivity database developed in cooperation with the Japanese Agency for Industrial Science and Technology (see superconductivity);
- development and implementation of the STEP protocol for the exchange of materials data, under the auspices of the ISO 10313 activity;
- the NACE/NIST Corrosion Performance Database developed to provide a means to select structural alloys for corrosive applications; and
- the Crystal Data Center which provides fundamental crystallographic data on inorganic materials.

**PROGRAM TITLE:** Evaluated Materials Data

**PROJECT TITLE:** Ceramic Phase Diagrams

**Principal Investigator:** Stephen W. Freiman and Mary Clevinger

**Technical Objective:**

The primary objective of this project is to deliver critically evaluated phase equilibria data to industrial and academic customers.

**Technical Description:**

The technical evaluation of the phase diagrams obtained from the literature is carried out under NIST supervision. The preparation of the evaluated diagrams for dissemination is carried out at NIST with direct collaboration of on-site personnel of the American Ceramic Society (ACerS). The ACerS personnel are primarily supported by funds raised by them from industry. The collaboration represents an over-60-year agreement with ACerS to provide evaluated phase diagrams for the ceramic industry. The phase diagrams are supplied either in printed form or in computerized versions, and are distributed through the ACerS.

The second major area of activity has been on a monograph containing all know phase equilibria information relative to Zr and its compounds. This monograph will bring together new as well as previously published evaluated diagrams; it will also contain bibliographic references to publications containing phase equilibria data, but no diagrams. Publication of this volume is scheduled for the Fall of 1997.

**External Collaborations:**

American Ceramic Society Research Associates, Christina Cedeno, Thomas Green, Evans Hayward, and Niels Swanson, participate in the evaluation, computerization, and production of the phase diagram publications developed in this cooperative program.

**Accomplishments:**

During the past year, considerable progress was made in the development of two new phase equilibria outputs. The first is the second edition of a monograph containing phase diagrams pertinent to high $T_c$ superconducting materials. The first monograph on this subject was published by ACerS/NIST in 1993. This monograph will be ready for publication in February, 1997.

**Publications:**

Volume 12, focusing on oxides, was completed and published in 1996. This compilation contains 443 commentaries and approximately 800 diagrams.

Version 2.0 of the CD-ROM Database for Phase Equilibria Diagrams was completed, and is being marketed through the ACerS. This database contains more than 10,000 diagrams, including those previously published in Version 1.0. The database allows search capabilities of bibliographic information as well as powerful graphics capabilities with regards to the diagrams.

"ACerS/NIST Phase Equilibria Update," Richard M. Spriggs and Stephen W. Freiman, Bull. Am. Cer. Soc. 75 [1] 83-85 (1996).

**PROGRAM TITLE:** Evaluated Materials Data

**PROJECT TITLE:** NIST Informatics Web Site in Support of Advanced Ceramics Research

**Principal Investigator:** Edwin F. Begley

**Objective:**

To establish a World Wide Web site for representing, archiving, accessing, manipulating, utilizing, and applying information related to advanced ceramics research at NIST.

**Technical Description:**

During fiscal year 1996, the Systems Integration for Manufacturing Applications Program (SIMA) funded initial development of a prototype World Wide Web version (WebHTS) of the NIST High Temperature Superconducting (HTS) Materials Database. This task was designed to address on-line access to standard reference data which is a key SIMA program area for testbeds and technology transfer. In fiscal year 1997, renewed SIMA funding is being used to complete WebHTS and to expand the testbed to include demonstrations of electronic collaboration and, also, the transfer of different types of technical information. The expansion will be accomplished through the development of three new tasks: 1. "WWW Demonstration: Ultrasonic Characterization of Particulates, Technology and Applications Development in MSEL," 2. "NIST Guide to International Materials Databases", and 3. "NIST Equilibria Expert."

WebHTS Materials Database

Presently, the HTS materials database exists in stand-alone Microsoft Windows™ 3.1 format and is being distributed by the NIST Standard Reference Data Program (Standard Reference Database #62). The HTS database is described in the high temperature superconductor portion of this report. Adapting the HTS database to the WEB environemnt will help address major issues in the delivery of NIST standard reference data. These issues include:

- Can existing database structures be utilized efficiently?
- Can DOS and Windows interface logic be preserved and completely supported on the Web?
- Can output displays maintain their flexibility and robustness?
- Can solutions for these questions be developed so that making additional NIST standard reference databases available on the Web becomes an incremental task?

WWW Demonstration: Ultrasonic Characterization of Particulates, Technology and Applications Development at MSEL

This task will focus on acoustic-based measurements for particle characterization and process control and will serve as the cornerstone for a future, more general treatment of powder processing and characterization information and research. This approach was selected for development because it directly addresses the need to provide a computing and communications testbed in support of electronic collaboration and demonstration. Features will include scientific meeting announcements, distribution of computational tools and application notes, and serve as a repository of property data. Additionally, access will be provided to technical and scientific information derived from on-site research.

NIST Guide to International Materials Databases
Over the years, scientists and engineers have requested a directory that will assist them with locating computerized and non-computerized sources of materials specific information. The Web will provide an effective forum for disseminating, maintaining, and expanding this guide. In many cases, hyperlinks exist to the data sources, if not the data themselves.

NIST Equilibria Expert
The NIST Equilibria Expert (EE) is an attempt to capture expertise, via computer, in a manner leading to persistence with a meaningful output: multimedia software devoted to the interpretation and determination of phase equilibria diagrams. The software will be publicly distributed on the Web and, therefore, widely accessible.

Five modules are planned for the Equilibria Expert: a glossary of concepts and definitions, sections on unary, binary, and ternary systems, and, lastly, a module on how one develops or determines a phase diagram. The glossary has been completed for the Windows™ environment and covers over fifty concepts which are illustrated using digital audio, still images, text, animations, and, where needed, digital video.

**Planned Outcome**:

This project will result in a World Wide Web site which will provide visitors with access to a wide variety of information related to advanced ceramics research at NIST, data, analysis methods and expertise.

**Accomplishments:**

At present, a server has been installed to support the NIST Web Site for Advanced Ceramics, an evolving Ceramics Division homepage has been constructed to host the planned content, and the described tasks are being developed and installed on the web server as they reach a reasonable level of maturity.

**PROGRAM TITLE**: Evaluated Materials Data

**PROJECT TITLE**: Structural Ceramics Database

**Principal Investigator**: Ronald G. Munro and Edwin F. Begley

**Technical Objective**:

The objectives of this project are to provide evaluated data, database standards, and data evaluation methodologies to advance the application and understanding of structural ceramics.

**Technical Description**:

This project is designed to facilitate technological advances in materials science by providing evaluated thermal, mechanical, and corrosion property data for the broad class of materials cariously called advanced technical ceramics, structural ceramics, engineered ceramics, or fine ceramics.

**External Collaboration**:

The Russian Research Center for Standardization, Information, and Certification of Materials is providing evaluated property data for selected oxide and carbide structural ceramics from Russian language sources. This effort provides data that previously have been inaccessible to U. S. industry or have been available only in Russian language publications.

**Planned Outcomes**:

Several significant results are expected from this project: (1) a comprehensive set of evaluated data; (2) a software interface to the database; (3) standards and methodology for data evaluation; and (4) relations and models for properties and performance characteristics.

**Accomplishments:**

The data set for Version 3 of the NIST Standard Reference Database Number 30: Structural Ceramics has been completed. The new data set contains a broad range of thermal and mechanical property data for oxide, carbide, nitride, boride, and oxynitride materials, including such materials as alumina, mullite, zirconia, silicon carbide, boron carbide, silicon nitride, aluminum nitride, titanium diboride, and SiAlON. A new Windows (TM) interface for viewing the data has been developed and is undergoing internal testing prior to its release to the Standard Reference Data Program.

**Publications:**

Database:

NIST Standard Reference Database Number 30: Structural Ceramics Database, Version 2.

Technical Papers:

"Material Specifications of Advanced Ceramics in Corrosion Studies," R. G. Munro, ASTM Journal of Testing and Evaluation, Vol. 23 (5), 395-398 (1995).

"The Role of Corrosion in a Material Selector Expert System for Advanced Structural Ceramics," R. G. Munro, in Computerization and Networking of Materials Databases: Fourth Volume, ASTM STP 1257, C. Sturrock and E. F. Begley, eds. (American Society of Testing and Materials, 1995) pp. 127-135.

"Material Specifications of Advanced Ceramics and Other Issues in the Use of Property Databases with Corrosion Analysis Models," R. G. Munro, ASTM Journal of Testing and Evaluation, in press.

# HIGH TEMPERATURE SUPERCONDUCTIVITY

# HIGH TEMPERATURE SUPERCONDUCTIVITY

A significant program in critical transition temperature superconductivity is being conducted in MSEL and other Laboratories at NIST. The primary focus of the MSEL program is on bulk superconducting materials for wire and magnet applications. In carrying out this program, researchers in MSEL work closely with their counterparts in other NIST Laboratories, and collaborators in U.S. industry, universities, and other National Laboratories.

The primary thrusts of the program are as follows:

- Phase equilibria - Work is being performed in close collaboration with the U.S. Department of Energy (DOE) and its national laboratories to provide the phase diagrams necessary for processing these unique ceramic materials. A prime objective is the development of the portions of the phase diagram for the Pb-Bi-Sr-Ca-Cu-O system relevant to production of the high $T_c$ materials.

- Flux pinning - Use is made of a unique magneto-optical imaging facility to examine flux pinning in a variety of materials, with much of this work being conducted in collaboration with American Superconductor Corporation. In addition techniques for better interpretation of magnetic measurements are being developed. Structure and dynamics of flux lattices and melting phenomena, critical to applications, are investigated with small-angle neutron scattering techniques.

- Damage mechanisms - Work is being carried out under a joint CRADA (cooperative research and development agreement) with American Superconductor Corporation as part of the "Wire Development Group" which involves a number of DOE National Laboratories and the University of Wisconsin to elucidate the effects of strain on the loss of current in superconducting wires. The primary tool being employed is the use of microfocus radiography available at the NIST beamline at the Brookhaven National Laboratory.

- Database - A high temperature superconductor database has been developed in collaboration with the National Research Institute for Metals (NRIM) in Japan. The High Temperature Superconductor (HTS) Database includes evaluated open-literature data on numerous physical, mechanical, and electrical properties of a variety of chemical systems. The first version of the database is now for sale by the Office of Standard Reference Data.

- Crystal structure - Thermal neutron scattering techniques and profile refinement analyses are being utilized to investigate crystal and magnetic structures, composition, dynamics and crystal chemical properties. This research is being carried out in collaboration with a number of industrial and university experts and researchers at National Laboratories.

**PROGRAM TITLE:** High Temperature Superconductivity

**PROJECT TITLE:** Damage Characterization in High-Tc Tapes

**Principal Investigator:** Richard Spal

**Technical Objective:**

The electrical and mechanical behaviors of high-Tc superconductor composite tapes under tensile strain is of special concern because high-Tc superconductors are brittle. The objective of the current research is to test a fracture model of Bi-2223/Ag tapes under tensile strain derived from earlier microradiography studies.

**Technical Description:**

To study fracture in high-Tc superconductor tapes, a Bi-2223/Ag tape consisting of 19 Bi-2223 filaments sheathed in a Ag matrix was microradiographed at zero strain (as received) , then tensilely strained along its axis to 0.80% and microradiographed again. The microradiography was done at 24.75 keV photon energy with an asymmetric Bragg-diffraction x-ray microscope operating at 38X magnification, and equipped with an x-ray sensitive two-dimensional charged-coupled device (CCD) array.

**External Collaborations:**

We are developing techniques for the microradiography of superconducting tapes in cooperation with G. N. Riley and C. J. Christopherson, American Superconductor Corp.

**Accomplishments:**

The microradiography data were used to provide parameters for electrical and mechanical models of the tape. Subsequently, nonlinear voltage-current (V-I) curves were calculated from the model, taking into account current flow in the Ag matrix around cracks in the Bi-2223 filaments. Calculated and measured curves agree, thus confirming the model.

**PROGRAM TITLE:** High Temperature Superconductivity

**PROJECT TITLE:** Magneto-Optic Imaging of High Temperature Superconductors

**Principal Investigator:** Debra Kaiser

**Technical Objective:**

The objective of this research is to provide U.S. industry with evaluation techniques and data that will accelerate the commercialization of high temperature superconductors for electrical power transport.

**Technical Description:**

High flux pinning densities are needed for increasing the electrical current carrying capabilities of high temperature superconductors. Flux pinning mechanisms in high temperature superconductors are being studied by means of a magneto-optic imaging technique that was originally developed at the Russian Academy of Sciences. Magneto-optical imaging is proving to be highly useful in visualizing how various microstructural features of the superconductors pin flux and in evaluating the flux pinning densities.

**External Collaborations:**

American Superconductor Corporation provides the $(Bi,Pb)_2Sr_2Ca_2Cu_3O_x$ (BSCCO)/Ag composites which are characterized by magneto-optic imaging studies in cooperation with Marina Turchinskaya, University of Maryland.

**Planned Outcome:**

This research should provide producers of high temperature superconducting materials with a routine diagnostic tool to evaluate flux flow and flux pinning in their materials.

**Accomplishments:**

Our recent studies have demonstrated that magneto-optic imaging can be used for nondestructive analysis of flux flow in BSCCO/Ag composites. Superconducting BSCCO filaments can be imaged directly through the outer silver sheath of the composite tape. The images reveal: the morphology and alignment of filaments located as much as 112 μm below the unpolished tape surface; the depths of the filaments; the homogeneity of the magnetic flux distribution within these filaments; longitudinal thickness variations in the filaments; and the effects of neighboring filaments on flux flow in a filament. Magnetic induction profiles derived from analyses of the images indicate the magnitude and distribution of the magnetic field in each filament in a composite tape. These characteristics may prove to be useful in predicting the performance of the composite in service.

**Publications:**

"Nondestructive Magneto-optical Imaging Analysis of Superconducting $(Bi,Pb)_2Sr_2Ca_2Cu_3O_x$ Composites," M. Turchinskaya, D. L. Kaiser, A. J. Shapiro, G. N. Riley, Jr., and C. Christopherson, J. Mater. Res. 11, 1597 (1996).

**PROGRAM TITLE:** High Temperature Superconductivity

**PROJECT TITLE:** Materials Property Database for High Temperature Superconductors

**Principal Investigator:** Ronald Munro and Edwin F. Begley

**Technical Objective:**

The objectives of this project are to provide evaluated data, database standards, and data evaluation methodologies to advance the application and understanding of high temperature superconductors.

**Technical Description:**

This project is designed to facilitate technological advances in materials science by providing evaluated thermal and mechanical properties along with the principal superconductor characteristics for the broad class of materials commonly called high temperature superconductors.

**External Collaborations:**

The National Research Institute for Metals (Japan) is collaborating with NIST through a formal agreement to exchange property data on high-Tc materials.

**Accomplishments:**

Version 2 of the NIST Standard Reference Database 62: High Temperature Superconductors (HTS) has been completed. This new version contains data for cuprate, bismuthate, and relatively new borocarbide superconductors. This version also includes data provided by a unique Japanese study of high-Tc superconductors, primarily of the Bi(Pb)-Sr-Ca-Cu-O family. This set of data was obtained as part of a data exchange agreement between NIST and the National Research Institute for Metals (NRIM) in Japan. This collaboration has enabled U.S. efforts to access data that would not be readily available otherwise.

**Planned Outcomes:**

High temperature superconductors form the most intensely studied class of materials among all the types of materials that may be considered advanced or high-technology materials. The average publication rate since the discovery of the materials in 1986 has been on the order of 5000 papers per year. The resulting abundance of data has created serious challenges to accessing the essential data and to resolving the wealth of inconsistencies that may be found among the sets of properly data. The HTS database is designed to overcome barriers to the key technological information.

**Publications:**

Database:

NIST Standard Reference Database Number 62: High Temperature Superconductors, Version 1, 1995.

Technical Papers:

"Reference Relations for the Evaluation of the Materials Properties of Orthorhombic $YBa_2Cu_3O_x$ Supercondcutors," R. G. Munro and H. Chen, J. Am. Cer. Soc., Vol. 79, pp. 603-608 (1996).

"Dependence of the Critical Temperature on Atomic Structure in Orthorhombic Yba2Cu3Ox," H. Chen and R. G. Munro, Physical Review B, Vol. 53, pp. 12496-12501.

"Data Evaluation Methodology for High Temperature Superconductors," R. G. Munro and H. Chen, Computerization and Networking of Materials Databases: Fifth Volume, ASTM STP 1311, S. Nishijima and S. Iwata, eds. (American Society of Testing and Materials).

**PROGRAM TITLE:** High Temperature Superconductivity

**PROJECT TITLE:** Phase Equilibria Relations of High $T_c$ Superconductors

**Principal Investigators:** Terrell A. Vanderah, Winne Wong-Ng, and Lawrence P. Cook

## Technical Objective:

The objective of this research is to develop experimental phase-equilibria diagrams of superconducting materials with emphasis on regions pertinent to wire processing needed to improve the synthesis of higher quality (purity, texture) superconducting phases in bulk applications such as wires.

## Technical Description:

The high-temperature superconducting copper oxide phases are complex four-, five-, and even higher-component systems with complex crystal chemistries and variable stoichiometries. For practical reasons, experimental phase equilibria studies are deliberately focussed on selected regions and conditions, e.g. temperature (T) and oxygen partial pressure ( P), pertinent to wire processing. The co-existence of high-quality superconducting solid plus a liquid phase is required for the production of wires with high current-carrying capacities ($J_c$) and excellent superconducting properties ($T_c$); i.e., the superconducting phase must be both pure and textured to eliminate weak links. The phase diagram work is therefore directed toward determining the location in composition-P-T space of the primary crystallization fields of selected superconducting phases; that is, the regions where only 2 phases are present - the superconductor solid plus liquid. Recent efforts have been directed toward the BiSCCO 2212 ($T_c$ ~ 90 K) and Pb-2223 ($T_c$ ~ 110 K) superconducting phases.

## External Collaborations:

This project is supported in part by the DOE Superconductivity Program for Electric Systems which emphasizes development of bulk conductors; participants include government, academic, and industrial laboratories. The NIST group interacts and collaborates with Los Alamos National Laboratory (LANL), Oak Ridge National Laboratory (ORNL), and Argonne National Laboratory (ANL).

## Planned Outcomes:

Experimentally determined phase diagrams will be available that map out the primary crystallization fields of the BiSCCO 2212 ($T_c$ ~ 90 K) and Pb-2223 ($T_c$ ~ 110 K) phases. The primary crystallization fields are regions where only 2 phases are present - the superconductor solid plus liquid.

**Accomplishments:**

Determination of the approximate primary crystallization field of the BiSCCO "2212" superconductor in air and in the presence of silver impurities has been completed. At 830°C in air 2212 was found to be in equilibrium with 10 phases. Sixteen stable four-phase compatibility fields surrounding the 2212 phase have been identified at this temperature. The melting events associated with each stable four-phase region were studied with differential thermal analysis (DTA), quenching experiments, and wicking experiments in which samples of the first liquids formed were absorbed by capillary action. The chemical compositions of these liquids were obtained by quantitative energy dispersive X-ray spectrometry (EDS) and were used to locate the vertices of a multi-faceted polygon in compositional space that approximates the primary phase field of 2212. The addition of silver depresses the melting temperatures in the vicinity of the 2212. Ag was found to enter the melt at a mole fraction saturation level of 2% to 8%. In the copper-rich liquids, Ag replaced some of the copper, resulting in a shift of the 2212 crystallization field away from the copper oxide corner.

Experimental determination of the primary phase field of the five-component lead-substituted 2223 BiSCCO system as a function of oxygen partial pressure and in the presence of silver impurities has been initiated. In order to complete the first step of the study; i.e., subsolidus identification of all phases in equilibrium with the superconductor, it was necessary to complete the underlying ternary equilibrium diagrams for which information is incomplete or not available in the literature. In particular, subsolidus equilibria and melting behavior in the systems $PbO_x$-SrO-CaO, $Bi_2O_3$-CuO-$PbO_x$, and $PbO_x$-SrO-CuO have required experimental determination this year in order to proceed with determination of the crystallization field for the superconducting phase.

**Impact:**

"Processing maps" in the form of composition-temperature-pressure phase diagrams indicating the location of the primary crystallization fields for the BiSCCO 2212 and Pb-2223 phases will assist wire developers in synthesizing higher quality (purity, texture) superconducting phases and hence wires with higher critical current capacities. Though the BiSCCO 2212 results have not yet appeared in print, numerous copies of the pre-print have been requested by U.S. companies including the leading developer of superconducting wires.

**Publications:**

"The Primary Crystallization Phase Field of Bi-Sr-Ca-Cu-O (BSCCO) "2212" in Air and the Effect of Ag Addition," W. Wong-Ng, L.P. Cook, and F. Jiang; submitted to J. Am. Cer. Soc.

"Subsolidus Phase Relationships of the Pb-Sr-Ca-O System at 840 °C to 850 °C in Air," W. Wong-Ng, L.P. Cook, and F. Jiang; submitted to Physica C.

"Subsolidus and Melting Study of the $Bi_2O_3$-$PbO_x$-CuO System in Air," W. Wong-Ng, L.P. Cook, and F. Jiang; submitted to J. Appl. Supercon.

"Subsolidus and Melting Phase Relationships of the Pb-Ca-Cu-O System in Air," W. Wong-Ng, L.P. Cook, W. Greenwood, and F. Jiang; submitted to Physica C.

A.R. Drews, J.C. Cline, T.A. Vanderah, and K. Salazar, "High Temperature X-Ray Diffraction Studies of a Precursor Mixture for Pb-Substituted Bi-2223 Superconducting Wires," submitted to J. Mat. Res.

# MAGNETIC MATERIALS

# MAGNETIC MATERIALS

Magnetic materials are pervasive throughout our society. They are used, for instance, in magnetic recording media and devices, in all motors, in all transformers, on credit cards, as permanent magnets, as magnetic sensors, on checks, in theft control devices, in automotive and small engine timing devices, in xerographic copiers, in magnetic resonance imaging (MRI) machines, in microwave communications, in magnetic separation, and in magnetic cooling. Magnetic materials include metals, ceramics and polymers at different size scales ranging from large castings to particulates, thin films, multilayers and nanocomposites.

In the present trend to make devices smaller, thereby reducing weight or increasing storage density, new magnetic materials are constantly being developed. One critical need for implementation of these materials is the development of the measurement science needed for their characterization, both in terms of material properties and performance. This is the focus of the Magnetic Materials Program. Proper measurements of key magnetic data,, determination of the fundamental science behind the magnetic behavior of these new materials, analysis of the durability and performance of magnetic devices and development of standard reference materials are key elements of this program. Some information is only obtainable by the use of unique measurement tools at NIST like the NBS reactor, or the magneto-optic indicator film apparatus for observation of magnetic domain motion. Of particular interest is understanding the magnetic behavior of low dimensional systems, in which one or more characteristic dimensions have been reduced to nanometer sizes. For these new materials, however, it is not known whether their exciting novel behavior is due to new physics or to a logical extension of large-size behavior to small dimensions. Consequently, implementation of this new type of material into marketable products is significantly delayed. NIST is providing the measurement science to answer this critical unknown.

Areas of present study include the following:

- processing of magnetic multilayers for optimal giant magnetoresistance effects
- measurement and modeling of the enhanced magnetocaloric effect in nanocomposites
- observation and micromagnetic modeling of magnetic domains for understanding magnetization statics and dynamics in advanced and conventional materials
- nanotribology of magnetic hard disk, measurement of stiction, friction, and wear at the nanometer scale
- development of magnetic sensors of mechanical properties for incorporation as *in situ* controls in a steel mill

- development of a measurement system for the preparation of an absolute magnetic moment standard

- development of a magnetoresistance microscope for micrometer scale magnetic measurements in industrial environments

- a study of magnetic signatures of engineered surfaces such as those created by ion implantation of ferrous materials

By experimentally addressing important issues in magnetism, by bringing together the industrial and scientific communities through the organization of workshops and conferences in the area, and by the development and preparation of appropriate standards, NIST acts to accelerate the utilization of advanced magnetic materials by the industrial sector, and to enable industry to take advantage of new discoveries and innovations. In addition, close linkage with the national storage industry consortium (NSIC) which consists of 38 companies and a score of universities allows industrial relevance and partnership. Additional collaborations With Xerox, General Motors, Hewlett Packard, IBM, Seagate, and Motorola Corporations, for example, enable NIST to leverage its activities with the much larger, but complementary, capabilities of other organizations.

**PROGRAM TITLE:** Magnetic Materials

**PROJECT TITLE:** Nano-Tribology of Magnetic Hard Disk Systems

**Principal Investigators:** Stephen M. Hsu, Richard S. Gates, Patricia McGuiggan, and Daniel A. Fischer

**Technical Objectives**:

The project focuses on assisting industry in providing critical measurement tools in the areas of friction, wear, stiction, and durability necessary for the development of new generation of data storage technology with a bit density of (1.5 to 6) $x10^{-9}$ $cm^{-2}$.

**Technical Description:**

We are exploring different surface chemistries to enhance durability of hard disks at rapidly reducing flight heights. Various monomolecular films are deposited on ultra-smooth disks over different carbon overcoat materials and varying thicknesses. Part of the disks are evaluated by industrial collaborators using Constant Start and Stop (CSS) tests. Part of the disks are evaluated internally using tests developed at NIST. Surface characterization techniques are being developed to measure molecular orientation, film thickness, and surface bonding strengths.

**External Collaboration:**

Working in conjunction with The National Storage Industry Consortium (NSIC, some thirty companies) tribology working group we are developing techniques for the measurement of friction on magnetic storage devices.

**Planned Outcomes:**

In conjunction with the information technology industry, three areas of research are being conducted leading to anticipated outcomes of: (1) development of laboratory scale test procedures to evaluate new materials, coatings, and surface chemistry of the magnetic hard disk system, (2) understanding of how mono-molecular films interact and protect the magnetic disks, (3) determine The relationship between thin film structures and their mechanical properties. These outcomes will assist U.S. industries to develop the next generation data storage technologies.

**Accomplishments:**

Experiments were done on a model system as well as on the actual disks. Stearic acid monolayer and submonolayer were deposited on a copper surface and examined using Fourier Transform Infrared Spectroscopy, Time-resolved Raman Spectroscopy, and Ultra-soft X-ray Absorption Spectroscopy. The

# MECHANICAL PROPERTIES OF BRITTLE MATERIALS

# MECHANICAL PROPERTIES OF BRITTLE MATERIALS

Mechanical properties are the source of some of the greatest benefits as well as the most serious limitations of ceramics. With their high strength-to-weight ratio, their relatively inert behavior in aggressive environments, their high hardness and wear resistance, and their ability to withstand significantly higher temperatures than metals or polymers, ceramics potentially offer major improvements for component design in a wide range of applications. On the debit side, ceramic materials typically exhibit statistically variable brittle fracture, environmentally enhanced subcritical crack growth, a sensitivity to machining damage, and creep/deformation behavior at elevated temperatures. Additionally, a lack of techniques, which can detect and quantify critical flaws before failure occurs, severely curtail current uses of ceramics. The unpredictable failure behavior of ceramics stems from three sources: (1) limited data and a deficiency of basic understanding of failure processes in ceramics; (2) limited standard test techniques to permit inter-laboratory comparisons of materials behavior and to collect engineering data; and (3) inadequate models and statistical techniques for life prediction and reliability analyses. The Mechanical Properties of Brittle Materials Program in the Ceramics Division has components specifically addressing each of these issues.

Basic understanding of mechanical behavior of ceramics is investigated at both room temperature and elevated temperatures. Mechanical properties and failure processes in fiber-reinforced ceramic matrix composites are being investigated as a function of both temperature and fiber load. Changes in stress associated with crack bridging in microstructurally toughened alumina are being measured via micro-Raman techniques and correlated with micro-mechanical modeling. At elevated temperatures, the basic mechanisms responsible for crack growth, creep and creep rupture are being investigated for various silicon nitride compositions, and for membrane and fuel cell materials.

To improve interlaboratory comparisons and to increase confidence in generated data, new standard test techniques for hardness and toughness are being developed and tested in round-robin experiments. Research and inter-laboratory studies with instrumented indentation address the use of this technique in measuring the elasticity and hardness of thin films and coatings. Micro-Raman techniques are being developed and calibrated so that a quantitative assessment of microstructural residual stresses can be mapped for a heterogeneous microstructure. At elevated temperatures, new creep specimen designs were designed which permit higher stresses, reduce non-gage section failures, and permit smaller specimens to be fabricated from ceramic components. Intra- and inter-laboratory studies have demonstrated the robustness of these geometries.

Finally, techniques to predict lifetimes of ceramics under constant and variable loading conditions are being developed. The nonparametric bootstrap approach for assessing the confidence of lifetime predictions is investigated and compared with analytical techniques. Work includes applying these techniques to aluminum nitride materials for thermal management systems, and to fused silica windows for spacecraft applications. At elevated temperature a new experimental procedure is being developed for characterizing time-dependent failure under static loads.

**PROGRAM TITLE:** Mechanical Properties of Brittle Materials

**PROJECT TITLE:** Creep of Ceramics

**Principal Investigator:** Bernard J. Hockey and Sheldon Wiederhorn (MSEL)

**Technical Objectives:**

This research is designed to assist industry in the evaluation, design, and development of advanced structural ceramics for use as high-temperature components in land-based heat engines for power generation and vehicles, and in the development of measurement methodologies for the evaluation of the necessary high-temperature mechanical properties.

**Technical Description:**

Using our extensive creep facilities (12 machines) we can generate the quantity of data necessary to make databases that allow statistical interpretation of collected data. We can make predictions of mean failure time as well as times for very low probability of failure. This ability is especially important in the interpretation of intermediate-temperature delayed failure results, where failures exhibit extreme-value statistics behavior.

**External Collaborations:**

In cooperation with General Electric Power Generation, Schenectady, NY and W. E. Luecke, Case Western Reserve University, Cleveland, OH we are developing a database of creep properties for silicon nitride which will be utilized for materials selection and component design.

**Planned Outcomes:**

Major outcomes of this research are expected to include: (1) development of failure mechanism maps for structural ceramics proposed for use as ceramic engine components, including estimations of regions of low probability of failure; (2) development of standardized tensile testing methodologies for material comparison; and (3) elucidation of relationships between the microstructure of these materials and resultant elevated-temperature mechanical properties.

**Accomplishments:**

NIST and GE continued with the CRADA, signed in September 1994. We have conducted over 60 creep rupture, 50 strength, 70 static fatigue, and 20 dynamic fatigue tests on two candidate silicon nitride materials. Using this data, we constructed failure maps showing regions of safe operation (i.e., low probability of failure and/or long-term creep life) from room temperature up to 1400 °C. Several creep tests have lasted over 3,000 hours under load, and three are ongoing.

Using the deformation data generated as part of the CRADA, and other data collected in our laboratory, we have refined our model for the creep of silicon nitride materials. We are now focussing on the distribution of the intergranular phase as the source of the observed behavior.

We also completed our initial round-robin creep study. Two ceramic industry research laboratories (Allied Signal, Norton/St. Gobain), a university laboratory (Lehigh University, Department of Materials Science) and one government research laboratory (Oak Ridge National Laboratory) participated. Agreement between the laboratories exceeded our expectations.

Buoyed by the success of our initial round-robin, we launched a second, wider ranging interlaboratory study. In this effort we will include laboratories using different specimen geometries and strain measurement techniques. Already, researchers from Japan and Europe have agreed to participate.

The creep and rupture data gathered in this project demonstrate that silicon nitrides possess the requisite properties and reliability for use in high-temperature engines.

**Publications:**

William E. Luecke and Jonathan D. French; "Sources of Strain Measurement Error in Flag-Based Extensometry," J. Am. Ceram. Soc., **79** [6], 1617-1626 (1996).

Jonathan D. French and Sheldon M. Wiederhorn, "Tensile Specimens from Ceramic Components," J. Am. Ceram. Soc, **79** [2], 550-552 (1996).

B. Anne Fields and Sheldon M. Wiederhorn, "Creep Cavitation in a Siliconized Silicon Carbide Tested in Tension and Flexure," J. Am. Ceram. Soc., **79** [4], 977--986 (1996).

William E. Luecke and Sheldon M. Wiederhorn, "Interlaboratory Verification of Silicon Nitride Tensile Creep Properties," J. Am. Ceram. Soc., (1996), in press.

Michael G. Jenkins, Robert K. Shiffer and Sheldon M. Wiederhorn, "Creep Testing of Advanced Ceramics," in *Mechanical Testing Methodology for Ceramic Design and Reliability*, D. C. Cranmer and D. W. Richerson, eds., (Marcel Dekker, New York, 1996), submitted.

**PROGRAM TITLE:** Mechanical Properties of Brittle Materials

**PROJECT TITLE:** Damage Accumulation in Actuator Materials

**Principal Investigator:** Grady S. White

**Technical Objectives:**

The objective of this project is to identify the failure mechanisms in cyclically loaded actuator materials, so that meaningful reliability estimates can be made for smart materials systems. The interactions between stress and piezoelectric properties, the generation of microcracks and the effects of thermal excursions are being investigated for both "hard" lead zirconate titanate (PZT), i.e., PZT with tightly fixed domain structure, and "soft" PZT.

**Technical Description:**

This work is directed to determining failure mechanisms, both piezoelectric and mechanical, of PZT under cyclic loading conditions. Because all applications of actuator materials include cyclic loads and because actuators are frequently used to apply motion or forces under conditions in which component replacement is difficult or failure is dangerous, reliability is a fundamental concern.

For this study, poled bars of PZT (hard and soft) have been driven at longitudinal resonance frequency to generate alternate tensile and compressive stresses in the bars. Other poled bars of hard PZT have been driven at 20 Hz on a 4-point bend test rig. Temperature was monitored for both loading conditions. After cyclic loading, piezoelectric, elastic and dielectric constants, as well as mechanical Q, have been measured as a function of time and positions within the specimens. Transmission electron microscopy has been done on some of the hard PZT specimens.

**External Collaborations:**

Measurement and modeling of actuator failure mechanisms is being done in collaboration with Q. Jiang and D. Breiner, University of Nebraska, Department of Engineering Mechanics; materials are being provided by Edo Corporation.

**Planned Outcome:**

The outcome of this work will be an understanding of residual stress relief mechanisms in soft and hard PZT which will allow development of accurate reliability and lifetime prediction models.

**Accomplishments:**

We have determined that, during cyclic loading of hard PZT, both microcracking and 90° domain reorientation appear to be stress relief mechanisms which reduce the residual stresses generated during poling. At elevated temperatures, both domain reorientation and microcracking occur while, near room temperature, there is not enough thermal energy to allow domain reorientation and only microcracking is observed. For similar measurements in soft PZT, domain reorientation is observed at elevated temperature and not near room temperature. No evidence for microcracking has yet been observed for the soft PZT.

**Publications:**

M. D. Hill, G. S. White, C. S. Hwang, and I. K. Lloyd, "Cyclic Damage in Lead Zirconate Titanate," J. Am. Ceram. Soc. 79 [7], 1915-20 (1996).

G. S. White, M. D. Hill, and I. K. Lloyd, "Response of PZT-8 to Cyclic Loading," in Proceedings of the 6th International Symposium on Fracture Mechanics of Ceramics, in press.

**PROGRAM TITLE:** Mechanical Properties of Brittle Materials

**PROJECT TITLE:** Fracture Behavior of Ceramic Matrix Composites

**Principal Investigator:** Linda M. Braun

**Technical Objectives:**

This research project is designed to assist industry by assessing the applicability of fracture mechanics in the description of failure modes and reliability of fiber-reinforced ceramic matrix composites. Goals are to relate damage and fracture behavior to microstructure, and to develop testing methodologies to quantify damage.

**Technical Description:**

This project is designed to elucidate failure modes, damage generation, and damage accumulation in fiber-reinforced ceramic matrix composites through the development of new tests for the measurement of mechanical behavior and new test methodologies. Fracture processes in the composite matrix, individual fibers, fiber bundles, and at the fiber/matrix interface are studied as a function of processing methodology and microstructure.

**External Collaborations:**

Collaboration involves investigation of materials suppled by Jay Morrison, Westinghouse Electric Corporation, Orlando, FL, and Atul Shah, DuPont Lanxide Composites, Newark, DE, in order to determine failure mechanism in composites.

**Planned Outcomes:**

Major outcomes expected from this research are: (1) development of testing methodologies to quantify damage in fiber-reinforced, ceramic matrix composites; and (2) reliable damage and failure property data for design and manufacture of fiber-reinforced, ceramic matrix composites.

**Accomplishment:**

A new local technique was developed for evaluating damage generation and damage accumulation in fiber-reinforced, ceramic matrix composites. The technique uses the constrained shear stress-state beneath a spherical indentor to induce shear damage without concomitant tensile failure modes. The constrained shear test was used to investigate damage in two commercial SiC fiber-reinforced SiC composites. Damage was related to the microstructure and further correlated with the processing methodology. Load-displacement curves correlated with the amount of generated damage.

**PROGRAM TITLE:** Mechanical Properties of Brittle Materials

**PROJECT TITLE:** Mechanical Test Development

**Principal Investigator:** George D. Quinn

**Technical Objective:**

Procedures are developed for characterizing ceramics and standard test methods are prepared for ASTM and ISO consideration. Our objective is to develop procedures that are as technically rigorous as possible while remaining practical and useable by industry.

**Technical Description:**

Mechanical testing methods for ceramics are created, developed, improved, refined, and standardized. Testing is conducted to gain first-hand experience with a method. Upon reaching a mature prestandardization level, a method is evaluated by round robin(s) which verify the suitability of the method and generate precision and bias data. Foundation work for standard reference materials is performed. Current work is targeted towards fracture toughness, hardness, and diametral compression strength tests.

**External Collaborations:**

Industry is consulted for test method standardization needs. The Department of Energy, Office of Heavy Vehicle Technologies, provides programmatic support for some portions of this project. ASTM Committees such as C-28, Advanced Ceramics, and F-04, Surgical and Medical Devices are consulted and used as forums for creating standards. International collaborations are maintained through the VAMAS program and other avenues as warranted. International standardization is pursued through ISO Technical Committee 206, Fine Ceramics and contacts in CEN Technical Committee TC 184, Advanced Technical Ceramics.

**Planned Outcomes:**

Wherever possible, standard practices or test methods are prepared in the appropriate forum so that accurate and precise mechanical property data results can be obtained by NIST, industry, government labs, and academia. Emphasis is on preparing ASTM and ISO standards. This project also serves as a lead in to standard reference material projects. Round robin projects are conducted as necessary.

**Accomplishments:**

In the last year, three standards were shepherded through ASTM and adopted as standards based on the work done in this project:

C 1322-96 "Standard Practice for Fractography and Characterization of Fracture Origins in Advanced Ceramics,"
C 1326-96 "Standard Test Method for Knoop Indentation hardness of Advanced Ceramics,
C 1327-96 "Standard Test Method for Vickers Indentation Hardness of Advanced Ceramics,

Revisions to these standards were also prepared and adopted in 1996. In addition, FY 96 work in this program has contributed to the following draft standard that is balloting in ASTM C-28 and E-08:

C-xxxx "Standard Test Methods for the Determination of Fracture Toughness of Advanced Ceramics"

Also, a new draft world standard was prepared for ISO TC 206:

ISO - xxxx "Test Method for Flexural Strength of Monolithic Ceramics at Room Temperature"

In conjunction with these activities the following work was performed:

- A new concept of "Brittleness" was developed and a major paper prepared. This work was an outgrowth of our meticulous work on fracture toughness and hardness measurement techniques.

- Extensive fracture toughness testing by the Surface Crack in Flexure method was performed. Ten new materials were evaluated. Refinements to precrack measurements techniques and investigations of the influence of slow crack growth upon the precracks were will help refine the ASTM draft standard.

- Diametral compression strength testing commenced. This method is a strong candidate for standardization.

- A summary paper on the topic of comparing calculated to measured flaw sizes was written to aid fractographic investigations and to support the new fractography standard, C 1322-96.

- Hardness data was furnished for a VAMAS round robin organized by the Japan Fine Ceramics Center. Preliminary findings show that the best data (reproducibility and repeatability) was obtained *with the ASTM C 1326 Knoop 2 kg test procedure.* This will impact ISO standardization.

- Specimens, administrative and technical support were furnished to BAM Berlin for a new instrumented (recording) hardness VAMAS round robin. NIST prototype SRM 2830 Knoop hardness blocks are featured and are gaining widespread acceptance as one of the best reference ceramics in the world.

- Extensive work was performed to support ASTM Committee C-28 Advanced Ceramics, VAMAS Technical Working Area #3, Ceramics, and ISO Technical Committee 206, Fine Ceramics. This work ranged from managing these entities (or working groups in them) to helping other parties prepare standards or projects.

**Impacts:**

Refined and standardized test methods are now available. The ceramics community now has procedures that generate data of high quality and data which is readily comparable between laboratories, benefitting both the industrial and research communities. Data suitable for design and design data bases are now easily obtained. *The structural ceramics community now takes ceramics more seriously and are more inclined to utilize this class of materials.*

Tangible benefits also include significant cost savings. For example, the adoption of standard specimen sizes and surface preparation treatments has driven the cost of flexure specimens (the bread and butter strength test for ceramics) from $15-20 to $8 per specimen, a 50% savings. The two most prominent ceramic machine shops in the United States are now fabricating over 500 flexure specimens per week each. Considering the existence of many other small shops that also fabricate standard flexure specimens, we estimate that the total savings to American industry per year are *over $500,000 per year.*

As another example, fractography of ceramics has heretofore been a highly interpretive "art." Work in this project has standardized some elements of fractographic analysis. Consistent results and interpretations are more readily obtained and can be related better to mechanical property results. *The fractography standard is used as a teaching aid in courses at several universities and by a course offered by the American Ceramic Society.*

In some instances, new research findings are developed as a consequence of prestandardization work. For example, an entirely new concept for brittleness has been discovered following meticulous conventional hardness experiments.

**Publications:**

Thirty-four reports and papers have been written to document the progress in this project. These have ranged from papers summarizing progress in standardization activities in general, to detailed papers on test methods and procedures, to round robin summaries. In this year the following papers were written:

G. D. Quinn, R. J. Gettings, and J. J. Kübler, "Fracture Toughness of Ceramics by the Surface Crack in Flexure (SCF) Method," pp. 203-218 in *Fracture Mechanics of Ceramics*, eds. R. C. Bradt, D. P. H. Hasselman, D. Munz, M. Sakai, and V. Yashevchenko, (Plenum, 1996).

G. D. Quinn, R. J. Gettings, and J. J. Kübler, "Fractography and the Surface Crack in Flexure (SCF) Method for Evaluating Fracture Toughness of Ceramics, pp 107 - 144 in *Fractography of Glasses and Ceramics,*" Ceramic Transactions, Vol. **64**, (American Ceramic Society, Westerville, OH, 1996).

J. J. Swab and G. D. Quinn, "The VAMAS Fractography Round Robin: A Piece of the Fractography Puzzle," in *Fractography of Glasses and Ceramics,*" Ceramic Transactions, Vol. **64**, (American Ceramic Society, Westerville, OH, 1996).

G. D. Quinn and J. J. Swab, "Fractography and Estimates of Fracture Origin Size from Fracture Mechanics," Ceram. Eng. and Sci. Proc., 1996, in press.

J. B. Quinn and G. D. Quinn, "Hardness and Brittleness of Ceramics," Ceram. Eng. and Sci. Proc., 1996, in press.

J. B. Quinn and G. D. Quinn, "Indentation Brittleness of Ceramics: A Fresh Approach," J. Mat. Sci., 1996, submitted.

J. B. Quinn and G. D. Quinn, "Hardness and Brittleness of Advanced Ceramics," in the proceedings the 2nd Pac Rim Conference, Cairns, Australia, July, 1996, submitted.

M. G. Jenkins and G. D. Quinn, "ASTM Standards for Monolithic and Composite Advanced Ceramics: Industrial, Governmental and Academic Cooperation," American Society of Mechanical Engineers paper 96-GT-270, June 1996. Presented at the International Gas Turbine and Aerospace Congress, Birmingham, UK, June 10, 1996.

C. R. Brinkman, G. D. Quinn, and R. W. McClung, "Overview of ASTM Standard Activities in Support of Advanced Structural Ceramics Development," pp. 97 - 108 in *Challenges in Ceramic Product Development, Manufacturing and Commercialization*, Ceramic Transactions, Vol **66**, (American Ceramic Society, Westerville, OH, 1996).

**PROGRAM TITLE:** Mechanical Properties of Brittle Materials

**PROJECT TITLE:** Raman Spectroscopy for Residual Stress Detection

**Principal Investigators:** Grady S. White and Linda Braun

**Technical Objectives:**

This research project is designed to develop measurement procedures to evaluate localized residual stresses which can control mechanical, electrical and optical properties over a wide range of industrial applications. Measurement of changes in Raman spectra will be used to evaluate local stresses on a scale comparable to the microstructure.

**Technical Description:**

Raman spectra are generated by the interaction of light with phonon modes in the unit cell. Consequently, stress induced changes in unit cell symmetry will cause shifts in Raman peak position and intensity. To measure stresses, these peak shifts must be calibrated as a function of stress. A major emphasis of this work involves investigating crystallographic effects on calibration curves. Peak shift/stress relationships were determined for [0001], $[11\bar{2}0]$, and $[22\bar{4}3]$ crystallographic orientations in sapphire using an *in situ* biaxial stressing rig. Effects of incident light polarization were also investigated in order to relate crystallographic orientation to Raman spectra. In the polarization studies, incident polarization angle was changed relative to the known crystallographic orientation. Crystallographic orientation was determined using electron backscatter techniques.

Preliminary investigations of sapphire windows, used in optical applications, have been made to correlate changes in stress observed by Raman spectroscopy to those detected by x-ray topography and polarized light microscopy.

**External Collaborations:**

Modeling of stress effects on Raman spectra is being done in collaboration with M. Bell of NRL. Stresses in sapphire windows are being investigated with R. Polvani of the Precision Engineering Division, NIST.

**Planned Outcomes:**

This work has demonstrated that specimen crystallographic orientation must be known for Raman peak positions to be related to stress state. An anticipated outcome from this work is the development of standardized calibration procedures which will allow quantitative stress estimates to be determined for materials which exhibit sharp Raman peaks and for which single crystal calibration specimens can be obtained.

**Accomplishments:**

A micro-Raman laboratory has been designed and constructed. Measurements of Raman peak shift vs applied biaxial load were made on sapphire specimens with normal orientations of [0001], $[11\bar{2}0]$, and $[22\bar{4}3]$. Slopes of the peak shift curves have been demonstrated to be orientation dependent. Preliminary findings have shown that slopes for the $[11\bar{2}0]$ and $[22\bar{4}3]$ orientations are over an order of magnitude greater than the slope for the [0001] orientation. This result shows that the crystallographic orientation of the material under investigation must be known in order to use the appropriate calibration curve to quantify stresses.

Polarization results suggest that relative peak height measurements made as a function of incident polarization angle can provide estimates of crystallographic orientation in sapphire. Therefore, appropriate calibration curves can be determined without Laue or electron backscatter measurements.

Slopes of peak shift vs stress curves obtained for three randomly chosen grains in an alumina specimen were compared with the slopes obtained from the single crystals. The slopes obtained for the alumina grains fell into the same two ranges as those obtained for the single crystals.

Correlations have been made, as a function of position within sapphire windows, of changes in stress/strain, as determined by x-ray topography, with peak shifts in Raman spectra.

**PROGRAM TITLE:** Mechanical Properties of Brittle Materials

**PROJECT TITLE:** Test Development for Aluminum Nitride Substrates

**Principal Investigators:** Jay S. Wallace and Edwin R. Fuller

**Technical Objectives:**

The primary objective of this research is to design and characterize standard test methods which are applicable to measuring strength and mechanical properties of aluminum nitride (AlN), and other thin ceramic substrates, used in the electronics industry. A secondary objective is to characterize mechanical properties and mechanical reliability of commercial and research AlN materials to ascertain microstructural factors that control mechanical reliability in these materials.

**Technical Description:**

This project is designed to investigate the parameters involved in performing reliable mechanical property evaluations of thin ceramic substrates for electronic applications, and other uses where material configuration dictates testing thin, flat samples. Design of a fixture to test strength of substrate materials had several design constraints. A primary concern was that typical production specimens could be measured without further material preparation; any material preparation, such as cutting, grinding or polishing, would change the in-service material condition and could distort the measurements. Due to specimen geometry, thin flat plates, a biaxial flexure design was mandated. Several biaxial flexure fixture configurations were evaluated and a coaxial ring (ring-on-ring) configuration with polymer loading rings was chosen. Several possible sources of experimental errors, including friction and contact stresses between the loading rings and the substrate, specimen deflection beyond the small deflection limit of the elasticity calculations, and stresses on the outside specimen edges, dictated the final fixture configuration. Initial round robin testing of AlN substrates has been performed by the four laboratories involved.

**External Collaborations:**

This research is part of the *Japan-U.S. Research Collaboration in Aluminum Nitride* for pre-competitive research in the development of AlN materials. It is a four-way collaboration between Dow Chemical Co. In Midland, Michigan, who provides AlN powder to Toshiba's Research and Development Center in Japan to made test specimens. NIST develops and conducts tests for characterizing the mechanical behavior of AlN substrates, and Japan's National Industrial Research Laboratory of Nagoya (NIRIN) is responsible for processing studies and microstructural characterization.

**Planned Outcome:**

The major outcomes expected from this research are: (1) development of testing methodologies for evaluating structural properties and reliability of thin ceramic substrate materials and (2) an understanding and characterization of microstructural factors that control mechanical reliability in these materials.

**Accomplishments:**

A coaxial ring test fixture for testing electronic substrates was designed and tested. A primary design goal was to develop a technique which would allow testing of substrates in the in-service material condition. In collaboration with Dow Chemical, Toshiba and NIRIN, the mechanical properties of a series of AlN materials, both commercial and prototype materials, have been examined. Primary focus concerned reliability of AlN materials in the presence of atmospheric moisture. A crack growth parameter, N', of approximately 125 indicated that there was a minimal statistically significant influence of atmospheric moisture on long-term strength.

Measurements of the fracture properties of several AlN materials have shown that there are significant differences in strength depending upon the processing and material preparation conditions. Low strengths and Weibull Modulii could be correlated with the appearance of surface layers which had a dramatically different fracture appearance as compared to the intergranular fracture found in the specimen interior. The behavior of the sample with this surface layer strongly supported the initial decision to develop a testing technique which measures the properties of the samples in the in-service material condition. The methods used here also permit the study of the effects of production techniques which modify the surface condition on the strength.

Finally, strengths of AlN samples were measured by the four laboratories in this research collaboration using a standardized coaxial ring fixture, and results were compared. Possible reasons for the systematic differences between results from the four laboratories are being discussed and investigated.

To date, three meetings have been held between participants to exchange data. At the conclusion of the project in March, 1998, an international symposium is being planned to disseminate the information and methodology developed in the project.

**Publications:**

Jay S. Wallace, Edwin R. Fuller, Jr., and Stephen W. Freiman, "Mechanical Properties of Aluminum Nitride Substrates," NISTIR 5903, September 26, 1996.

Jay S. Wallace, "Coaxial Ring Fixture and Testing Procedure for Ceramic Substrates," NISTIR 5891, August 21, 1996.

**PROGRAM TITLE:** Mechanical Properties of Brittle Materials

**PROJECT TITLE:** Test Development for Membrane Materials

**Principal Investigators:** Edwin R. Fuller and Tze-jer Chuang

**Technical Objectives:**

This research is designed to assist industry through the development of techniques for the structural characterization of dual purpose oxygen conducting ceramic materials. Additionally, critical mechanical property data are collected for newly developed materials to facilitate design and fabrication of a ceramic membrane reactor for processing gas streams. Techniques for determination of mechanical properties and residual stress and methodologies for assurance of durability and reliability under specific service conditions are the primary NIST focuses. Mechanical properties include: Young's modulus, strength distribution, residual stress evaluations, subcritical crack growth behavior, and fracture toughness.

**Technical Description:**

Ceramic ionic and mixed conductors hold promise for application as high temperature gas separation devices which can improve the thermal efficiency of chemical processes. This research is focused on one ionic conductor: modified $La_{1-x}Fe_{1-y}M_yO_{3-z}$ (where M = Cr, Co, Mn or Mg). Testing methods are evaluated, improved, and refined for measuring mechanical properties of small, brittle tubular specimens at elevated temperatures and in controlled environments. Key mechanical properties affecting design include: strength, residual stress state, and elastic modulus. Those properties affecting lifetime and reliability include: Weibull properties, residual stress state, subcritical crack growth behavior, and fracture toughness. Special considerations are needed due to the interplay between component geometry, compositionally driven residual stresses, and environmental history. Efforts have focused on an O-ring testing configuration for characterizing strength and a C-ring configuration for evaluating Young's modulus. Existent candidate materials are evaluated to validate testing techniques and to provide preliminary data to facilitate design and fabrication of reactor components. Finite element and analytical analyses support the test method development. Coupled diffusional equations with misfit stress calculations aid in evaluating the influence of the compositionally driven residual stress state.

**External Collaborations:**

Part of the research is done in collaboration with Terry J. Mazanec and Ajit Sane, BP Chemicals Inc., Cleveland, OH and G. Whichard and V. Bergsten, Praxair Surface Technologies, Indianapolis, IN, with which NIST has a CRADA. BP and Praxair provide materials for testing and collaborate on test methodologies.

**Planned Outcomes:**

The major outcomes expected from this research are: (1) development of testing methodologies to quantify structural properties and reliability of oxygen conducting ceramic membranes; (2) an understanding and characterization of failure and damage mechanisms in these materials, and (3) an understanding of compositionally driven residual stress states in these materials and their influence on structural behavior and lifetime.

**Accomplishments:**

Techniques were developed for testing small O-ring specimens in controlled environments from room temperature to 1000 °C. Mechanical strengths were measured on specimens cut directly from ceramic membrane tubes at room temperature in air and at 1000°C in nitrogen. Weibull properties were evaluated. A theory was derived for the time-dependent residual stresses that result from diffusion induced misfit strains. The residual stress state of a membrane tube was evaluated for boundary conditions such that the tube is initially in an oxygen depletion state. An analysis, both analytical and via finite elements, of the gap displacement for a C-ring testing geometry illustrates that this testing configuration provides a viable technique for measuring Young's modulus at elevated temperatures.

# SYNCHROTRON RADIATION

# SYNCHROTRON RADIATION

The Materials Microstructural Characterization Group in the Ceramics Division currently operates two beam stations and is a partner in the operation of a third beam station at the National Synchrotron Light Source (NSLS). At these facilities, a wide range of material characterization measurements is carried out. Scientific problems currently being addressed include microstructure characterization of ceramics and plasma-sprayed ceramic coatings, crystal perfection in a variety of basic and applied materials, and the atomic-scale and the molecular-scale structures at surfaces and interfaces in polymeric, metal/semiconductor, catalytic, and other systems of technological importance.

MSEL has entered a Collaborative Access Team (CAT) agreement with the University of Illinois, Oak Ridge National Laboratory, and U.O.P. Corporation to build and operate a sector at the Advanced Photon Source (APS) at the Argonne National Laboratory. The CAT is called UNI-CAT in recognition of the University, National Laboratory, and Industrial components of this team. The APS offers a 100 to 10,000-fold increase in brilliance compared to the best synchrotron x-ray sources of today.

In the years to come the APS will supplant the NSLS as this nation's premier x-ray source. The APS beam lines, now under construction by UNI-CAT, incorporate the newest technology which will not only enable NIST scientists to significantly improve our real-time x-ray microscopy, ultra-small-angle x-ray scattering, in-situ x-ray topography and EXAFS capabilities, but will also offer opportunities for cutting-edge experiments in structural crystallography (and time-resolved structural scattering), surface/interface scattering, diffuse scattering, and magnetic scattering. NIST scientists anticipate extending our present portfolio of characterization capabilities to include an even wider range of materials measurements of importance to materials scientists and to U.S. industry.

Experimental capabilities include:

- *In situ* studies of surface relaxation and phase transitions in approximate monolayer coverages in semiconductor crystals, buried interfaces, and multilayers; the brilliance at the APS will make it possible for the first time to monitor surfaces and interfaces *in situ* during molecular beam epitaxy (MBE) or chemical vapor deposition CVD.

- Investigations of ceramics, coatings, and polymers; our sensitivity will be increased by a factor of 100 in small-angle x-ray scattering.

- Imaging of defects in semiconductor crystals, photonic materials, and superconducting crystals; real-time imaging will become a practical reality at the APS and resolution will reach below 1 $\mu$m.

- Structure determination from single crystals or powders; time-resolved studies during melting or phase transitions will become possible.

- Diffuse x-ray scattering determination of structures and the behavior of lattice imperfections in ceramics, metals, semiconductors, and superconductors.

- Determination of magnetic structure and defects in magnetic superlattices, high-$T_c$ superconductors, and magnetic Compton scattering; the brilliance and circularly-polarized x-ray beams will enable magnetic x-ray measurements that could never be made before.

- X-ray absorption spectroscopy in a reactive environment.

**PROGRAM TITLE:** Synchrotron Radiation

**PROJECT TITLE:** Beamline Operation and Development

**Principal Investigators:** Gabrielle G. Long, Andrew J. Allen, David R. Black, Harold E. Burdette, Daniel A. Fischer, Richard D. Spal, and Joseph C. Woicik

**Technical Objectives:**

To operate two X-ray beam lines at the National Synchrotron Light Source, Brookhaven National Laboratory-- X23A2 and X23A3--for EXAFS, DAFS, USAXS and imaging. To participate in the operation of two more beam lines--X24A and U7A-- for standing-wave x-ray measurements and for x-ray absorption measurements at the carbon, nitrogen, oxygen and fluorine K-edges.

To construct beam lines at the Advanced Photon Source, Argonne National Laboratory, with NIST's Collaborative Access Team (CAT) partners: University of Illinois, Oak Ridge National Laboratory, and U.O.P. Corporation to build and operate a sector at the Advanced Photon Source (APS) at the Argonne National Laboratory: In this area, we are engaged in the design and construction of experiments for the two beam lines on UNI-CAT sector 33 for high resolution diffraction, USAXS, surface and interface scattering, X-ray imaging, EXAFS, and diffuse scattering.

**Technical Description:**

The APS offers a 100 to 10,000-fold increase in brilliance compared to the best synchrotron x-ray sources of today. The Materials Microstructural Characterization Group in the Ceramics Division currently operates two beam stations and is a partner in the operation of two more beam stations at the National Synchrotron Light Source (NSLS). At these facilities, a wide range of material characterization measurements is carried out. Scientific problems currently being addressed include microstructure characterization of ceramics and plasma-sprayed ceramic coatings, crystal perfection in a variety of basic and applied materials, and the atomic-scale and the molecular-scale structures at surfaces and interfaces in polymeric, metal/semiconductor, catalytic, and other systems of technological importance.

In the years to come the APS will supplant the NSLS as this nation's premier x-ray source. The APS beam lines, now under construction by UNI-CAT, incorporate the newest technology which will not only enable NIST scientists to improve significantly our real-time x-ray microscopy, ultra-small-angle x-ray scattering, in- situ x-ray topography and EXAFS capabilities, but will also offer opportunities for cutting-edge experiments in structural crystallography (and time-resolved structural scattering), surface/interface scattering, diffuse scattering, and magnetic scattering.

**External Collaborations:**

The Ceramics Division collaborates with H. Chen, UIUC, T. Chiang, UIUC, B. Larson, ORNL, G. Ice, ORNL, and R. Broach, UOP Corporation who are our partners in the collaborative access team, UNI-CAT at the Advanced Photon Source.

**Planned Outcomes:**

With the commissioning of the new UNI-CAT beamlines at the Advanced Photon Source, NIST scientists anticipate extending our present portfolio of microstructural characterization capabilities to include an even wider range of materials measurements of importance to materials scientists and to U.S. industry.

**Accomplishments:**

In 1996, in situ strain measurements have been made on high-Tc superconductors, sapphire windows for anti-ballistic missiles have been evaluated, dislocation formation as a function of strain has been observed both by x-ray topography and statistically by ultra-small-angle x-ray scattering, and materials such as ultra-high-molecular-weight polymers, carbon blacks, and foams have been investigated by general users of the beam lines.

A new soft-x-ray (C,N,O,F) materials science end station to study the structure and chemical nature of diverse materials at the National Synchrotron Light Source has been designed, built and commissioned. This experimental station, which delivers state-of-the-art intensity, resolution, and detection sensitivity is the result of a collaboration between NIST, The Dow Chemical Co., Brookhaven National Laboratory, and NIST Small Business Innovation Research (SBIR) awardees, International Radiation Detectors and Osmic Inc. The Dow/NIST materials science endstation utilizes polarized ultra soft x-rays as a search light for chemical bond identification, orientation and quantification in the bulk and surface of materials. The facility is a direct result of DOW / NIST co-funding synchrotron radiation technology in a value driven partnership with industry and government scientists. Practical industrial problems, are currently being investigated, such as model catalyst systems, polymer surfaces and their interfaces, hard disk lubricants and high Tc superconducting tapes.

The Dow Chemical Company, NIST and IBM are using USXAS to probe the surface and bulk of selected lubricants applied to various magnetic hard disk substrates in order to determine the bonding and orientation of the lubricant layers at a molecular level. USXAS is an ideal non destructive tool for studying the disk lubricant system since it has both elemental and chemically sensitivity, with great selectivity in carbon bond type. In addition the average orientation of chemical bonds may be measured via the polarization anisotropy of the soft x-ray absorption spectra. Current investigations are focusing on lubricant aging and wear (i.e. head disk crashes), lubricant surface chemistry, and hard disk surface composition.

The tribochemical and thermochemical reaction of stearic acid monolayers (adsorbed in air) on metal surfaces was studied by means of ultra soft x-ray absorption spectroscopy (USXAS). A detailed chemical and structural understanding of molecular bonding in the lubricant-to-substrate interface was obtained. The monolayer focus of this project was motivated by the need for a detailed chemical and mechanistic understanding of how a monolayer influences the friction and wear processes. This understanding is essential for the development of new lubrication technology for micro-machines, computer head-disk interface, smart material architecture and other nanometer scale technologies.

Research on thin diamond films, homoepitaxially-grown on diamond substrates, has been performed using new thin-film x-ray topography techniques at the MSEL Beam line at the National Synchrotron Light Source. The data have revealed the nature of the influence of the substrate on the prefection of the deposits. In particular, the dislocation structure terminating on the substrate was seen to continue -- one for one-- into the films. These results have influenced the processing of bulk substrates to reduce the number of defects in the films.

A beam conditioning table for the high-resolution x-ray diffraction experimental station on the UNI-CAT sector 33 at the Advanced Photon Source has been designed and constructed. Installation and commissioning of this table is scheduled for March 1997. Capabilities of the table presently include ultra-small-angle x-ray scattering and x-ray filtering. In the future, capabilities will include x-ray polarization creation and analysis and milli-electron volt x-ray beam creation.

Currently, the APS is undergoing commissioning, and is filling routinely to 100 mA, is operating with positrons at 7 GeV, is storing positrons with a lifetime of ~11 hours, takes ~20-30 minutes to refill after faults, and has reduced orbit motion significantly and improved orbit stability to better than 10% of the particle beam size. The facility is scheduling user time at ~250 hours per run of three weeks (with an additional three weeks maintenance period), with x-ray availability increasing from ~165 hours to ~224 hours between August and October, 1996.

UNI-CAT is currently going through shielding verification of its first and second optical enclosures and is engaged in beamline installation activities. Commissioning of the experimental stations on the insertion device beamline is scheduled to begin in March, 1997.

**Publications:**

Pehr Pehrsson, Terri McCormick, Brock Alexander, Mike Marchywka, David Black, James Butler and Steven Prawler, "Homoepitaxial Mosaic Growth and Liftoff of Diamond Films,"in *Diamond for Electronic Applications*, (Proc. MRS Symp., 1996) in press.

S. Han, G. Rodriguez, A. Taylor, M. A. Plano, M. D. Moyer, M. A. Moreno, L. S. Pan, D. R. Black, H. E. Burdette, J. Agers and A. Chen, "Correlation of Electrical Properties with Defects in a Homoepitaxial

Chemical-Vapor-Deposited Diamond Film," in *Diamond for Electronic Applications*, (Proc. MRS Symp., 1996) in press.

W. B. Alexander, P. E. Pehrsson, D. Black, and J. E. Butler, "X-Ray Diffraction Analysis of Strain and Mosaic Structure in (011)-Oriented Diamond" in *III-Nitride, SiC and Diamond Materials for Electronic Devices* (Proc. MRS Symp., 1996) in press.

S. X. Huang, D. A. Fischer and J. L. Gland, "Aniline Adsorption, Hydrogenation and Hydrogenolysis on the Ni (100) Surface," for submission to *J. Phys. Chem.*

S. X. Huang, D. A. Fischer and J. L. Gland, "In Situ Studies of Cyclohexylamine Dehydrogenation and Hydrogenation on the Ni (111) Surface," for submission to *J. Phys. Chem.*

Y. Fukumoto, A. R. Moodenbaugh, M. Suenaga, D. A. Fischer and J. L. Gland, "Effect of Oxygen Partial Pressure during Post Heat-Treatment on $Bi_2Sr_2CaCu_2O_y$/Ag Tapes," for submission to *J. Appl. Phys.*

D. A. Fischer, Z. Hu and S. M. Hsu, "Molecular Orientation and Bonding in Monolayer Stearic Acid on a Copper Surface in Air," for submission to *Tribology Letters.*

D. A. Fischer, G. E. Mitchell, A. T. Yeh and J. L. Gland, "Functional Group Orientation in Surface and Bulk Polystyrene Studied by Ultra Soft X-Ray Absorption Spectroscopy," for submission to *J. Appl. Poly. Sci.*

D. A. Fischer, Z. S. Hu and S. M. Hsu, "Tribochemical and Thermochemical Reactions of Stearic Acid on Copper Surfaces in Air as Measured by Ultra Soft X-Ray Absorption Spectroscopy," for submission to *Tribology Letters.*

M. X. Yang, P. W. Kash, D.-H. Sun, G. W. Flynn, B. E. Bent, M. T. Holbrook, S. R. Bare, D. A. Fischer and J. L. Gland, "Chemistry of Chloroethylenes on Cu (100): Bonding and Reactions," for submission to *Surf. Sci.*

M. X. Yang, J. Eng, Jr., P. W. Kash, G. W. Flynn, B. E. Bent, M. T. Holbrook, S. R. Bare, J. L. Gland and D. A. Fischer, "Generation and Reaction of Vinyl Groups on a Cu (100) Surface," for submission to *J. Poly. Sci.*

**PROGRAM TITLE:** Synchrotron Radiation

**PROJECT TITLE:** Characterization of Sapphire Windows

**Principal Investigators:** David Black, Linda Braun, and Robert Polvani (Manufacturing Engineering Laboratory)

**Technical Objectives:**

Because of its combination of optical and thermal properties, large single-crystals of sapphire are being used as uncooled windows and domes for anti-ballistic missiles. In these applications, the crystals experience thermal shocking and large thermal-induced stresses which may lead to failure. One factor affecting the fracture strength of these brittle materials is surface flaws. To produce the strongest windows and domes at the lowest cost, processing-induced surface and subsurface damage must be identified and controlled. Therefore, the technical objectives of this project are to: 1) develop diagnostic tools that can detect surface and subsurface damage in single-crystal sapphire; 2) apply these techniques to characterize damage created during growth and/or fabrication; 3) correlate the observed damage to measured fracture strength; and 4) evaluate the effect that post-fabrication processing techniques such as annealing have on surface and subsurface damage.

**Technical Description:**

Most of the technical objectives are being met through a series of experiments on a large set of sapphire modulus-of-rupture (MOR) bars. The MOR bar experiments involve three crystal growers, four sample fabricators, two crystallographic orientations, two surface finishes, and two post-fabrication processes. This represents all combinations currently used in antiballistic missile programs. The samples will be examined by the following techniques: light microscopy, polariscope, polarimetry, wavefront quality, surface finish, bidirectional reflectance distribution function (BRDF) measurements, x-ray topography, Raman spectroscopy, neutron diffraction, cathodoluminescence, and dimpling. These techniques combine the expertise available in the Ceramic Division with that in the Reactor Radiation Division and the Precision Engineering Division. Observations made by different techniques on the same samples will allow us to select the best combination of diagnostic tools. Comparisons of observations made by means of the best techniques on different samples will allow us to investigate the relationship between growth and processing on surface and subsurface damage as well as the effects of the post-fabrication processing. An additional set of 90 MOR bars will be used to correlate defects observed by x-ray topography to measured fracture strength. A surface topograph will be recorded from the tensile surface of each bar prior to fracture testing. After testing, samples that break into only two pieces will be examined again. Images of the weakest samples will be examined in an attempt to identify critical flaws or general features correlated to weak fracture. Post-fracture images will be used to identify specific flaws that initiated fracture.

**External Collaboration:**

Case Western Reserve University, Crystal Systems, Inc., Meller, Inc., Naval Air Warfare Center, Pacific Optical, Inc., University of Dayton Research Institute, and Zygo, Inc. are participating with NIST in the sapphire window program.

**Planned Outcomes:**

The strongest windows and domes will be produced, at the lowest cost, when processing-induced surface and subsurface damage are identified and controlled.

**Accomplishments:**

Using a preliminary set of 15 MOR bars, x-ray topography data have been used to identify specific surface features correlated with fracture strength. Differences in bulk defect density between different growth methods have been observed. Grazing incidence asymmetric diffraction images have shown microstructural differences between different surface-finishing methods. X-ray topography data have identified large variations in surface damage on the edges of windows. The techniques of topography and polarized light microscopy, which yield a global image, have been combined with the probing technique of Raman spectroscopy. Specific locations for the acquisition of the Raman spectra were selected from the global pictures.

**Publications:**

D. Harris, F. Schmid and D. Black, "Factors that Influence the Mechanical Failure of Sapphire at Elevated Temperature," SPIE Conference: *Window and Dome Technologies and Materials, V*, Orlando World Convention Center, Orlando, FL (April 21 - 25, 1997).

R. S. Polvani, D. R. Black, B. J. Hockey, and C. J. Evans, "Subsurface Damage: the Hidden Problem," SPIE Conference: *Window and Dome Technologies and Materials, V*, Orlando World Convention Center, Orlando, FL (April 21 - 25, 1997).

**PROGRAM TITLE:** Synchrotron Radiation Characterization

**PROJECT TITLE:** Semiconducting Materials Evaluation

**Principal Investigators:** Joseph C. Woicik and Joseph G. Pellegrino (Electronic and Electrical Engineering Laboratory)

**Technical Objectives:**

The objective of this program is to characterize quantitatively structures to obtain a unifying picture of bond lengths and elasticity in strained-layer semiconductors.

**Technical Description:**

The progress in crystal growth techniques in the past two decades has made it possible to manufacture novel devices by synthesizing artificially-layered materials built up of structurally and chemically dissimilar constituents. In a pseudomorphically-grown heterostructure, the buried film is constrained to have the same lattice parameters as the substrate in the plane parallel to the film, while it is free to relax in the growth direction. This results in a tetragonal distortion of the unit cell. This strain, induced by lattice misfit, has a number of effects on the stability, growth mode and surface morphology of the heterolayer. It also plays a crucial role in determining the optical and electronic properties of the film. X-ray standing wave measurements and extended x-ray absorption fine structure (EXAFS) measurements are used to determine the strain and bond distortions in strained-layer semiconductor structures. These highly-precise nondestructive probes enable the perpendicular strain within the layer and the strain-induced displacement in the growth direction to be measured directly.

**External Collaboration:**

K. E. Miyano, Brooklyn College and M. J. Bedzyk, Northwestern U. and ANL are collaborating on other measurements on the semiconductor materials.

**Planned Outcomes:**

Heterojunction devices are increasingly important. Our improved understanding will be expected to lead to new and more stable structures with better performance.

**Accomplishments:**

A GaAs/1 monolayer InAs/GaAs(001) heterostructure grown by molecular-beam epitaxy was characterized. The measured strain in the InAs layer agrees with macroscopic elasticity theory in the 1 monolayer limit. The epitaxy of the heterostructure was also studied as a function of depth in the structure.. The depth-selective method was used to measure the displacement of the GaAs cap layer in the growth direction, which could be related directly to the perpendicular strain in the InAs layer.

**Publications:**

J. C. Woicik, J. G. Pellegrino, and K. E. Miyano, "Bond Lengths and Elasticity in Strained-Layer Semiconductors," for publication in *J. de Phys.*

A. C. Carter, C. E. Bouldin, K. M. Kemner, M. I. Bell, J. C. Woicik, and S. A. Majetich, "The Surface Structure of Cadmium Selenide Nanocrystalites," for publication in *Phys. Rev. B.*

T.-L. Lee, Y. Qian, P. F. Lyman, J. C. Woicik, J. G. Pellegrino, and M. J. Bedzyk, "The Use of Standing Waves and Evanescent-Wave Emission to Study Buried Strained-Layer Heterostructures," *Physica* **B 221** (1996) 437.

J. C. Woicik, K. E. Miyano, J. G. Pellegrino, P. S. Shaw, S. H. Southworth, and B. A. Karlin, "Strain and Relaxation in InAs Films Grown on GaAs (001)," *Appl. Phys. Lett.* **68** (1996) 3010.

A. Herrera-Gomez, P. M. Rousseau, G. Materlik, T. Kendelewicz, J. C. Woicik, P. B. Griffin, J. Plummer, and W. E. Spicer, "X-Ray Standing Wave Study of the Crystalline Position of Electrically-Active and Inactive Arsenic Impurities in Heavily-Doped Silicon," for publication in *Phys. Rev. B.*

V. G. Harris, K. M. Kemner, W. T. Elam, B. N. Das, N. C. Koon, J. P. Kirkland, J. C. Woicik, P. Crespo, A. Hernando, and A. Garcia Escorial, "Near-Neighbor Mixing and Bond Dilation in Mechanically-Alloyed CuFe," for publication in *J. Appl. Phys.*

K. M. Kemner, V. G. Harris, V. Chakarian, Y. U. Idzerda, W. T. Elam, C.-C. Kao, Y. C. Feng, D. E. Laughlin, and J. C. Woicik, " The Role of Ta and Pt in Segregation within Co-Cr-Ta and Co-Cr-Pt Thin Film Magnetic Recording Media," for publication in *J. Appl. Phys.*

# OTHER PROGRAMS

**PROGRAM TITLE:** Other

**PROJECT TITLE:** Characterization of Cements using SANS

**Principal Investigator:** Andrew J. Allen

**Technical Objectives:**

The objective of this project is to characterize microstructural evolution, during hydration, of cements to characterize their microstructural degradation due to environmental effects, and to probe the effects of additions of silica fume, fly ash, and other additives that would lead to superior performance.

**Technical Description:**

This project makes use of small-angle neutron scattering and ultra-small angle x-ray scattering to characterize microstructural evolution during the hydration of cements, as a function of environmental effects and additives, as it affects highway infrastructural concretes.

**External Collaboration:**

R. A. Livingston, Department of Transportation is the program monitor and aids in the analysis of the SANS data.

**Planned Outcome:**

These studies are enabling a quantitative assessment of the different microstructural modifications that underlie the variable effectiveness of different silica fume and fly ash additives in forming cements and concretes of improved strength and durability.

**Accomplishments:**

The effects of pozzolanic additives on the microstructure of cement during hydration has been extensively studied using small-angle neutron scattering (SANS) and ultra-small-angle x-ray scattering (USAXS). A semi-fractal model, developed earlier, was modified to extract microstructural parameters from the SANS data. A link was established between the existence of coarse particles in the silica-fume particle size distribution (determined mainly by means of USAXS) and possible deleterious effects on the subsequent microstructural evolution during cement hydration (determined mainly by means of SANS). Also, utilizing the strong isotope effect between hydrogen and deuterium in neutron scattering by hydrogenous systems, our fundamental SANS studies have been able to explain how the different values for the internal surface areas within hydrating cements are obtained by means of different industrial methods.

**Publications:**

R. A. Livingston, D. A. Neumann, A. J. Allen, and J. J. Rush, "Application of Neutron Scattering Methods to Cementitious Materials," in *Neutron Scattering in Materials Science, II*. D. A. Neumann, T. P. Russell and B. J. Wuensch, Eds. (MRS Symp. Proc. **376** (Materials Research Society, Pittsburgh, PA, 1995) 459 - 469.

A. J. Allen and R. A. Livingston, "Small-Angle Scattering Study of Concrete Microstructure as a Function of Silica Fume, Fly Ash or Other Pozzolanic Additions," (SP153-62) in Proc. 5th CANMET / ACI International Conference on Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete, June 1995. V. M. Malhotra, Ed. (Amer. Concrete Inst., Detroit, MI, 1995) 1179 - 1200.

R. A. Livingston and A. J. Allen, "Application of Small-Angle Neutron Scattering Method to the Study of Durability of Historic Brick and Mortar," in *Ceramics in Architecture*, Proc. 8th CIMTEC World Ceramic Congress and Forum on New Materials, P. Vincenzini, Ed. (CIMTEC, Faenza, Italy, 1995) Vol. A, 573 - 580.

A. J. Allen and R. A. Livingston, "The Relationship between Different Fume Additives and the Fine Scale Microstructural Evolution in Cement-Based Materials," to appear in *Advanced Cement-Based Materials*, MRS Fall, 1996.

A. J. Allen and R. A. Livingston, "Scattering Methods" talk at the Gordon Research Conference on the Chemistry and Physics of Cement-Based Materials, Plymouth State College, Plymouth, NH, July 31, 1996

**PROGRAM TITLE:** Other

**PROJECT TITLE:** Diamond Film Research

**Principal Investigator:** Albert Feldman

**Technical Objectives:**

The objective of this work is to develop thermal wave measurement techniques for evaluating thermal properties and adhesion of diamond and of other thin film materials and to relate these measurements to thin film microstructure.

**Technical Description:**

Thermal wave imaging by the photothermal radiometry technique is being used to reveal thin film thermal and mechanical properties.

Indentation is a method frequently used to measure adhesion of coatings. It involves measuring the diameter of a delaminated region as a function of the applied load to a conical indenter pressed into the film. When the films are transparent, the region of delamination is usually observable visually, however, when the film is opaque, the region of delamination is not evident. Thermal wave imaging is being used to reveal the region of delamination around an indentation that may not be readily observable by other techniques.

Thermal wave imaging is also being used to determine whether structure in thermal wave images of diamond coated tungsten carbide (WC) can be used to reveal properties of the film/substrate interface. Thermal wave radiometry is being used to measure the thermal properties of diamond and other thin film materials. One new procedure being developed will be used to measure the transverse (parallel to the surface) thermal conductivity of CVD diamond. Another, comparator type photothermal method will be used to measure the normal component of insulating thin films.

Computer methods will be used to model the experimental procedures and to interpret the experimental results in terms of thin film and film/substrate interface microstructure.

**External Collaborations:**

Westinghouse Corp., Crystallume Corp., Norton Diamond Films, and Advanced Refractory Technologies are providing materials for the project.

**Planned Outcomes:**

Development of new measurement methodologies for rapid convenient methods of measuring thin film thermal conductivity.

A nondestructive procedure for predicting premature failure of CVD diamond coated cutting tools.

**Accomplishments:**

We have employed photothermal radiometry to obtain thermal wave images in the vicinity of indents in WC-6 Mole %Ni coated with CVD diamond obtained from Westinghouse. The images reveal a structure beyond the immediate location of the indent suggesting a region of delamination. The spatial features of both the magnitude and phase of the thermal signal and their dependence on modulation frequency can be explained on the basis of a one dimensional thermal wave theory that assumes: 1) an air gap between the diamond and the substrate extending well beyond the visibly observable indented region; 2) a thermal resistance interface between the diamond film and the substrate extending over the entire coated surface. The theory allows us to estimate the air gap thickness which decreases as the distance from the indented region increases. Air gap variations of the order of 10 nm in width are easily detectable.

The last in a NIST sponsored series "Workshop on Characterizing Diamond Films IV" was held at NIST March 4-5, 1996. Twenty-eight people from industry and universities registered for the workshop. The main part of the workshop addressed the technical problems associated with adhesion of CVD diamond to cutting tool materials. The principal conclusions of the workshop were:

- Considerable progress has been made in the development of diamond coatings that adhere adequately to tungsten carbide (WC) cutting tool substrates. Some expressed the view that the adhesion problem has been solved as attested to by the availability of off-the-shelf diamond coated cutting tool inserts.

- To promote the use of diamond coated cutting tools, protocols for their use will have to be developed. However, a considerable effort would be required due to the large range of machining conditions that can be encountered.

- The reasons for the relatively large laboratory-to-laboratory variations in our prior round robin on thermal conductivity measurement can be attributed to specimen inhomogeneity and specimen anisotropy. A new round robin based on specimens with significantly better homogeneity has been organized.

**Publications:**

"Workshop on Characterizing Diamond Films IV," A. Feldman, A.P. Malshe, and J. Graebner, NISTIR 5837.

"Workshop on Characterizing Diamond Films IV," A. Feldman, A.P. Malshe, and J. Graebner, Conference Report, J. of Res. NIST, Vol. 110, 383-385 (1996).

"Thermal Diffusion in a Stratified Medium with a Modulated Heat Source," A. Feldman, NIST IR 5928, December 1996.

"Thermal Wave Imaging of Indented Diamond Coated WC", A. Feldman, accepted for publication in Journal of Materials Research.

**PROGRAM TITLE:** Other

**PROJECT TITLE:** Single Crystal Standards

**Principal Investigators:** Winnie Wong-Ng, Richard DesLattes (Physics Laboratory) and Jay Armstrong (Chemical Science and Technology Laboratory).

**Technical Objectives:**

The purpose of this research is to provide industry, academic and government laboratory with an SRM (ruby spheres) for the alignment of single crystal diffractometers. The auxiliary data on the chromium content will also be useful for microanalytical calibrations.

**Technical Description:**

The development of this standard includes two main activities which have been carried out as a team effort between NIST, Hauptman-Woodward Medical Research Institute, Bell Laboratories, Carnegie Institution of Washington and the U.S. Geological Survey. These activities include an international round robin and the certification of the lattice parameters using several x-ray diffraction techniques.

The international round robin entails dispatching sets of SRM ruby spheres and zeolite test crystals to 50 laboratories. Instructions were provided for the participants to measure data pertinent to the evaluation of the crystal centering algorithm and the alignment of the instrument. This procedure was based on the method developed by Finger et al. in 1979, in which the measured angles for a single reflection, or Friedel pair of reflections, in eight different orientations are used to determine the values for various errors associated with the mounting of the crystal and alignment of the diffractometer.

The lattice parameters of the ruby spheres are currently being certified by using a 4-circle single crystal diffractometers (with both Cu and Mo radiation), a modified Bond diffractometer adapted for single crystal measurements and a Guinier-Hagg powder camera using the transmission technique.

The homogeneity and the quantity of the chromium content of these spheres were investigated by using both the microprobe and quantitative SEM/EDX techniques.

**External Collaborations:**

The round robin participants are: G. DeTitta, Hauptman-Woodward Medicial Research Institute, Inc., Buffalo, T. Siegrist, Bell Laboratories (Lucent Technology), L. Finger, Carnegie Institution of Washington and H. Evans, US Geological Survey.

**Planned Outcome:**

This work is expected to enhance the alignment capability of single crystal x-ray diffractometers in industrial, government and academic x-ray laboratories.

**Accomplishments:**

The ruby spheres were found to be suitable standard material. The chromium was relatively homogenous with a mass fraction of 0.45 ±0.04% among 14 spheres being studied. The crystals have very small Mosaic spread (0.015° full width at half maximum (FWHM) x-ray rocking curve).

To date, we have received 37 sets of international round robins reports. Data analysis are being conducted and a comparison of the various results of lattice parameters and orientation matrix of both the SRM and the test crystal clearly indicates the spheres to be extremely useful for diagnosis of various possible sources of errors (including misalignment of crystal in x,y,z coordinates, zero settings for the instrument, error in counter or tube height, etc.), therefore enabling accurate alignment of the instrument. These findings will be reported back to the participants for assisting them to evaluate the conditions of their diffractometers.

Twenty sets of 4-circle diffractometer data are currently being analyzed. The analysis includes estimation of various contributions to systematic errors such as absorption, horizontal divergence, vertical divergence, thermal expansion and refraction. Analysis of the Guinier-Hagg camera powder data using 5 samples (each by grinding 20 spheres) have been completed and the result shows good agreement with the single crystal diffractometer data.

**PROGRAM TITLE:** Other

**PROJECT TITLE:** SRMs for Powder Diffraction

**Principal Investigators:** James P. Cline, Richard D. Deslattes and Jean-Louis Staudenmann (Physics Laboratory), and Brian H. Toby (Reactor Radiation Division).

**Technical Objective:**

To provide SRMs which extend the NIST measurement capabilities to the powder diffraction user community. This insures that measurements can discern ever smaller changes in sample character which allow for more effective property optimization.

**Technical Description:**

In the most general sense, powder diffraction patterns consist of a set of intensity values, x-ray or neutron, measured over a range of crystallographic d-spacings. These patterns exhibit peaks which result from the interference of coherent scattering of incident radiation from the periodic crystal structure of the specimen. The form of the pattern indicates the qualitative, quantitative, crystallographic, and microstructural aspects of the sample. Therefore, proper analysis of diffraction patterns can provide considerable information about the specimen, giving rise to a wide range of applications for this technique.

The three variables associated with diffraction equipment which can be evaluated with NIST powder diffraction SRMs are: 1) the d-spacing or line position, 2) line intensity as a function of position, or instrument sensitivity, and 3) instrumental and sample contributions to the shape of reflection profiles. Additional powder diffraction SRMs are designed for quantitative analysis with the use of the internal standard method.

We are presently pursuing a new generation of line position SRMs which will be certified via a robust linkage to the iodine stabilized HeNe laser length standard. This project has involved the construction of a multi-axis diffractometer with a rotational resolution in the arc-second range. In order to obtain independence from sample position errors, the equipment utilizes a graded multilayer parabolic mirror to focus the divergent beam from the conventional x-ray source into a high intensity parallel beam. The silicon powder to be used for the SRM is being prepared from boules of intrinsic material grown by the float zone method. The lattice parameters of the single crystal material are being investigated with respect to interstitial, vacancy and impurity concentration. The surface character of the powder is also being considered; the surface energy will result in stresses on the particles which will effect the measured lattice parameter. We anticipate that the lattice parameters will be certified to the parts per million range.

The observed diffraction profile from the diffractometer consists of a sample profile convolved with an instrument profile and superimposed with noise. The sample profile characterizes the broadening due to crystallite size and micro-strain effects within the sample. Although there exist several methods of determining the sample profile they often require specific assumptions concerning the functional form of the sample profiles being made or result in ill-conditioned solutions. The approach which has been developed to solve this problem is to apply the Maximum Entropy method (MaxEnt). The MaxEnt method incorporates the *a priori* information about the instrument profile, noise distribution as constraints and determines the solution which maximizes the entropy with respect to these constrains.

At present research work is concentrating on developing a generalized MaxEnt/Bayesian method which could be applied to deconvolving and separating overlapped profile peaks and adopted for crystallite size and micro-strain analysis.

The instrumental contribution to observed line profile shape from x-ray diffraction equipment can be characterized with SRM 660 ($LaB_6$). This material was selected through an ICDD sponsored round robin which found that it was free of peak broadening due to crystallite size and micro-strain effects. Refinements of the SRM's evenly spaced, high intensity diffraction lines yield precise values for parameters of the selected profile shape function. Due to its certified lattice parameters, SRM 660 can also be used for determining instrumental parameters through a Rietveld refinement. Under development is an SRM which will display the effects of particle size induced profile broadening

Conventional methods of quantitative analysis are based on the Reference Intensity Ratio, RIR, method. A more accurate and precise method is Quantitative Rietveld Analysis, QRA, in which the powder diffraction data are analyzed with Rietveld method. This method entails the calculation of the pattern from crystallographic, microstructural and equipment characteristics which are related to the form of the pattern through a series of model functions. The difference between the calculated and observed pattern is then minimized by sequentially refining the physical parameters contained in the model functions to obtain an accurate and precise description of the specimen. The baseline for this method is the quality of the fit between the calculated and observed patterns.

While both of these methods can be used to perform quantitative analysis without the use of an internal standard, this is predicated by the assumption that the specimen has no amorphous component. In order to perform an accurate quantitative analysis which includes the amorphous content, a standard of known phase purity must be used. Thus, a major focus of the work in this area has been the development of a measurement and certification method for the amorphous content of SRM 676, a non-orienting alumina powder which is presently certified with respect to lattice parameters and eight relative intensity values.

The experimental approach is based on the comparison of the phase abundance of two phase mixtures determined from the preparation procedure using an analytical balance, which includes the amorphous component, to that determined from the diffraction data, which does not. Specimens consisted of 50-50 mixtures of SRM 676 and silicon powder which was obtained from crushed and jet milled from single crystal, electronic grade boules. This microstructure allowed for the assumption that all amorphous material in the silicon powder was confined to a surface layer on the particles, and that the thickness of the layer was constant with respect to particle size. Thus, by systematically varying the surface area of the silicon powder, we could model it's effect on the data. However, prerequisite to the success of this method was an unbiased measurement method. Potential for bias was judged from the plausibility of the refined results obtained from a number of powder diffraction methods. Data were collected via time-of-flight, TOF, and constant wavelength, CW, neutron powder diffraction and synchrotron and conventional x-ray powder diffraction. Analysis of the refinements indicated that the TOF data were the least biased and thus the amorphous content of the alumina was credibly determined.

SRM 674a consists of a set of five powders: $\alpha$ $Al_2O_3$, ZnO, $TiO_2$ (rutile), $Cr_2O_3$, and $CeO_2$, which range in x-ray mass attenuation coefficients from (126 to 2203) $cm^{-1}$ (Cu K$\alpha$). The materials available with this SRM permit the minimization of absorption contrast between the standard and the specimen. SRMs 1878a ($\alpha$ Quartz) and 1879a (cristobalite) were certified with respect to amorphous content for analysis of silica containing materials in accordance with health and safety regulations. Quantitative analysis of the silicon nitride system can be performed with SRM 656 which consists of two powders, one high in $\alpha$ content while the other is high in $\beta$. They are certified with respect to $\alpha/\beta$ ratio and amorphous content.

**External Collaborations:**

Robert B. Von Dreele (Los Alamos National Laboratory), Walter Kalceff and Nicholas Armstrong (University of Technology, Sydney, Australia) are collaborating in the analysis of x-ray data.

**Planned Outcomes:**

Development of a powder diffractometer capable of lattice parameter measurements in the parts-per-million range has been completed. This will permit certification of a new generation of line position SRMs with roughly an order of magnitude improvement in certainty of the certified lattice parameters.

**Accomplishments:**

A powder diffractometer capable of first principle lattice parameter measurements to the parts per million range has been constructed.

The amorphous content of SRM 676, alumina powder, has been determined to within a few tenths of a percent.

The Maximum Entropy Method has been applied to the deconvolution of the X-ray diffraction line profiles for the determination of sample induced profile broadening.

The effect of equipment optics on the observed position of profile maxima has been characterized and evaluated with a fundamental parameters approach.

**PROGRAM TITLE:** Other

**PROJECT TITLE:** Wear of Biomaterials

**Principal Investigators:** Stephen M. Hsu and John Tesk (Polymers Division)

**Technical Objectives:**

This project aims to develop a quick, low cost, effective test methods to evaluate biomaterials used in total joint replacement in conjunction with an industrial consortium.

**Technical Description:**

The biomaterials industry is a rapidly growing business. The development of new materials offers an opportunity for technological advances in this important area. The cost of qualifying a biomaterial in the U.S. is high as well as time consuming. An efficient, effective screening test method will reduce costs, cut the lead time, and help to maintain the competitive edge of the U.S. biomaterials industry.

The orthopedic consortium consists of six companies whose major business is in the supply of hip and knee joint replacement parts. A technology survey will be conducted to evaluate the current state of the art of the materials screening methodology. NIST will conduct research as well as organize a round robin to examine the precision, precedural adequacy, and significance of thė tests currently in use. If necessary, a new test will be developed to simulate the hip and knee wear mechanisms.

**External Collaborations:**

The orthopedic consortium members are: Zimmer, Inc., Smith and Nephew, Johnson and Johnson, Biomet, Osteomics, and Wright Medical Technology.

**Planned Outcomes:**

The consortium was formed in October, 1996. The anticipated outcomes will be in: 1) wear mechanism understanding of how motion and surface roughness of different materials affect the generation of wear and wear particles; 2) the development of a test procedure that can evaluate biomaterials for joint replacement; and 3) the development and compilation of materials characterization measurement methods before, during, and after the wear event.

**Accomplishments:**

The primary accomplishment has been the formation of the Orthopaedic Accelerated Wear Resistance Consortium.

# RESEARCH STAFF

*The Ceramics Division Staff E-mail addresses can be accessed using the fname.lname.@nist.gov, except as otherwise noted. (Example: stephen.freiman@nist.gov)*

## DIVISION OFFICE

| | |
|---|---|
| Fogarty, Gerard<br>(No longer a NIST employee) | • Non-linear optical processes<br>• Nature, genesis, distribution, and effects of irregularities in monolithic crystals and multilayers<br>• High-resolution diffraction imaging |
| Freiman, Stephen W.<br>301/975-6119 | • Electronic ceramics<br>• Mechanical properties<br>• Superconductivity |
| Jahanmir, Said<br>301/975-3671 | • Ceramic machining<br>• Mechanisms of material removal<br>• Mechanics of contacts<br>• Effects of machining on mechanical properties |
| Steiner, Bruce W.<br>301/975-5977 | • High-resolution diffraction imaging<br>• Defects in monolithic crystals and multilayers<br>• Non-linear optical processes |

## POWDER CHARACTERIZATION AND PROCESSING

| | |
|---|---|
| Cline, James P.<br>301/975-5793 | • Standard reference materials<br>• High-temperature x-ray diffraction<br>• Microstructural effects in x-ray diffraction<br>• Rietveld refinement of x-ray diffraction data |
| Hackley, Vincent A.<br>301/975-5790<br>vince.hackley@nist.gov | • Electrokinetic and electroactive measurement<br>• Slurry rheology<br>• Surface chemistry of powders. |
| Kelly, James F.<br>301/975-5794 | • Quantitative scanning electron microscopy<br>• Image analysis<br>• Microstructure analysis<br>• Powder standards |

| | | |
|---|---|---|
| Lum, Lin-Sien H.<br>301/975-3674 | • | Powder characterization |
| | • | Instrumental analysis |
| Malghan, Subhas G.<br>301/975-6101<br>(No longer in the Ceramis Div.) | • | Powder and dense slurry characterization |
| | • | Colloidal processing and forming |
| | • | Interfacial and surface chemistry of powders |
| | • | Standards development |
| Minor, Dennis B.<br>301/975-5787 | • | Analytical scanning electron microscopy of ceramics and particulates |
| | • | Powder test sample preparation |
| | | Powder characterization |
| Onoda, George Y.<br>301/975-4489 | • | Ceramic Processing Science |
| | • | Physics of Particulate Materials |
| | • | Characterization of Powders |
| Pei, Patrick T.<br>301/975-3681 | • | Spectroscopic and thermal characterization |
| | • | Chemical coating |
| | • | Powders characterization |
| Ritter, Joseph J.<br>301/975-6106 | • | Chemistry of powders synthesis |
| | • | Specialty powders synthesis |
| | • | Nanomaterials |
| Wang, Pu Sen<br>301/975-6104<br>pu.wang@nist.gov | • | Solid-state nuclear magnetic resonance |
| | • | Spectroscopic characterization |

## MECHANICAL PROPERTIES

| | | |
|---|---|---|
| Braun, Linda M.<br>301/975-5777 | • | Raman stress measurements |
| | • | Ceramic matrix composites |
| | • | Toughening mechanisms |
| Carter, W. Craig<br>301/975-3971<br>w.carter@nist.gov | • | Materials thermodynamics |
| | • | Advanced mathematical and computational techniques |
| | • | Computation of materials processes |

| | | |
|---|---|---|
| Chuang, Tze-Jer<br>301/975-5773 | • | Creep/creep rupture<br>Fracture mechanics<br>Finite-element modeling<br>Lifetime predictions |
| Fuller, Edwin, R., Jr.<br>301/975-5795 | • | Influence of microstructure on fracture<br>Toughening mechanisms<br>Microstructural modeling and simulation |
| Hockey, Bernard J.<br>301/975-5780 | • | Electron microscopy<br>High-temperature creep |
| Kauffman, Dale A.<br>301/975-5764 | • | Glass melting |
| Krause, Ralph F., Jr.<br>301/975-5781 | • | Creep in flexure and tension<br>Fracture mechanics<br>Hot pressing<br>Chemical thermodynamics |
| Quinn, George D.<br>301/975-5765 | • | Mechanical property test standards<br>Standard reference materials<br>Creep testing |
| Roosen, Andrew J.<br>301/975-6166 | • | Microstructural modeling<br>Computer simulation |
| Smith, Douglas T.<br>301/975-5768 | • | Surface forces<br>Charge transfer at interfaces<br>Adhesion and friction<br>Colloidal processing |
| Wallace, Jay S.<br>301/975-5984 | • | Processing and microstructure<br>Silicon nitride densification<br>Thermal analysis |

<u>PHASE EQUILIBRIA</u>

| | | |
|---|---|---|
| Burton, Benjamin P.<br>301/975-6043 | • | Calculated phase diagrams<br>Dielectric ceramics |

| | | |
|---|---|---|
| Cook, Lawrence P.<br>301/975-6114<br>larry.cook@nist.gov | • | High-temperature chemistry |
| | • | Phase equilibria |
| McCormack, Ryan P.<br>301/975-5786 | • | Phase Equilibria Calculations |
| Vanderah, Terrell A.<br>301/975-5785 | • | Solid-state chemistry |
| | • | Phase equilibria of microwave dielectrics |
| Wong-Ng, Winnie<br>301/975-5791 | • | X-ray crystallography and reference patterns |
| | • | Phase equilibria/crystal chemistry of high-$T_c$ superconductors |
| | • | Molecular orbital calculations |

**ELECTRONIC MATERIALS**

| | | |
|---|---|---|
| Blendell, John E.<br>301/975-5796 | • | Ceramic processing and clean-room processing |
| | • | Sintering and diffusion controlled processes |
| | • | Processing high-$T_c$ ceramic superconductors |
| | • | Activation chemical analysis |
| Bonnell, David W.<br>301/975-5755 | • | Computer automation |
| | • | Molecular-beam mass spectrometry |
| | • | Thermodynamic modeling |
| | • | Laser/plasma sputtering |
| Gonzalez, Eduardo<br>301/975-6102 | • | Ceramic Processing |
| | • | Nano-scale sintering |
| | • | Texture analysis |
| Hastie, John W.<br>301/975-5754 | • | High-temperature chemistry |
| | • | Phase equilibria thermochemistry |
| | • | Molecular-beam mass spectrometry |
| | • | Thin-film deposition |
| | • | Vapor deposition process control and modeling |
| Hill, Michael D.<br>(No longer a NIST employee) | • | Mechanical properties of PZT |
| | • | Ceramic processing |
| Paul, Albert J.<br>301/975-6004 | • | Laser physics |
| | • | Plasma diagnostics |

| | |
|---|---|
| | • Laser spectroscopy<br>• Laser mass spectroscopy<br>• Gasdynamic modeling |
| Piermarini, Gasper J.<br>301/975-5734 | • Ceramic processing and high-pressure sintering<br>• Pressure-induced transformation toughening<br>• High-pressure physical properties and structures<br>• High-pressure x-ray diffraction and spectroscopy |
| Schenck, Peter K.<br>301/975-5758 | • Emission and laser spectroscopy<br>• Thin-film deposition<br>• Computer graphics and image analysis<br>• Laboratory automation<br>• Plasma monitoring and control |
| Sessoms, Arthur B.<br>301/975-5757 | • Molecular beam mass spectroscopy<br>• Thin film deposition |
| Vaudin, Mark D.<br>301/975-5799 | • Electron microscopy<br>• Microscopy and diffraction studies of interfaces<br>• Computer modelling of grain-boundary phenomena<br>• Dielectric films |
| White, Grady S.<br>301/975-5752 | • Thin films<br>• Nondestructive evaluation<br>• Subcritical crack growth<br>• Stress measurements<br>• Cyclic fatigue |

## OPTICAL MATERIALS

| | |
|---|---|
| Bouldin, Charles E.<br>301/975-2046 | • X-ray absorption spectroscopy<br>• Diffraction anomalous fine structure<br>• GeSi heterojunction bipolar transistors |
| Farabaugh, Edward N.<br>301/975-5747 | • Chemical vapor deposition of diamond<br>• Structure and morphology analysis<br>• Scanning electron microscopy |

| | | |
|---|---|---|
| Feldman, Albert<br>301/975-5740 | • Chemical vapor deposition of diamond<br>• Thermal properties<br>• Modelling thermal wave propagation<br>• Thin-film optical properties |
| Kaiser, Debra L.<br>301/975-6759 | • Physical properties and structures of high-temperature superconductors<br>• Interfaces in high-temperature superconductors<br>• Chemical vapor deposition of ferroelectric oxide thin films |
| Robins, Lawrence H.<br>301/975-5263 | • Defect identification and distribution<br>• Cathodoluminescence imaging and spectroscopy<br>• Photoluminescence spectroscopy<br>• Raman spectroscopy |
| Rotter, Lawrence D.<br>301/975-6603 | • Measurement of electro-optic coefficients<br>• Photorefractive effect<br>• Optical spectroscopy of thin films |

## MATERIALS MICROSTRUCTURE CHARACTERIZATION

| | |
|---|---|
| Allen, Andrew J.<br>301/975-5982 | • Small angle x-ray scattering<br>• Ceramic microstructure analysis |
| Black, David R.<br>301/975-5976 | • Defect microstructure in diamond<br>• Polycrystalline diffraction imaging<br>• X-ray imaging of photonic materials |
| Burdette, Harold E<br>301/975-5979 | • X-ray optics<br>• X-ray diffraction imaging<br>• Crystal growth<br>• Instrumentation |
| Fischer, Daniel A.<br>516/344-5177<br>fishcher@x23a3df.nsls.bnl.gov | • X-ray absorption fine structure<br>• X-ray scattering<br>• Surface science |
| Long, Gabrielle G.<br>301/975-595975 | • Small-angle x-ray and neutron scattering<br>• Ceramic microstructure evolution as a function of processing<br>• X-ray optics |

| | |
|---|---|
| Spal, Richard D. | • X-ray optics<br>• Diffraction physics<br>• X-ray scattering |
| Woicik, Joseph C.<br>516/344-5236<br>woicik@ssrl01.slac.stanford.edu | • UV photoemission<br>• X-ray standing waves<br>• Surface and interface science |

## SURFACE PROPERTIES

| | |
|---|---|
| Gates, Richard S.<br>301/975-3677 | • Tribo-chemistry<br>• Surface chemical properties of ceramics |
| Hsu, Stephen M.<br>301/975-6120 | • Ceramic wear mechanisms<br>• Engineered ceramic surfaces<br>• Lubrication and machining of ceramics |
| McGuiggan, Patricia M.<br>301/975-4599 | • Microtribology<br>• Surface force measurement |
| Ives, Lewis K.<br>301/975-6013 | • Wear of materials<br>• Transmission electron microscopy<br>• Machining of ceramics |

## DATA TECHNOLOGIES

| | |
|---|---|
| Begley, Edwin F.<br>301/975-6118 | • Database management methods<br>• Engineering database structures<br>• Digital video interactive technology |
| Carpenter, Joseph A., Jr.<br>301/975-6397 | • Functional ceramics applications<br>• Technical assessments<br>• Industrial liaisons |
| Cellarosi, Mario<br>301/975-6123 | • Glass standards<br>• Machining Data |
| Clevinger, Mary A.<br>301/975-6109 | • Phase diagrams for ceramists<br>• Computerized data |

| | |
|---|---|
| Dapkunas, Stanley J.<br>301/975-6119 | • Structural ceramics applications<br>• Technical assessments<br>• Coatings |
| Harris, Joyce F.<br>301/975-6045 | • Data acquisitions<br>• Digitization and data entry |
| Munro, Ronald G.<br>301/975-6127 | • Materials properties of advanced ceramics<br>• Data evaluation and validation<br>• Analysis of data relations |

## GUEST SCIENTISTS AND GRADUATE STUDENTS

| | |
|---|---|
| Armstrong, Nicholas | University of Technology, Sydney |
| Balzaretti, Naira | Institute de Fisica, Brazil |
| Belmonte, Manuel | Autonoma University, Spain |
| Blackburn, Douglas | Consultant |
| Breiner, David | University of Nebraska |
| Brower, Daniel | Optex Corporation |
| Cedeno, Christina | American Ceramic Society |
| Chen, Chun-I | Pennsylvania State University |
| Chen, Hailong | University of Tokyo |
| Chen, Shi-Yew | Purdue University |
| Chu, Steven | State University of New York at Stony Brook |
| Diao, Jianli | University of Maryland |
| Dong, Xiaoyua | University of Medicine & Dentistry of New Jersey |
| Fang, Hsu-Wei | University of Maryland |
| Farabaugh, Edward | Consultant |
| Frederiske, Hans | Consultant |
| Green, Thomas | American Ceramic Society |
| Greenwood, William | Unversity of Maryland |
| Haller, Wolfgang | Abbott Laboratories |

| | |
|---|---|
| Hayward, Evans | American Ceramic Society |
| Hill, Michael | Trans-Tech Inc. |
| Hryniewicz, Piotr | University of Delaware |
| Ilavsky, Jan | State University of New York at Stony Brook |
| Jemian, Peter | University of Illinois at Urbana/Champaign |
| Jiang, Feng | University of Maryland |
| Jiang, Qing | University of Nebraska |
| Job, Lenox | University of Maryland |
| Kailas, Satish | Indian Institite of Science |
| Kim, Bong-Ho | Changwan National Laboratory |
| Kim, Myong-Ho | Chang-Won National University |
| Larsen-Basse, Jorn | National Science Foundation |
| Lee, Soo-Wohn | Sun Moon University |
| Levinson, Lionel | General Electric |
| Liu, Daqing | Columbia University |
| Liu, Haiyan | University of Maryland |
| Loezos, John | University of Maryland |
| McMurdie, Howard | Joint Center for Powder Diffraction Studies |
| Nagarajan, Mala | University of Maryland |
| Nagarajan, Venkatta | Indian Institute of Science |
| Ondik, Helen | American Ceramic Society |

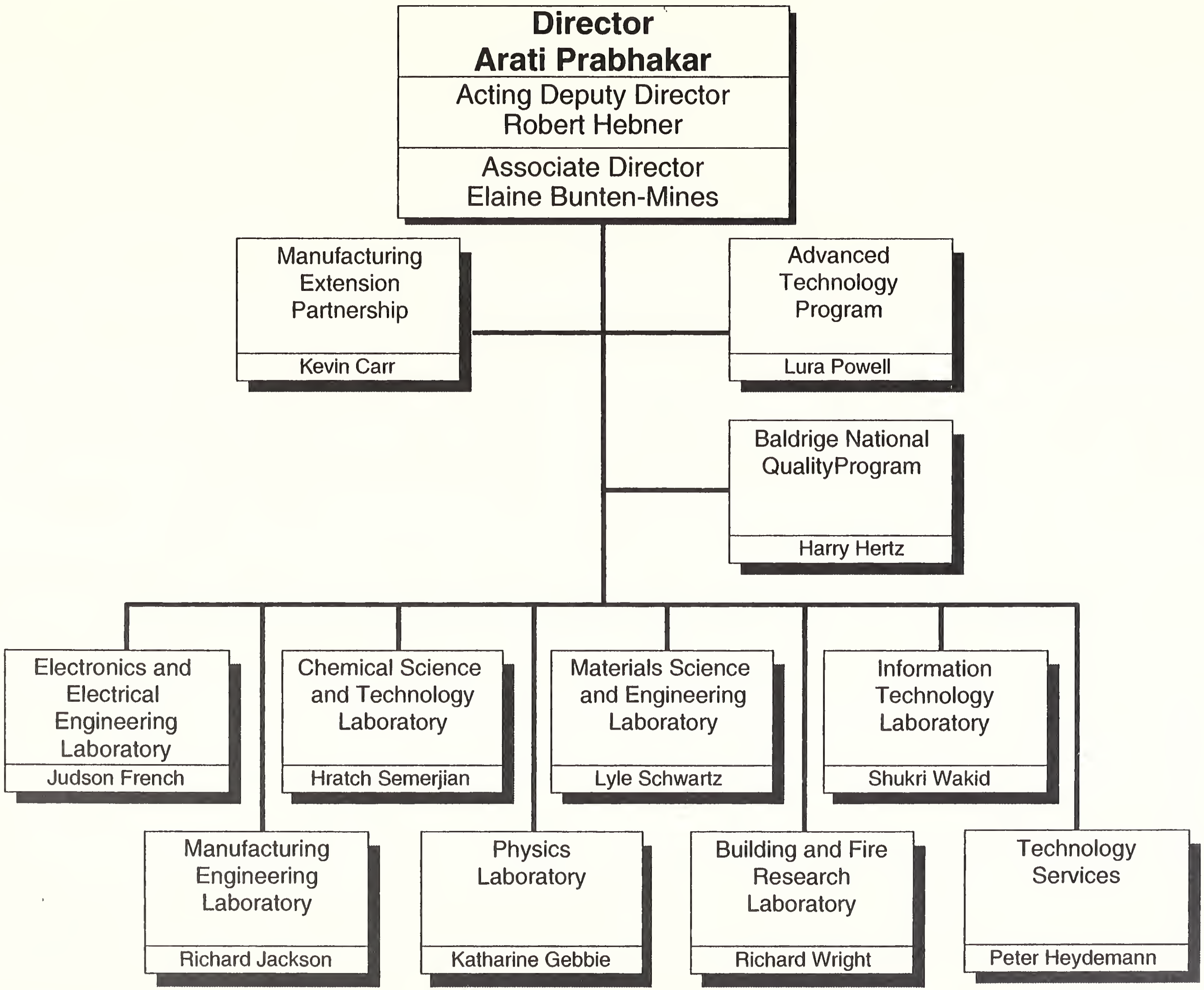
| | |
|---|---|
| Orlando, Stefano | Instituto Materiali speciali del (CNR) |
| Paik, Ungyu | Changwan National Laboratory |
| Pan, Yi-Ming | Southwest Research Institute |
| Piermarini, Gasper | University of Maryland |
| Pothier, Brian | Army Research Laboratory |
| Quinn, Janet | Consultant |
| Raman, Rajkumar | BDM Federal |
| Ritchie, Kevin | University of Maryland |
| Ritter, Joe | Consultant |
| Roberts, Ellis | Consultant |
| Roth, Robert | Viper Group |
| Ruff, Arthur | Consultant |
| Shen, Ming | University of Illinois |
| Selinger, Robin | Catholic University |
| Serra, Pere | University De Barcelona |
| Smith, Milisa | University of Maryland |
| Smith, Peter | Pacific Norhwest Laboratory |
| Swab, Jeffrey | Army Research Laboratory |
| Swanson, Nils | American Ceramic Society |
| Turchinskaya, Marina | Consultant |
| Wachtman, John | Consultant |

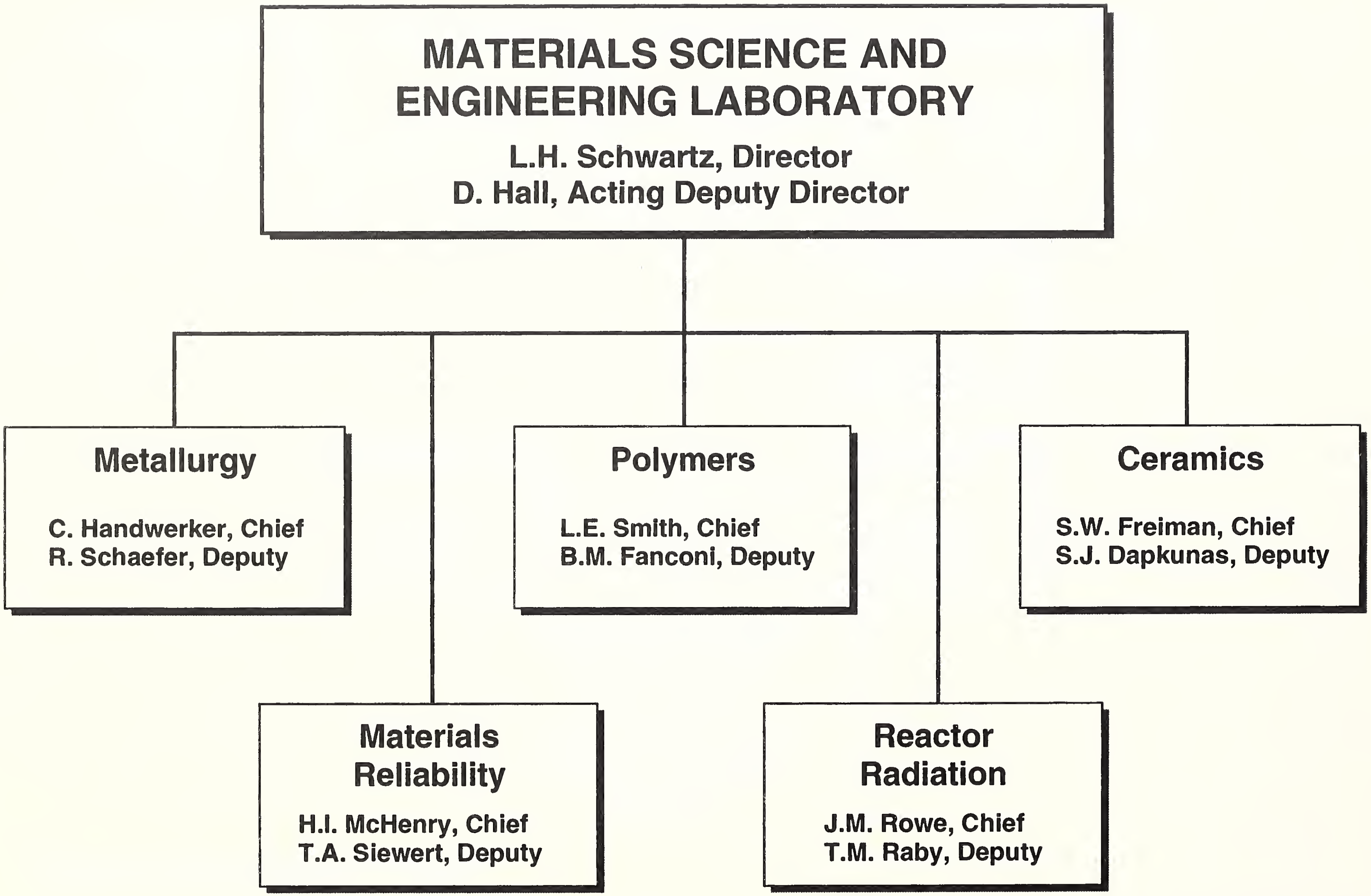
| | |
|---|---|
| Wang, Tong | Jiao Tong University |
| Wang, Yinglong | University of Maryland |
| Wang, You | University of Illinois |
| Xu, Huakun | University of Maryland |
| Ying, Tsi-Neng | University of Maryland |
| Ying, Zhanfeng | University of Illinois |
| Zhang, Jun | Lanzhou Institute of Chemical Physics |
| Zhang, Xian-Hua | University of Maryland |

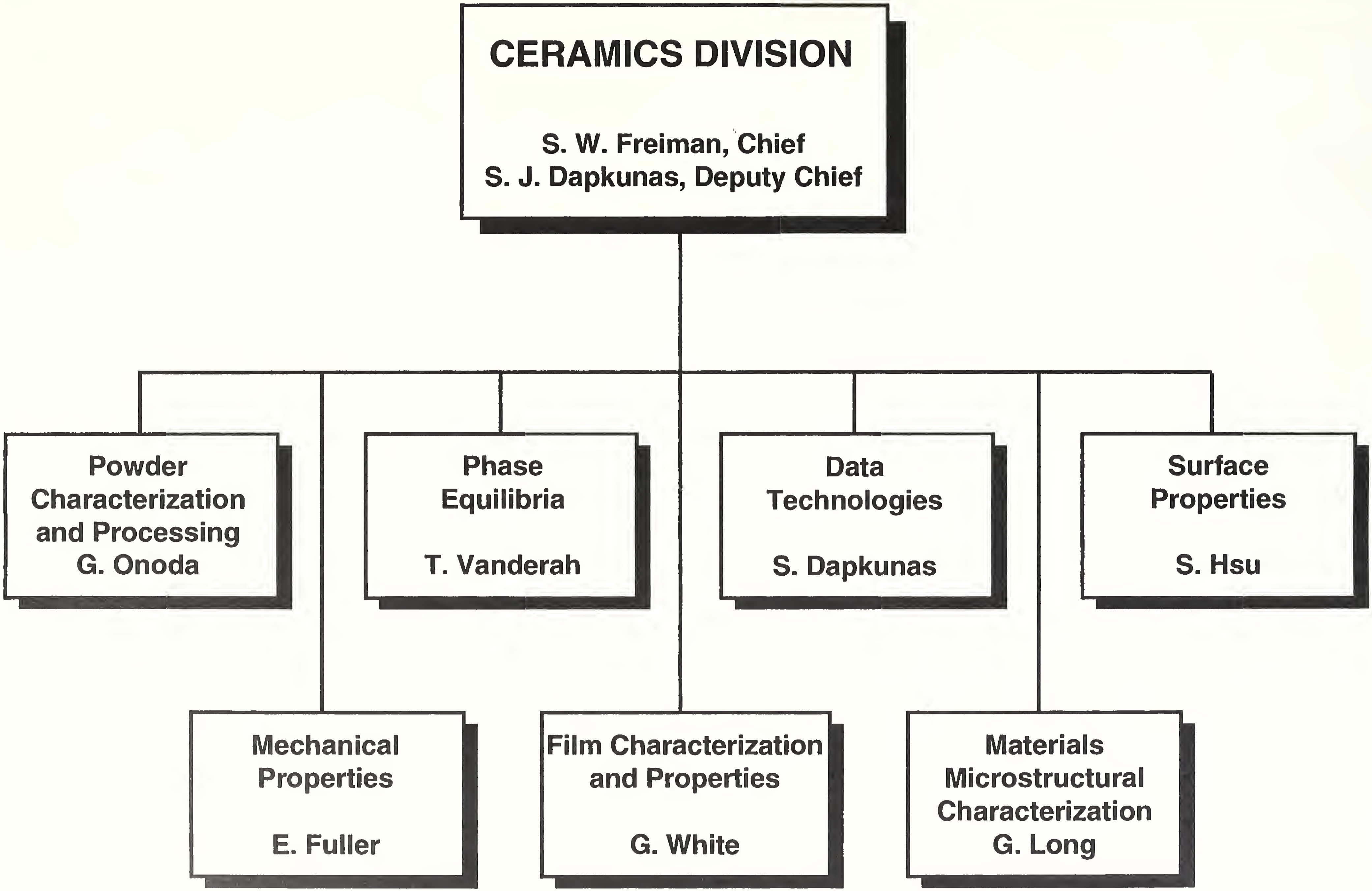
# APPENDIX

# National Institute of Standards and Technology

## Organizational Chart




MATERIALS SCIENCE AND ENGINEERING LABORATORY
L.H. Schwartz, Director
D. Hall, Acting Deputy Director
Metallurgy
C. Handwerker, Chief
R. Schaefer, Deputy
Materials Reliability
H.I. McHenry, Chief
T.A. Siewert, Deputy
Polymers
L.E. Smith, Chief
B.M. Fanconi, Deputy
Reactor Radiation
J.M. Rowe, Chief
T.M. Raby, Deputy
Ceramics
S.W. Freiman, Chief
S.J. Dapkunas, Deputy


CERAMICS DIVISION
S. W. Freiman, Chief
S. J. Dapkunas, Deputy Chief
Powder Characterization and Processing
G. Onoda
Phase Equilibria
T. Vanderah
Data Technologies
S. Dapkunas
Surface Properties
S. Hsu
Mechanical Properties
E. Fuller
Film Characterization and Properties
G. White
Materials Microstructural Characterization
G. Long