Impact of NIST Research and Services

December 2000

NIST Transfers New Polymer Structure Analysis Method to Industry

A new method, developed by MSEL's Polymers Division, for determining the molecular architecture of polymers was transferred successfully to chemists at Dow-Corning Corp. of Midland, Mich. The transfer was facilitated by a recently completed Cooperative Research and Development Agreement (CRADA) in which Polymers Division staff demonstrated their method on materials custom-designed by Dow Corning chemists. Dow Corning scientists applied the technique to their commercial materials to reveal aspects of the chemical structure that were unexpected and impossible to detect by other means.

The new measurement procedure developed at NIST facilitates elucidation of the molecular structure of a class of materials called silsesquioxanes. Dow-Corning is a leading supplier of polymeric silsesquioxanes, which have application in a wide array of industries from microelectronics to dental implants. Silsesquioxanes are based on a trifunctional silicon-oxygen monomer having pendant organic side groups. The trifunctional property of the monomer results in condensation polymers with a wide variety of possible three-dimensional configurations. However, industry lacked methods to accurately determine the structure, how the structure develops during manufacture and how the structure influences properties. The analysis challenge facing Dow-Corning scientists was further complicated by a chemical composition that resulted from the use of two different monomers co-polymerized together.

MSEL's researchers had developed a method using matrix-assisted time-of-flight mass spectrometry (MALDI-TOF-MS), along with autocorrelation analysis of the resulting mass spectra, to determine the topological nature of the molecules as a function of molecular mass. For any molecule having a particular number of silicon atoms, the method can determine the relative number that show a closed topology—polyhedral in shape—versus the number that show an open topology—highly branched in shape. A manuscript that will report on the general method and the results for this example is in preparation.

February 2001

Calibration Standards for Determination of Molecular Mass

MSEL's Polymers Division certified three new polyethylene standards for calibration and performance evaluation of size exclusion chromatographs. Size exclusion chromatography (SEC) is the most convenient and widely used method for determining the mass distribution of synthetic polymers. The molecular mass distribution is the molecular characteristic of polymers that controls both processibility and properties. The three new mass standards, together with three previously certified standards, cover the range from 5,000 g/mol to 200,000 g/mol. These provide the polymer industry with an adequate set of molecular mass calibrants for polyethylene.

Calibrations of SEC are carried out with a series of narrow fraction molecular mass standards covering the mass distribution range of the polymer of interest. Narrow fraction molecular mass polymers are only available for a selected few polymers. In the absence of suitable standards, crude approximations are used which introduce uncertainties in the measurement results. Although polyethylene is the most prevalent synthetic polymer, there are no commercial standards consisting of narrow mass fractions, other than those provided by NIST. The lack of commercial standards arises from difficulties obtaining narrow molecular mass fractions of polyethylene and in measuring absolute molecular masses by light scattering or osmometry at temperatures as high as 150 degrees C. The new standards were prepared from fractionation of a broad distribution polyethylene that provided the fractions previously certified by NIST.

March 2001

NIST Data Facilitates Materials Development for Next Generation IC Chip

Data provided by MSEL's Polymers Division have been used to facilitate development of new interlevel dielectric (ILD) films for next-generation integrated circuit (IC) chips. The drive toward increased density, enhanced performance and cost effectiveness in IC technology requires the development and integration of low dielectric constant (or low k) materials as ILD for deep-submicrometer on-chip interconnects. Over the past year, Rohm and Haas initiated a new research program to pursue low k ILD development. Owing to successes achieved by NIST scientists in characterizing related materials in collaboration with SEMATECH, Rohm and Haas scientists sought NIST assistance to provide critical characterization data on structure and properties. Under a cooperative research and development agreement between NIST and Rohm and Haas, scientists in the Polymers Division provided Rohm and Haas characterization data on four different experimental materials. During a recent joint conference, Rohm and Haas personnel disclosed that the NIST data correlated well with their internal dielectric data and confirmed their working model.

NIST originally developed the methodology for characterization of low-k ILD under a CRADA with International SEMATECH (ISMT). Internal support was also provided by the NIST Office of Microelectronics Programs. The methodology is based on a unique combination of X-ray and neutron scattering measurements that provide critically needed data on the structure of porous thin films. Over the past three years, more than 30 candidate materials from ISMT and its member companies have been characterized by NIST. The data provided by NIST have helped ISMT establish a low k ILD database for selection of viable candidate materials for process integration. It has also enabled ISMT to provide feedback to the material suppliers for further improvement of their ILD materials

August 2001

NIST Instrumentation Installed at Plastics Film Manufacturing Facility

Instrumentation developed in the MSEL's Polymers Division has been installed in a polymer processing plant to facilitate development of manufacturing conditions for polymer films. The instrumentation addresses the need of polymer film producers for a more rapid measurement of molecular orientation and temperature during film production to avoid costly time delays and rejected product runs. The performance properties of biaxially stretched films are determined by their molecular orientation (or anisotropy) and the temperature at which they are processed. Currently, film processors measure orientation in post processing quality control experiments that are carried out with a considerable time delay after processing.

Under a CRADA arrangement with Exxon/Mobil Chemical of Macedon, N.Y., and NIST, scientists in the Polymers Division have developed a sensor and measurement system for real-time monitoring of temperature and molecular orientation during processing of biaxially stretched polypropylene film. At the Exxon/Mobil facility, film processing is carried out in a continuous manner using a tenter stretching frame in an oven that stretches a plastic ribbon in two perpendicular directions: the process flow direction (machine direction) and the direction perpendicular to the process flow (transverse direction).

The NIST measuring technique relies on the presence of a fluorescent dye molecule that is doped into the polymer resin at very low concentrations. Temperature monitoring is carried out by measuring temperature induced changes in the shape of the fluorescence spectrum. Molecular orientation is determined by measuring fluorescence anisotropy of the fluorescent probe molecule whose orientation mimics the orientation of the resin matrix. A sensor head containing optical fibers, focusing lenses, and polarization elements is lowered into the stretching oven and is positioned directly above the processed film. The optical fibers transmit light from the light source to the film and collect fluorescence light for transmission to the detectors. As the film is transported past the sensor, three quantities are measured: orientation in the machine direction, orientation in the transverse direction, and temperature. Exxon/Mobil scientists are using this new information to develop processing strategies that are designed to tailor product performance to specific applications.

September 2001

High Temperature Lead-free Solders

Several industries have identified needs for solders that perform reliably at ever-higher temperatures, temperatures which approach the melting point of the industry-standard tin-lead eutectic alloy (T_m = 183 degrees Celsius). For instance, automotive under-the-hood microelectronics are subject to higher ambient temperatures due to low hood profiles (less air circulation) and the need to place assemblies, such as engine control modules, near the point of application to reduce wiring harnesses. Such harsh environment applications require solders with melting points higher than that of tin-lead eutectic in order to achieve the required reliability. In addition, recent legislative and marketing pressures in Europe and Japan have pushed U.S. manufacturers to pursue lead-free solders for all microelectronics applications, leading to the double challenge of developing high temperature, Pb-free solders.

This year the National Center for Manufacturing Sciences (NCMS) completed the four-year High Temperature Fatigue Resistant Solder Project with the assistance of the MSEL’s Metallurgy Division. Consortium members include Allied Signal, Amkor Technologies, Delphi Delco Electronics Systems, Ford Motor Company, Heraeus Corporation, Indium Corporation, Johnson Manufacturing, Rockwell International Corporation, Iowa State University, and NIST. The goal of the project was to determine whether highly reliable, non-toxic, cost-effective substitutes could be found for industry-standard high lead and Sn-Ag eutectic solders in harsh environments.

NIST played a leadership role in this research project, chairing the Alloy Task Group and providing definitive, timely phase diagram data and critical analyses needed for evaluating candidate solders. NIST also coordinated the final analysis of the data, the determination of conclusions and recommendations, and the writing of the NCMS final report. Six lead-free solder compositions were identified that exhibit fatigue performance during cycling up to 160 degrees Celsius of a wide range of surface mount components which is superior to the industry standard eutectic Sn-Ag alloy. In addition, seven lead-free alloys cycled with ball grid array packages through -40 to 125 degrees Celsius strongly outperforming Sn-Pb eutectic solder.

The High Temperature Fatigue Resistant Solder Project was summarized in an invited article in *Advanced Materials and Processes*, April 2001, written by NIST staff. In addition, a technical paper presented by NIST was selected as one of the five best papers out of 58 presented at the TMS 2001 Annual Meeting Symposium on "Recent Progress in Pb-Free Solders and Soldering Technologies.

October 2001

NIST Aids Development of New Bone Graft Materials

Scientists from the MSEL Polymers Division and research associates from the American Dental Association Health Foundation have demonstrated a new approach to bone regeneration. More than 100,000 bone grafts are performed each year in the United States, but the amount of available autologous bone is limited and available material is difficult to shape. Furthermore, the number of bone grafts will likely increase as the population ages. Thus, the development of a synthetic, moldable bone graft is the primary goal of tissue engineered products industry.

The new approach extends previous work by the American Dental Association Health Foundation at NIST on a self-setting calcium phosphate cement that can be sculpted to fit the contours of a wound. This cement was improved in recent work by making it macroporous and osteoconductive through inclusion of polymer microspheres and a bone growth factor, respectively. The polymer microspheres are made of a biodegradable polymer that initially stabilizes the graft, but then can degrade gradually, leaving pores of the appropriate size for colonization by osteoblasts. The calcium phosphate cement matrix would be reabsorbed and replaced by new bone. The NIST research has shown that in cell media the polymer-modified cement undergoes complete degradation of the polymer microspheres and porogens, leaving a porous structure. Osteoblast-like cells were shown to adhere, attain a normal morphology, proliferate and remain viable when cultured on the new composite graft. The calcium phosphate cement is further improved by providing controlled release of an osteoinductive protein that facilitates growth of new bone. Studies have shown that adjusting the amount of porogens could modulate the protein release kinetics.

The NIST work has attracted the interest of biotechnology companies that focus on the development of synthetic bone grafts.

Recommended Practice Guide Success Story

First available in the spring of 2001, the NIST *Recommended Practice Guide on Rockwell Hardness Testing of Metallic Materials* (Special Publication 960-5) has been requested at a rapid rate. Nearly 5,000 copies have been requested, and the first printing is almost exhausted. The MSEL guide documents preferred methods for measuring hardness of metals, the most widely used technique employed by industry worldwide for characterizing mechanical properties. Manufacturers of hardness testing equipment are now distributing the guide, and several include it with each new hardness tester they sell.
As noted by the Vice President of United Calibration Corporation, “This publication is a good step in bringing metrological methods to the calibration and operation of Rockwell hardness testers. It is educating users and auditors in the fine points of Rockwell testing.” In addition to the hard copy, the guide is available at www.nist.gov/practiceguides.

Patent Issued For Reverse-Angle X-Ray Diffraction

Patent 6,269,144 was recently issued to NIST for a “Method and Apparatus for Diffraction Measurement Using a Scanning X-ray Source.” The NIST inventors were Bill Dube, Dale Fitting, and Tom Siewert, all of the MSEL Materials Reliability Division. The Digiray Corp. inventor was Richard Albert. The concept combines the high-energy X-ray diffraction technology that has been developed in the Materials Reliability Division during the past five years with the unique area-scanned X-ray tube developed by Digiray Corp. The technique differs from conventional X-ray scanning systems in that the X-ray source is scanned through a pattern instead of the specimen. The technique is particularly appropriate for rapid determination of texture or identifying the phases present in a specimen.

In 1999, Digiray received the exclusive license to this joint NIST-Digiray invention. Digiray will develop the method into commercial products.

MSEL Programmatic/Technical Accomplishments

This section contains selected highlights of MSEL research. The highlights are arranged by programs within the four major program groups: Materials Characterization, Measurement Facilities, Materials Manufacturing, and Functional Materials. Significant advances were achieved in combinatorial methods, materials for microelectronics and wireless communications, x-ray characterization, modeling and metals processing.

MATERIALS CHARACTERIZATION

Combinatorial Methods

Novel Combinatorial Methods for Inorganic Thin Films (July 2001)

Over the past decade, combinatorial chemistry, which involves high throughput synthesis and analysis of a multivariable "library" containing a large number of miniaturized samples, has revolutionized the drug discovery process in the pharmaceuticals industry. Recently, materials scientists have been applying combinatorial principles to the discovery and optimization of inorganic thin films for electronic, photonic, and magnetic devices; this requires unique tools for library fabrication and characterization. Researchers in the MSEL's Ceramics Division have developed a novel dual-beam, dual-target pulsed laser deposition process for the fabrication of compositionally-graded thin film libraries. The deposition system has high-speed, *in-situ* diagnostics, which permit real-time fine-tuning of the two laser plumes to optimize the deposition parameters. This technique is applicable to a wide range of complex oxides, metals, and metal/oxide composites. To date, libraries of $BaTiO_3$-$SrTiO_3$, a material of interest for wireless communication devices, have been deposited on silicon substrates. Film thickness has been mapped at a spatial resolution of 0.3 millimeter using a spectroscopic reflectometry apparatus designed by MSEL researchers. Composition and dielectric properties of the libraries are being characterized by high throughput measurement techniques in CSTL.

Combinatorial Characterization of Block Copolymer Film Morphology (July 2001)

Combinatorial methods have been successfully applied by researchers in the NIST Polymers Division within MSEL to observe novel morphologies and to establish fundamental kinetic relationships in the ordering properties of block copolymer films. Copolymers are a class of polymer materials that have large potential for commercial applications. Unique properties in melts, blends and solutions lead to their use as adhesives, emulsifying agents, thermoplastic elastomers, compatibilizers, etc. Block copolymers are an important sub-class of copolymers consisting of polymers of different chemistry that are covalently linked.

A key question in block copolymers is the nature of interactions between blocks, as well as block interactions with different materials. To address this question NIST researchers exploited the ability of block copolymers to form quantized periodic structures, such as lamellae, that directly reflect molecular parameters such as block lengths, chemical interactions between the block constituents, and interactions with an external (substrate) material in thin films. The work of the NIST researchers (available online in NVL journals: *Physical Review Letters & Journal of*

Polymers Science Polymer: Part B Polymer Physics) demonstrates that these fundamental properties can be very efficiently determined in a high-throughput manner using a combinatorial approach. This was accomplished by flow-coating multiple films having different molecular masses and gradients in film thickness. Each "library", the size of a standard microscope slide, contains as many as 1,500 differentiable experimental conditions, including process variables of temperature and time. Novel morphologies observed including a labyrinthine (or spinodal) surface patterns as well as extended smooth regions. These morphologies are related to an enthalpic vs. entropic balance of interactions in block copolymers. In addition, the size of the surface patterns unexpectedly displayed an inverse relationship with molecular mass that can be attributed to the copolymer surface elasticity.

Metals Characterization

New Microscopy Capability in MSEL (April 2001)

MSEL has a new field-emission scanning electron microscope (FE-SEM) capable of high spatial resolution microstructural characterization of a wide variety of metal, ceramic, and polymer structures. This microscope has accelerating voltages from 500 V to 30 kV with spatial resolutions of 1.5 nm at 15 kV and 2.5 nm at 1 kV. The ability to maintain high resolution even at lower voltage allows the investigation of uncoated, non-conducting specimens, such as ceramics and polymers. The microscope is equipped with an energy dispersive X-ray spectrometer (EDS), back-scattered electron (BSE) detector, and faraday (picoampere) cups. The microscope has an improved objective lens electron detector system, which can be continuously adjusted to allow for imaging with secondary or backscattered electrons. This improved design allows BSE imaging at low voltages (less than 5 kV) where conventional BSE detectors are unsuitable. The new FE-SEM is expected to benefit a wide range of NIST research programs through high resolution materials characterization. The microscope is currently being used to evaluate the structures and compositions of thin- film multilayers, highly deformed metals, copper on-chip metallization, ceramic fracture surfaces, nanostructured powders, polymers with nano-scale porosity, and lithography masks.

Multiphase Polymeric Materials

Advances in Process Visualization Reveals Novel Polymer Structure (January 2001)

Scientists from MSEL's Polymers Division have utilized in-situ visualization technology to discover novel structures formed during processing of polymer blends. The observations, which will appear in *Physical Review Letters*, are the consequence of new measurement tools developed for elucidating the structure of polymer blends during processing. The novel structure results when the dimension of a manufactured part approaches the size of one of the components in an incompatible mixture of polymers. Under such conditions, the NIST measurements show that there is a massive reorganization of the structure of the dispersed polymer droplets. In a four-stage process, tens of thousands of the droplets join together to form extremely large strings. Instead of micrometer-sized droplets typical of polymer blending, these strings can be 10 centimeters in length, and have been observed to wrap around the processing flow. Once the strings form, they are extremely stable; in fact, it is hard to get rid of them.

Most engineering plastics are polymer blends. Polymer blending technologies are well developed for the case where the final part, such as a car bumper, is much larger than the size of the dispersed polymer droplet, typically one micrometer. The new observations suggest the need for alternative blending strategies when the size of the part becomes comparable to the size of the droplets. In addition, the string-like structure may lead to new applications, for example, conductive plastic wires, if the string component was a conductive polymer and the matrix was an insulator with good mechanical properties. If the string component formed a reinforcing fiber, one could have ultra-thin composite materials of high one-dimensional strength. Likewise dissolving out the string component from a biocompatible polymer could provide oriented pores for cell growth for tissue engineering.

New Test Capability Probes Failure Processes in Polymer Composites (November 2001)

A new measurement tool for visualizing and quantifying time-dependent failure mechanisms in polymer composites has been developed in the MSEL Polymers Division. The new test method produces optical images of multi-fiber test specimens as the specimens are deformed under mechanical load. Previous work, based on single-fiber tests, ignored how rupture of one fiber affects the failure of neighboring fibers and provided only limited information regarding the influence of the polymer matrix on mechanical failure.

Initial results from the new test apparatus show that the nucleation of critical flaws in unidirectional fibrous composites depends on the time-dependent redistribution of the mechanical stress in the polymer matrix. The behavior of the matrix determines how the rupture of one reinforcement fiber affects the integrity of neighboring fibers. In addition, new information regarding the role of matrix cracks and residual curing stresses on fibrous composite failure behavior has been revealed. A visual representation of the time dependent failure behavior in two-dimensional multi-fiber composites can be found at:
http://polymers.msel.nist.gov/researcharea/multiphase/project-detail.cfm?PID=56

Knowledge of the time-dependent failure processes in fiber-reinforced composites is critical to their use as structural parts in automotive applications. Automotive design engineers need better tools for predicting and managing how composite parts respond to crashes. To address this need Polymers Division researchers are adapting the MSEL object oriented finite element analysis (OOF) program to include viscoelastic materials. The data from the multi-fiber tests will be used to aid the development of failure models for the new OOF program.

New Test Method to Determine The Constituent Contents of Polymeric Composites (January 2002)

Researchers in the Polymers Division of MSEL are proposing a modification of the standard burn-off test to characterize carbon/glass hybrid composites, ASTM D3171-99. Hybrid composites are increasingly being used in infrastructure, aerospace, and automotive applications. These hybrids use two different fibers to reinforce the resin, thereby gaining some of the advantageous properties of both fibers. Typically, carbon and glass are used since this combination provides high performance and low cost. Critical issues in such materials are the fiber mix ratio and the fiber and void contents. At present, there is no simple way to determine these features, although many techniques exist for measuring the components of single reinforcement composites.

The proposed amendment calls for heating the specimen in a muffle furnace in a series of steps designed to sequentially separate out the resin, carbon fibers, and glass fibers. In addition, void contents of these composites can also be calculated. Results obtained with the proposed method on both commercial and laboratory-prepared samples were found to be in excellent agreement with values obtained by labor-intensive microscopic examinations.

Knowledge of the constituents in hybrid composites is needed for the development of models that accurately predict composite strength and failure behavior. The ultimate goal of our work is to use parameters such as those determined by this new test to establish a mathematical link between micromechanics properties that initiate and control the modes of composite failure and the physics of composite failure behavior.

Polymer Characterization

International Interlaboratory Testing Advances Mass Distribution Measurement Method for Synthetic Polymers (October 2000)

The quality of mass spectrometric measurements of mass distribution in synthetic polymers was assessed in a recent NIST report that described the results of an international interlaboratory comparison involving 21 laboratories, including MSEL's Polymers Division. MALDI-MS, a form of mass spectrometry in which laser ablation is used to produce volatile charged molecules, is being explored as an absolute method for molecular mass distribution of synthetic polymers. Most current methods yield only moments of the mass distribution. For instance, gel permeation chromatography yields the mass distribution but requires calibration with hard-to-find standards of known mass. Published results of mass distribution by mass spectrometry yield conflicting findings; hence the interlaboratory comparison was undertaken to determine the current status of measurements on a single, well-characterized polymer and to identify measurement issues that require attention. The polymer, polystyrene, evaluated in the round robin was custom synthesized to NIST specifications with molecular characteristics such that it could be investigated not only by mass spectrometry but also by traditional spectroscopic methods and light scattering.

Participants of the interlaboratory comparison reported the mass spectrum of the polystyrene and moments of the distribution calculated from mass spectrometric data. NIST staff calculated the moments from the submitted data as well. In some cases, the moments calculated by NIST using the participants' data differed significantly from moments reported by the participants. The distribution in values of moments calculated by NIST was very narrow, with a standard deviation of one polystyrene repeat unit, approximately. Furthermore, analysis of these data yielded moments of the mass distribution lower than those obtained from current methods but within the measurement uncertainty. Nonetheless, it was found that calibration of mass spectrometers was not performed correctly by several participants and that methods of data analysis differed widely with some participants reporting moments of the distribution that differed significantly from the mean. The findings of the report will be used to improve the quantification of the new mass spectrometric method for the determination of synthetic polymer mass distributions.

Standard Non-Newtonian Fluid for Rheological Measurements (September 2001)

A new Standard Reference Material, SRM 2490, is available for calibration of rheometers, instruments used to measure the flow behavior of fluids. Complex fluids, such as suspensions or polymer melts and solutions, often do not follow the simple Newtonian ideal in their flow behavior. Such fluids are found in numerous applications in everyday life (injection molding, paints and coatings, food products, etc.), and the ability to measure accurately and characterize their behavior is very important to optimizing their processing conditions. Since there are a number of commonly used methods to measure the flow behavior of polymers, the new Standard Reference Material will provide a means for comparing the performance of different instruments, as well as a tool for research into better methods of measuring the rheological properties of polymeric fluids. The new standard fluid is certified by MSEL's Polymers Division for the shear-rate dependence of viscosity and first normal force difference at shear rates from 0.001 s^{-1} to 100 s^{-1} over a temperature range from 0 to 50 degrees Celsius. The linear viscoelastic storage modulus and loss modulus are also certified at frequencies from 0.04 rad/s to 100 rad/s over the same temperature range.

The new fluid supersedes the previous Standard Reference Material 1490 Non-linear Fluid Standard, which was composed of a high-molecular-mass polyisobutylene dissolved in normal hexadecane. The new standard fluid SRM 2490 consists of a similar high-molecular-mass polyisobutylene dissolved in 2,6,10, 14-tetramethylpentadecane (common name pristane). Pristane is a branched alkane of a slightly higher molecular mass than the normal hexadecane; the branching prevents crystallization or vitrification down to -60° degrees Celsius, while the higher molecular mass reduces the rate of evaporation of pristane as compared to normal hexadecane.

Powder Measurements

NIST Recommended Practice Guide—Particle Size Characterization (April 2001)

Researchers in MSEL's Ceramics Division have completed the first in a new series of NIST publications, *NIST Recommended Practice Guide—Particle Size Characterization* (NIST SP 960-1). The uniqueness of this document lies in its integration of all of the critical aspects of particle size characterization. The guide is designed primarily for non-expert users in the ceramics industry, such as plant engineers, laboratory technicians, and students. The guide describes important aspects of powder sampling and focuses on four techniques of size analysis: sieving, gravitational sedimentation, microscopy and laser light diffraction. Issues related to reporting size data are also discussed. Each size analysis technique is addressed in a separate chapter with attention to principles of the technique, general procedures, strengths and limitations, applicability, sources of error and variation, and data collection and interpretation. Examples of issues encountered in particle size analysis based upon NIST-led interlaboratory tests have been included. Another feature of this guide is the description of numerous national and international standards pertaining to these size analysis techniques, as well as other issues of particle size characterization. Feedback from industrial users was obtained to ensure relevance to their requirements. More information on this and other practice guides can be found at www.nist.gov/practiceguides.

MSEL & BFRL Develop Recommended Practice Guide on Dispersion Nomenclature (November 2001)

A new NIST Recommended Practice Guide (SP960-3), *The Use of Nomenclature in Dispersion Science and Technology*, is now available. The guide is the product of a cooperative effort between MSEL and BFRL researchers and should have wide appeal.

Ceramic suspensions, gels, and pastes are the starting materials for a wide variety of applications, playing critical roles in the manufacture of products ranging from concrete and sunscreens to multilayer ceramic capacitors and integrated circuits. Unfortunately, researchers and engineers working in these diverse fields often do not speak the same language. Even within the same field, variations in terminology are common. There is a clear and present need for a broadly accepted, uniform and precise nomenclature for describing experimental methods and instrumentation, for sharing technical ideas and concepts and to provide a sound basis on which to standardize measurement methods and data reporting practices. This new guide will serve as a resource for practitioners working in fields in which ceramic dispersions are used. The guide focuses on commonly encountered terminology, providing a consistent framework for improved technical communication.

Ultrasonic Characterization of Materials

Nondestructive Testing of Cables (December 2000)

Cables formed by twisting steel wires together to form a flexible rope with high-strength properties are found throughout industry. However, the nondestructive detection of internal flaws such as cracks or corrosion in the innermost wires is very difficult for conventional nondestructive testing techniques because of the naturally inhomogeneous nature of the cable’s construction. Recently, the Colorado School of Mines and MSEL’s Materials Reliability Division in Boulder collaborated on the development of a novel method of inspection of copper cables used for grounding power transformers in electrical substations. Here, the cables run underground with the only access being a short length between the transformer frame and the surface of the ground. A special ultrasonic transducer was designed that could be clamped around the exposed end of the cable. The transducer sends a torsional ultrasonic wave along the cable buried under the substation. By detecting and signal processing the echo signals returned by corroded regions, the damage can not only be located but its severity can be estimated. This inspection technique is now being applied to high-voltage transmission line cables made of steel and aluminum wires twisted together to optimize the conductivity-to-strength ratio. The work at the Colorado School of Mines is supported by a contract with EPRI.

Elastic Characterization Of Anisotropic Thin Films Using SAW Dispersion (July 2001)

The Materials Reliability Division within MSEL is developing theoretical and experimental techniques for non-destructive measurement of elastic characteristics of anisotropic thin films. Presently there is a strong industrial interest in elastic characterization of thin films because they have applications in electronic, photonic, and magnetic devices and are also used as wear and corrosion resistant coatings on ordinary materials. Material parameters of interest for elastic characterization of a film are the elastic constants of the film, its density, and thickness. In general, the films as well as the substrate in modern materials are elastically anisotropic. Current theoretical and experimental methods of non-destructive characterization are not convenient for anisotropic layered solids.

Experimentally, we measure the phase velocity of a surface acoustic wave (SAW) over a broad frequency range. We have created a laser-ultrasonic apparatus for broadband SAWs. The system incorporates a 0.2 ns pulsed laser for SAW generation and a Michelson interferometer detector with bandwidth over 800 MHz. We have used this apparatus to measure dispersion relations in several samples including titanium nitride films on single-crystal silicon and stainless steel samples. The thickness of these films ranged from about 250 nm to 3500 nm.

For the purpose of analysis of the dispersion data for SAWs, we have developed a computationally efficient representation of the Green's function to model the elastodynamic characteristics of an anisotropic thin film on an anisotropic substrate. In this model, the Green's function is represented in terms of a delta function of space and time in slowness space. For anisotropic solids, this representation is computationally more convenient than the convention Fourier reciprocal space and frequency representation. Our model can account for surface texture of the film and imperfect interfacial bonding between the film and the substrate. The elastodynamic model is used to calculate the dispersion of surface acoustic waves in the film and also provides an efficient algorithm for the inverse problem of characterizing the film from measured values of the dispersion. We have successfully applied this method to calculate SAW velocities in various isotropic and anisotropic films including textured polycrystalline films of TiN on single-crystal Si and to estimate the elastic constants of the films. Excellent agreement is obtained between the theoretical and measured values of the SAW velocities in most cases.

Improved Technique for Characterization of Texture in Thick Plates (November 2001)

Commercial metal alloys used for structures are usually produced by rolling or extrusion into the form of plates, bars or beams. These fabrication processes leave their mark on the material in the form of a texture or preferred orientation of the grains in the microstructure. In many applications, such as the nondestructive inspection and materials characterization of structural components, a knowledge of this texture is of vital importance.

It can be measured in the laboratory by X-ray techniques or by ultrasonic methods that involve precision machining of a specimen cut from the part. However, the information on texture is often needed in the field, at depths below the penetration of X-rays or on parts that cannot be cut up. For several years, the MSEL Materials Reliability Division has been developing ultrasonic measurement procedures for deducing the texture of materials using specimens carefully machined from the part. We have developed a texture measurement technique by combining electromagnetic acoustic transducers (EMATs), which excite and detect ultrasonic waves that propagate near or on the surface of a plate, with theoretical models for the elasticity of polycrystalline aggregates.

It is nondestructive and applicable to large objects found in the field, at rolling mills, or in foundries. It is being used to measure surface residual stresses that distort parts being machined from thick plates, to characterize ultrasonic reference blocks used to calibrate ultrasonic inspection systems, and to monitor the condition of surface layers used to extend fatigue life or improve wear resistance.

X-Ray Characterization

MSEL Collaboration Uses Microgravity to Improve Protein Crystal Growth (November 2000)

NIST scientists are collaborating with Biospace International in the growth of ribonuclease crystals in space. X-ray diffraction topography, which has only recently been applied to protein crystals, was used to probe the differences between crystals grown on the space shuttle and crystals grown at the same time on the earth. The topographs from the space-grown crystals showed that they were of higher crystalline perfection than the ground-grown crystals. The images of the space-grown crystals were more uniform and sharply defined. The symmetry was consistent with nucleation followed by homogeneous symmetric growth. This growth mechanism is possible in microgravity but not likely on earth where there is sedimentation and convection-induced asymmetry. On the other hand, the earth-grown crystals had a less well-defined microstructure with no clearly identifiable features and there was no consistent symmetry of the images. All of these features indicate lower quality crystals with a higher-defect density. In addition to quality improvements, microgravity also improves crystal harvesting. Approximately 80 percent of the crystals grown in microgravity were free-floating in the growth chamber, facilitating removal. In contrast, approximately 80 percent of the earth-grown crystals grew attached to the growth chamber making harvesting more difficult. These results clearly demonstrate the advantages of a microgravity environment for growing protein crystals.

New X-ray Imaging Technique Reveals Crystal Defects (December 2000)

The deformation of metals takes place primarily by the motion and interaction of defects in the crystal structure known as dislocations. Quantitative understanding of this deformation, needed for modeling of metal-forming processes, has been hampered by a lack of knowledge about the complex configurations assumed by these defect microstructures when the metals are deformed.

A new experimental technique, ultra small angle X-ray scattering (USAXS) imaging, has been shown jointly by the Metallurgy and Ceramics Divisions of MSEL to hold promise as a useful tool for studying microstructures in situ. The technique is based on forming an image of the sample using X-rays which have been scattered from defects in the crystal structure. Although these X-rays scattered from defects are very weak, the USAXS technique allows them to be isolated from the high-intensity background to form an image of the defects only. The scattering from these components can be detected down to around seven to ten times the intensity of the main transmitted X-ray beam. Preliminary tests of this technique were made at the Advanced Photon Source on March 11-13, 2000, using copper samples in which defects had been produced by a very slow deformation treatment. A more thorough study was conducted on May 17-21, 2000. The tests were very successful and microscopic damage was imaged using several different scattering conditions. A basic theory for the image formation process in USAXS imaging has been worked out and it was validated by experiments completed on Sept. 4, 2000. The technique is believed to be a major breakthrough with broad potential applications, including the study of the defects which control metal deformation behavior. A paper on USAXS imaging has been accepted for publication.

MEASUREMENT FACILITIES

Neutron Facility Operation

"DAVE": Data Analysis and Visualization Environment (January 2002)

Scientists at the NIST Center for Neutron Research have developed a new software tool for the reduction, visualization, and analysis of neutron inelastic scattering data. DAVE, short for Data Analysis and Visualization Environment, is an integrated suite of interactive software tools with a visual interface for treating and analyzing neutron inelastic scattering data sets. With a few clicks of the mouse, users can reduce their data from one of the inelastic spectrometers, make cuts through the scattering function, and fit them with the lineshape of their choice from a library of model functions. The integration of these functions greatly simplifies moving among the different inelastic spectrometers. Moreover the software is designed so that it is straightforward to add other instruments or more advanced analysis functions. DAVE is a standalone executable application freely available for PC, LINUX, and MAC platforms.

Neutron Characterization

Quasielastic Neutron Scattering Probes Protein Dynamics (October 2000)

The function of a protein depends critically on its ability to adopt a specific structure. Remarkably a protein can fold efficiently to this native state from the unfolded states on physiological time scales. Understanding how this process occurs is one of the great challenges in biology. Proteins can also form collapsed, partially folded states. Such partially folded proteins resemble the intermediate states along the protein folding pathway and play important roles in understanding the mechanisms of protein folding.

To understand the changes in protein dynamics that occur in the final stages of folding, scientists from the NCNR and MSEL's Polymers Division have used quasielastic neutron scattering to probe the differences in the dynamics between the native state and the almost completely folded, molten globule state of the protein bovine a-lactalbumin. The results, show that the side-chain protons in the molten globules are significantly more mobile than those in the native protein. Moreover, the length scale of the motion, information that is uniquely provided by neutron spectroscopic techniques, is substantially longer in the molten globule state compared to that in the more compact native state. (For further information, see Z. Bu, et al., *J. Mol. Biol.* 301, 525 (2000).)

NCNR Sets the Standard for Quantitative Phase Analysis (December 2000)

Personnel from the NIST Center for Neutron Research (NCNR) recently participated in an international round-robin on the use of diffraction techniques for the quantification of phase abundance in multiphase mixtures. This type of analysis is essential for the characterization, development, and performance of many industrial materials, such as thermal barrier coatings employed in aircraft engines. The round-robin included participants from X-ray, synchrotron, and neutron facilities worldwide, and was sponsored by the Commission on Powder Diffraction of the International Union of Crystallography.

Results to date show a wide variation in performance for various methods. For example, in one standard mixture containing 34.2 percent zinc oxide, results obtained using laboratory X-ray sources ranged from 25 percent to 42 percent, results from synchrotron sources ranged from 29 percent to 35 percent, and those from neutron sources ranged from 32 percent to 35 percent. NCNR analysis gave 34.4(1) percent. For all 10 mixtures analyzed, the NCNR results agreed within statistical limits with the nominal compositions and, overall, gave the best results in the study.

The results of this study again emphasize the importance of neutron methods in providing accurate data on phase composition in industrial materials.

Supercooling and Superheating of Vortex Matter (January 2001)

The behavior of quantized flux lines in type-II superconductors is of critical importance in a variety of high-current applications anticipated for “high temperature” superconductors, such as magnets for medical imaging and power transmission cables. These vortex systems also provide a prototypical system for the study of fundamental problems in phase transitions and melting phenomena. Unfortunately, vortex structures have been difficult to investigate in detail in the cuprate materials because of the intrinsically short superconducting length scales and because of materials quality problems. A current subject of wide interest concerns the possibility of a solid-liquid transition of vortex matter and its relation to the dramatic transport anomaly in superconductors known as the peak effect, in which the critical current exhibits a maximum rather than decreasing monotonically with increasing temperature. Researchers at Brown University and the NCNR have now carried out small angle neutron scattering measurements combined with in-situ ac magnetic measurements, on a high-quality niobium crystal where these experimental difficulties are averted. They report the first structural evidence for a first-order vortex solid-liquid transition associated with the peak effect. In particular, superheating of the vortex solid and supercooling of the vortex liquid have been observed directly for the first time. This is an important result for assessing future technological applications, since there is a definite limit, by virtue of being a first-order transition, to which the material’s properties can be tailored to achieve the highest critical currents. These results also open up the possibility to experimentally test the fundamental theoretical ideas of melting in bulk solids. For example, in conventional solids surface melting masks any superheating effects, while a superheated vortex lattice is stable for hours, but can be melted by applying a small perturbing ac magnetic field.

Characterizing Nanoscopic Disorder Using Quantum Molecular Tops (February 2001)

Researchers at the NIST Center for Neutron Research have recently carried out the first U.S. studies by cold neutron spectroscopy of molecular disorder induced by nanoscale confinement. In this work inelastic neutron scattering was used to probe the rotational dynamics of molecules adsorbed into porous glass disks with pores ranging from 2.5 nm to 7.5 nm.

In bulk molecular solids at ~5 K, the molecular rotors are classically forbidden from rotating due to the surrounding molecular field. However, quantum mechanics allows the molecules to rotate by tunneling through the barrier. The differences observed between the quantum tunneling in the bulk and confined molecular solids provide a powerful probe of the structure of the confined molecular solid. This information, which is key to useful properties of nanostructured materials, is very difficult to obtain using conventional structural methods. Using neutron inelastic scattering, NCNR scientists have measured the effect of both pore size and the surface chemistry on the degree of disorder in the local molecular environment for molecules such as CH3I confined in porous glasses.

Thus, novel cold neutron techniques that probe the dynamics of the adsorbed solid rather than the static structure could prove very useful in characterizing the next generation of engineered nanoporous materials, with applications including chemical separation.

A New "Twist" on Neutron Reflectometry: Imaging Exchange-Spring Magnets (March 2001)

Scientists of the NIST Center for Neutron Research (NCNR) have developed a new method of using polarized neutron reflectometry (PNR) to extract the structure of buried magnetic spirals in magnetic films. This technique improves upon earlier methods by being particularly sensitive to the presence of magnetic twists vis-à-vis structures in which the magnetization direction does not vary appreciably. Tracking the formation and growth of twists may solve a number of puzzles that hamper the development of magnetic thin film devices.

In collaboration with IBM scientists, the technique has been applied to a thin-film exchange-spring magnet. The results confirmed that current theory regarding the behavior of such magnets may be violated. The film consists of the hard ferromagnet $Fe_{55}Pt_{45}$ topped by the soft ferromagnet $Ni_{80}Fe_{20}$. It has been predicted that the combination of soft and hard ferromagnets in close proximity produces a composite which has a strong moment and does not readily demagnetize. As a side effect, when a small external magnetic field is opposed to the magnet, the portion of the soft ferromagnet farthest from the hard ferromagnet may twist into alignment with the field.

Techniques other than PNR typically measure only the average orientation of the magnetic spins and cannot readily distinguish a spiral from a structure in which all the spins are canted with respect to an external field. PNR can extract the depth-dependence of the structure. The new modification of the PNR method greatly enhances the contrast between various structures. First the reflectivity is measured with neutrons glancing off the front surface of the material, and then repeat with neutrons glancing off the back surface. Key features in the data immediately indicate the presence of a spiral, and by studying the film at a number of fields, it is possible to track the development of the spiral. Surprisingly, it is found that the spiral invades the hard ferromagnet even at extremely low fields, in contradiction to current theory.

With this new technique, NIST is now able to better characterize the magnetic properties of thin films, which can improve the capability and reliability of industrial devices for magnetic recording and sensing.

New High T_C Boron Superconductor (April 2001)

The surprise discovery very recently of superconductivity at 40K in the binary MgB_2 system has triggered enormous interest in the structural, electronic, and superconducting properties of simple systems in general and this class of compounds in particular. From the experimental viewpoint, it is important to determine whether MgB_2 is an isolated, special exception, or if it is representative of a broad class of new superconducting materials. The emerging picture of this system is quite interesting. The crystal structure is layered, similar to intercalated graphite, and the band structure shows that it is a good metal due to the boron orbitals at the Fermi surface, while the Mg does not contribute appreciably to the conductivity. The hole-type conduction band is reminiscent of the high-T_c cuprates, but, in contrast to the cuprates, the normal-state conductivity is three-dimensional in nature instead of being highly anisotropic, thus eliminating the “weak-link” problem that has plagued widespread commercialization of the cuprates. The conduction electron density and normal-state conductivity are also one to two orders-of-magnitude higher than either the Nb-based alloys or Bi-based cuprates used in present day wires, contradicting the conventional wisdom that good superconductors are poor conductors because of the strong electron-phonon interaction and at the same time providing encouragement that higher T_c materials will be found in this class.

From a fundamental point of view, the central question is whether the high T_c in this new system can be understood within the framework of a conventional electron-phonon mechanism, or a more exotic mechanism is responsible for the superconducting pairing. To answer this question, scientists from the NIST Center for Neutron Research, Princeton University, the University of Maryland and the University of Pennsylvania have carried out temperature-dependent neutron measurements of the crystal structure and phonon density of states, and have compared these results with detailed first-principles calculations of the lattice dynamics and electronic band structure for MgB_2. Excellent agreement is found between theory and experiment, demonstrating that the calculations are able to capture the essential physics of this class of materials. The numerical results demonstrate that the in-plane boron phonons are strongly coupled to the conduction electrons, providing the large electron-phonon interaction in this system. This coupling gives rise not only to strong anharmonicity for these phonon modes, but to a large non-linear electron-phonon coupling that explains the high T_c in MgB_2.

The many interesting properties described above, combined with the low cost, lightweight, and easy fabrication of wires and thin films, makes this new material quite attractive for many applications. Additional information can be obtained at http://webster.ncnr.nist.gov/staff/taner/mgb2/.

Neutrons Used To Characterize a Novel Lithium-Containing Zeolite (May 2001)

Zeolites are minerals with molecule-sized pores. Different materials have different-sized pores. In the past few decades, chemists have learned to produce new zeolite analogs that incorporate a variety of elements and have a variety of properties. These zeolitic materials are used widely for tasks ranging from the production of gasoline and medical oxygen to improved laundry detergents.

In collaboration with researchers from SUNY Stony Brook and the Ruhr-Universität-Bochum, MSEL researchers have characterized a new type of zeolitic material—the lithosilicate RUB29—built in part from LiO^4 building blocks. [S.-H. Park, et al., Journal of the American Chemical Society, 122, 11023 (2000).] Neutron diffraction performed at NIST was essential for a complete structural determination for this material. The novel LiO^4 building units found in RUB-29 are more flexible than others previously employed and allow formerly impossible configurations of pores to be achieved. Also, the Li atoms require proportionally more charge balancing cations than other building blocks. This means that lithosilicates have the potential for unprecedented ion-exchange capabilities. Further, in this work, an additional unique property of RUB-29 was discovered: the Li atoms in this material are mobile at relatively low temperature (<250 degrees C), indicating this class of materials could have possible applications in fuel cell or battery technology.

Small-Angle Neutron Scattering Uniquely Probes Gene Regulatory Protein/DNA Complexes (June 2001)

Scientists at the NIST Center for Neutron Research (NCNR), the Biotechnology Division, and the Center for Advanced Research in Biotechnology are using small-angle neutron scattering to obtain unique information about the structure of gene regulatory protein/DNA complexes in solution. Gene regulatory proteins control gene expression in developmental and cellular processes of many organisms. Some are activators, turning genes on and some are repressors, turning genes off. All gene regulatory proteins recognize and bind specific DNA sequences. The binding of gene regulatory proteins to DNA often results in a deformation of the DNA. There also has been recent indirect evidence that the proteins undergo a structural change as well upon DNA binding. Small-angle neutron scattering (SANS) is currently being used at the NCNR to study the structural changes in both the DNA and protein components of DNA/gene regulatory protein complexes. The goal is to better understand the interactions between DNA and proteins in these important biological systems.

SANS is ideal for studying protein/DNA complexes since the neutron scattering strengths of DNA and protein differ with respect to each other. By measuring the complex in solutions containing different amounts of D^2O, with respect to H^2O, different structural components can be highlighted, while others are suppressed. By measuring the protein/DNA complex under a sufficient number of solvent conditions, the structure of the two components can be separately determined, even though both components are bound together as one complex! Thus, SANS allows a unique determination of the structure of the individual components in the complex.

Recent SANS experiments have confirmed that the gene activator protein, cyclic AMP receptor protein (CRP), undergoes a significant structural, or conformational, change in solution upon DNA binding. Furthermore, the regions of the protein that undergo the conformational change contain the binding site for RNA polymerase, which plays a crucial role in the early stages of protein synthesis. This structural change may be necessary in order for CRP to interact with RNA polymerase during this process. Further SANS studies are under way on other protein/DNA complexes that play a role in gene regulation.

Biomimetic Membrane Studies Using Neutron Reflectometry (July 2001)

Structures that serve as models of cell membranes are of fundamental importance in understanding such key biological processes as phospholipid self-assembly, molecular recognition and cell-protein interactions. Recent improvements in neutron reflectometry at the NIST Center for Neutron Research within MSEL, coupled with advances in biomimetic film fabrication in the NIST Biotechnology Division of CSTL, afford enhanced sensitivity for the study of membranes and membrane-protein complexes.

New phase-sensitive measurement techniques and model-independent data analysis methods developed at the NCNR have demonstrated the feasibility of obtaining reliable depth profiles of supported membranes in contact with biologically relevant aqueous environments, achieving subnanometer spatial resolutions.

Using these methods, the depth profile of a biomimetic membrane consisting of a self-assembled alkanethiol monolayer, anchored to a gold film, and a phospholipid layer self-assembled *in-situ* from vesicles in solution has been measured. The results compare well with molecular dynamics simulations. The interaction of the peptide melittin with similar biomimetic films has also been probed, revealing that the small protein penetrates into the phospholipid leaflet of the film and perturbs the underlying alkane layer. Work using these advanced neutron capabilities is underway to study biomimetic films produced on engineered and cushioned surfaces which will enable the investigation of trans-membrane proteins.

Molecular Dynamics Simulations and Neutron Scattering Yield New Insights Into Protein Dynamics (September 2001)

Understanding the process by which a protein efficiently folds to the physiologically active native state is one of the great challenges in biology. Proteins can also form stable, partially folded states that are thought to resemble intermediate states along the protein folding pathway. Recently, a collaboration between the University of Pennsylvania, the University of California at Irvine, and MSEL’s Center for Neutron Research and Polymers Division have used molecular dynamics simulations and quasielastic neutron scattering techniques to elucidate dynamic changes in the protein alpha-lactalbumin for the native state and the partially folded molten globule state.

Molecular dynamics simulations are the ideal complement to neutron scattering because neutrons measure correlation functions that are based on the positions of the atoms as a function of time. For the case of alpha-lactalbumin, the neutron results show that the side-chain protons in the molten globules are significantly more mobile than those in the native protein. Molecular dynamics results, which reproduce the measured quasielastic neutron spectra extremely well, show that the observed dynamic changes arise primarily from the particular region of the protein that forms a beta sheet in the native state and unfolds to a random coil in the molten globule. Thus the spectroscopic results clearly reflect the formation of secondary structures that occur as a protein folds. Moreover, the techniques developed for the comparison of molecular dynamics simulations with neutron spectra are directly applicable to a wide variety of complex materials.

Stresses in Electron Beam Weld Joints of Superalloys (October 2001)

Single crystalline turbine blades are the pinnacle of a decade-long development and refinement of nickel-based superalloys. Because of the considerable investment in manufacturing, electron beam welding with a polycrystalline replacement material is used to repair minor structural damage of failed components of these otherwise poorly weldable materials. While both the fusion zone and the heat affected zone are small, about one millimeter, the cooling rates are high so that very high residual stresses are generated.

In order to study the efficiency of stress relief, scientists from the NIST Center for Neutron Research of MSEL and General Electric have investigated by means of neutron diffraction the residual stress distribution both in the as-welded state and after a heat treatment. The heat treatment includes a solution treatment and subsequent aging. The typical grain size of the polycrystal side of the weld joint was approximately one millimeter which is about the size of the incident neutron beam. Thus, stress measurements could be done only on the single crystal side of the joint.

It was found that the as-welded sample exhibits tensile stresses on the order of the yield stress both parallel and perpendicular to the weld. We have also found evidence for solution partitioning and a substantial level of plastic strain both in the fusion zone and in an approximately half-millimeter wide heat affected zone. Both effects are completely removed after the heat treatment. The heat treatment also removes very effectively and completely the detrimental tensile residual stresses in the extended weld zone. These results are the first on this type of system, in which single-crystal and polycrystalline constituents are joined.

Neutron Methods Link Microstructure to Processing and Performance for Thermal Barrier Coatings (December 2001)

Although coatings are used in the electric utility and aircraft industries to protect advanced gas turbines from increasingly high operating temperatures, there is presently no single industrial technique that can quantify the component void microstructures that control thermal barrier coating performance and reliability. NIST researchers in MSEL’s Ceramics Division have developed advanced small-angle neutron and X-ray scattering methods which, with appropriate models, provide a microstructure characterization for thick, free-standing material. Two innovations now extend these studies to submillimeter-thick coatings *in situ* on the substrate, and suggest that such characterization can provide calibration and validation of the partial information available from other methods.

In near-surface small-angle neutron scattering (NS-SANS), developed partly with the help of Advanced Technology Program Intramural Funds, reflection geometry is used to determine apparent internal void surface area distributions within thermal barrier coatings to typical mean depths of 0.1 mm. The method has been used to study the effects of thermal cycling on an yttria-stabilized zirconia plasma sprayed thermal barrier coatings deposited on a nickel superalloy substrate. The NS-SANS measurement has revealed a marked increase in intra-splat cracking perpendicular to the substrate, arising from thermal mismatch strains between the coating and the substrate. This effect contrasts with a preferential sintering of intra-splat cracks for free-standing deposits and it significantly modifies the properties and performance of thermal barrier coatings subjected to elevated service temperatures.

For 0.3 to 0.4-mm-thick thermal barrier coatings on substrates, microstructures can also be determined using a modified form of ultra-small-angle X-ray scattering, suitable for the study of anisotropic materials. It has been applied to thermal barrier coatings fabricated by plasma spray and by electron-beam plasma-vapor deposition.

By combining conventional SANS studies of free-standing thermal barrier coating microstructures with NS-SANS and SBUSAXS studies of the modifications introduced when the thermal barrier coating is in situ on the substrate, a valuable validation tool is becoming available to support industrial thermal barrier coating design.

A Model System for Scattering Studies of Membrane Proteins (December 2001)

Because of the difficulty in crystallizing membrane proteins, there is considerable interest in identifying systems that mimic biological membranes and facilitate structural studies of inserted proteins. Solutions of lipid-rich mixtures of phospholipids with certain detergents have shown promise in this regard. Over a range of conditions, these mixtures form isolated bilayer fragments that are stabilized by the segregation of the detergent molecules at the edges. The interior of these disk-shaped single-bilayer structures thus provides an environment for guest proteins that is topologically and chemically similar to that of cell membranes. It has also been possible to insert chelated magnetic ions into the bilayer fragments to align the bilayer normals parallel to an applied field, which in turn can be used to orient the fragments, and any inserted proteins, for a scattering experiment.

To assess the potential of using magnetically-doped, mixed lipid bilayers for structural studies of membrane proteins, we have carried out extensive small-angle neutron scattering (SANS) measurements of the morphology, phase behavior, and magnetic alignment of phospholipid detergent mixtures. These data have revealed a previously unrecognized phase at temperatures above 40 °C in which the bilayer fragments coalesce to form extended single-bilayer sheets. In this phase, the sheets readily align in moderate fields. Measurements in the aligned state reveal that the bilayer sheets are not homogeneous but have defects, probably due to perforations lined with the short chain detergent molecules. By reducing the detergent fraction by about 30 percent, we have extended the region of stability of this phase to physiologic temperatures while maintaining its basic structure and degree of alignment.

Protocols for inserting membrane proteins in this, the most promising membrane support system identified so far, are currently being developed to enable SANS measurements of the conformation the proteins have in actual cell membranes.

MATERIALS MANUFACTURING

Advanced Engine Materials

Thermal Conductivity Feature Added to OOF (October 2001)

OOF, an object oriented finite-element code developed to predict macroscopic material properties based on microstructure, has been expanded to include thermal conductivity. The public-domain software, developed by MSEL and ITL researchers in cooperation with MIT, initially addressed calculation of elastic properties. Prediction of thermal conductivity is valuable in many fields and has been the subject of collaborative research with industry focused on the microstructural design of ceramic thermal barrier coatings used in stationary gas turbines and jet engines. The OOF thermal conductivity program is available at www.ctcms.nist.gov/oof/download.

Metals Processing

Increased Accuracy for Particle Temperature Measurement (October 2000)

Scientists in MSEL's Metallurgy Division have obtained emissivity data that make possible more accurate measurements of the temperature of rapidly moving incandescent particles in thermal spray plumes. Thermal spray is used for many purposes, including deposition coatings for protection against heat, corrosion, and wear. However, it is difficult to obtain reproducible results or to determine the best instrument settings for processing new materials. One approach sought by industry is to use instrument control based on measured temperatures and velocities of particles in the spray plume.

The only method currently available to measure the temperatures of such rapidly moving particles (hundreds of meters per second) is two-color pyrometry, which derives a temperature from measurement of the light emitted in two different bands of wavelengths. It is normally assumed, due to lack of any specific knowledge, that the emissivity of the material does not depend on wavelength, so the intensity of the light in the two wavelength bands can be calculated from a standard Planck function. MSEL researchers use a special facility, which uses electrical resistance heating to heat wires and holds the wires at an elevated temperature during optical measurements. The researchers were able to make specific measurements of the wavelength dependence of emissivity of tungsten and molybdenum at temperatures up to those materials' melting points. The measurements allowed MSEL to derive a correction factor for the two-color pyrometry of these materials, which was several hundred degrees at the melting point of tungsten. Additional factors, such as oxidation, which can affect the accuracy of two-color pyrometry, will be the subject of future investigations.

Extended Temperature Range for Calibration of Two-Color Pyrometers (August 2001)

Properties of metallic and ceramic coatings produced by the thermal spray process depend strongly on processing conditions. Two-color pyrometry is the most common technique used to determine particle and substrate temperatures, but incorrect calibration procedures can result in significant errors. One error source of is the use of the radiance temperature rather than the absolute temperature to calibrate the pyrometer. The radiance temperature of a test surface is equivalent to the temperature of a perfectly radiating surface (e.g. blackbody, $\varepsilon=1$) with the same radiant intensity as the test surface at a specified wavelength. Tungsten ribbon lamps, the most readily available temperature standards, are usually supplied with calibrations to radiance temperature since they are normally intended for calibrating single-color pyrometers, where radiance temperature is appropriate. Another error occurs if the deviation of tungsten from gray body behavior (wavelength independent radiance) goes uncorrected. In addition to these errors, extrapolation beyond the range of the NIST calibrated tungsten ribbon lamps, will further degrade the accuracy of these temperature measurements.

Researchers in the MSEL's Metallurgy Division have developed calibration procedures for two-color pyrometers that improve the accuracy of thermal spray particle temperature measurements. The errors associated with the use of radiance temperature rather than true temperature in calibrations were quantified, and the relative accuracy of determining true temperature from literature emissivity data versus direct measurement are investigated by comparing both corrections to a blackbody calibration. Errors associated with the deviation of tungsten from gray body behavior were also investigated in this manner. In addition, the calibration range has been extended beyond that which can be achieved with lamp standards to the melting point of tungsten using facilities in the NIST's Subsecond Thermophysics Laboratory. More accurate particle temperature data will lead to an improved ability to predict coating characteristics from spray processing conditions.

High Nitrogen Stainless Steel Alloys Provide New Opportunities (January 2002)

During a project on the development of sensors for the powder metallurgy industry, the MSEL Metallurgy Division has developed a technique for production of nitrogenated stainless steel alloys with enhanced corrosion and mechanical properties. Discussions with metal powder producers are underway to develop commercial powder metallurgy alloys using the NIST process that will find applications in biomedical implant devices, light-weight armor plate, and other demanding environments. NIST developed this technique through work on a model for prediction of nitrogen solubility and microstructure in modified 300 series stainless steel alloys.

The new powder metallurgy nitrogenated stainless steel alloys are single phase (austenite) with no tendency to form the embrittling nitride and sigma phase compounds often found in high nitrogenated stainless steels. The unique microstructure results in consolidated parts with superior corrosion and mechanical properties compared to commercially available wrought alloys, and reduced costs compared to other powder metallurgy nitrogenated stainless steel alloys. Scientists Frank Biancaniello, Rodney Jiggetts, and Steve Ridder were awarded U.S. Patent 6,168,755 for the development.

FUNCTIONAL MATERIALS

Materials for Microelectronics

New Texture Measurement Software Now Available on MSEL Web (October 2000)

Many components and devices are fabricated from materials that have a preferred crystallographic orientation or texture. The properties and performance of these components and devices can be highly dependent upon the texture. For example, the remanent polarization in $PbZr_xTi_{1-x}O_3$ films used in non-volatile memory devices is orientation-dependent so the ability to switch domains in the devices during a writing operation is strongly influenced by the texture of the film. To optimize the development of textured materials it is desirable to quantify the effects of texture on properties, which requires accurate measurement of the texture. The specialized equipment typically used for texture measurements is not routinely available in most laboratories. MSEL has developed accurate techniques that use commonly available equipment for measuring fiber texture in thin film and bulk materials. The measurement protocol, as well as the TexturePlus software needed to correct and analyze the resulting data, are available on the web at www.ceramics.nist.gov/webbook/TexturePlus/texture.htm. To date, the techniques have been used to measure texture in thin films of $Ba_{1-x}Sr_xTiO_3$, $PbZr_xTi_{1-x}O_3$ and Cu as well as bulk samples of alumina and silicon nitride.

Database on Lead-Free Solders (November 2000)

MSEL's Materials Reliability Division is working with the Metallurgy Division, the Colorado School of Mines, and the National Electronics Manufacturing Initiative (NEMI) to expand a database on the properties of lead-free solders. With product cycle time being slashed to keep up with consumer demand and competitive pressure, new electronic products are going directly from computer-aided design to full-scale production. The worldwide movement in the electronics industry to replace lead-tin eutectic solders with lead-free solders creates a need for critical data on the industry's new lead-free solder compositions for these design and reliability models. The team is working with the NEMI Lead-free Alloy Task Group to gather existing physical and mechanical property data that have been developed by researchers around the world into a single database. In addition, the team is working with NEMI to develop a list of missing high-priority data, with the list serving as a roadmap for research in lead-free solders. NIST and NEMI are planning to host a joint national workshop on these issues. The most recent version of the database is posted on the Materials Reliability Website at: http://www.boulder.nist.gov/div853/eudora="autourl"http://www.boulder.nist.gov/div853/. The team plans to add additional data and to critically evaluate more of the existing data each month.

Electrodeposited Pb-Free Solder and Whisker Prevention (February 2001)

A technology important to electronics manufacturing is the electrodeposition of Sn-based protective coatings to guarantee solderability. It has been known for many years that the use of pure Sn as a protective coating on copper and copper alloys can result in the growth of hair-like Sn crystals known as “whiskers.” These whiskers can be 1 µm to 2 µm in diameter and several millimeters long, and are capable of carrying 10 ma to 20 ma of current. It has also long been known that the addition of Pb to the coating effectively suppresses whisker growth, but, with the advent of Pb-free electronics finishing, the risk of tin whiskers is again a significant concern. With today's finer pitch devices, the whiskers can cause electrical shorts and failure.

Whiskers are generally believed to grow to relieve residual stress in electrodeposited Sn. However, the origin of this stress is not at all clear. In the more than 50 years since the first documented observation of tin whiskers, a fundamental mechanism of tin whisker formation has never been fully elucidated. Without a good understanding of the mechanism of whisker growth, the electronics industry has yet to devise a good test for determining the propensity for coatings to grow whiskers. In the current program, MSEL researchers are focusing their efforts on developing an understanding of whisker formation in pure Sn and Sn-Cu alloy electrodeposits. This study is being carried out within the context of a study of the effect of plating methods on grain size, residual stress and alloy composition, and is expected to indicate plating approaches for prevention of whisker formation.

The MSEL study has revealed seven types (shapes) of tin whiskers that form on matte and bright pure Sn and Sn-Cu alloy coatings. The type is dependent on substrate material, such as rolled annealed Cu, electrodeposited Cu, evaporated Cu, rolled phosphor bronze, rolled brass, and mild steel. However, the study found that Sn whisker growth could be prevented on a substrate/Sn deposit combination known to grow whiskers by depositing a thin (0.1 µm to 2.0 µm) Ni coating on the substrate before deposition of the Sn or Sn-Cu coating. Currently the investigation of whisker formation is focused on intermetallic formation by copper-tin interdiffusion, substrate effects on tin nucleation, and inclusion of organic or inorganic impurities in the tin deposits. Special emphasis is being focused on the measurement of residual stress using X-ray diffraction analysis.

AFM Investigates Nanoscale Elastic Properties (August 2001)

The ever-decreasing length scales in many fields of technology require new non-destructive measurement tools that can cope with submicrometer dimensions. Specifically, the ability to determine mechanical properties on the nanoscale is needed in many applications, particularly in microelectronics. To meet these needs, we are developing measurement tools that exploit the spatial resolution of atomic force microscopy (~10-100 nm). Our approach, called atomic force acoustic microscopy (AFAM), involves vibrating the cantilever at ultrasonic frequencies to excite mechanical resonances. By measuring the resonant frequencies under both free space and surface-coupled conditions, quantitative information about the sample’s elastic properties can be extracted.

With AFAM, we obtained a value of 67 +/- 7 GPa for Young's modulus of a 1 mm aluminum film. This compares favorably with literature values of 67-71 GPa for bulk aluminum, and a value of 68.6 +/- 0.2 GPa obtained on the same film using surface acoustic wave methods. Furthermore, by holding the excitation frequency constant and measuring the cantilever's vibration amplitude as the tip is scanned across the sample, qualitative images can be created. We have obtained preliminary elasticity images of a damascene copper/Si_{O2} dielectric test structure for microelectronics. Such images of relative elasticity may provide valuable information about elastic stiffness variations from one sample region to another.

"Phase Field" Model of Electrodeposition (December 2001)

MSEL metallurgists, in collaboration with ITL, have for the first time applied the phase field method to the modeling of electrochemical processes. This method employs a phase-field variable, a function of position and time which describes whether the material at a certain location is a particular phase, such as liquid or solid. The behavior of this variable is coupled to the relevant transport equations for the material during electrodeposition of metals, such as copper for the wiring in integrated circuits. Interfaces between phases are described by smooth, but highly localized, changes of this variable. This approach avoids the mathematically difficult problem of applying boundary conditions at an interface whose location is part of the unknown solution. The phase field technique has been developed and applied with great success over the last decade, both by MSEL researchers and others around the world. The range of problems addressed includes the time evolution of complex solidification morphologies related to the casting of metals, the behavior of crystalline dislocations under stress, and surface electromigration on metals.

This new model also predicts the behavior of electrical charges at the electrode-electrolyte interface. The resulting relationships between electrostatic potential and surface energy (electrocapillary curves), surface charge, and differential capacitance are completely consistent with the traditional sharp-interface models of electrochemical interfaces. This new phase field method provides advantages over existing sharp-interface models in that details of interfacial behavior can be readily explored on complex morphologies, such as within the narrow trenches used in microelectronic fabrication or the dendrites formed during battery recharging.

Materials for Wireless Communication

Improving Crystal Resonators with New Materials (February 2001)

Accurate time and frequency standards depend critically on crystal resonators made of quartz because this material has extremely low internal dissipation of mechanical energy. This dissipation is measured by the Q of the resonator which is typically about three million for a 5 MHz AT cut quartz device. Achievement of this high a Q value was the result of extensive research in the 1950s into the mechanism of energy loss and the development of techniques to eliminate impurities and to grow more perfect crystals of quartz. Recently, a new class of synthetic crystals based on langasite—a lanthanum-gallium-silicate —and its isomorphs, langanite and langatate, have exhibited properties that could make them useful substitutes for quartz in many applications. However, the Q values are seldom as high as in properly prepared quartz. MSEL's Materials Reliability Division has developed a novel method of measuring the Q of piezoelectric crystals that minimizes energy loss to the surroundings and, hence, can measure the internal dissipation with unusual accuracy. Application of this method at a variety of temperatures and frequencies has exposed several mechanisms of internal loss in the langasite type materials and is being used to guide the development of manufacturing techniques that will insure the consistently high values of Q required for the next generation of crystal resonators.

Dielectric Behavior of Materials for Wireless Communications Predicted from First Principles (June 2001)

Dielectric materials for wireless communications applications must have high dielectric constant, low loss, and temperature stability. For high-power base station resonators, the only ceramic known with the required dielectric properties is $Ba_3ZnTa_2O_9$ (BZT). The drive to find low-cost alternatives to BZT motivates our interest in determining the microscopic origin of useful electronic properties. As part of this effort, MSEL researchers have performed first-principles calculations of the dielectric properties of $CaTiO_3$ (CT) and $CaAl_{½}Nb_{½}O_3$ (CAN). These systems are both components of solid solutions that contain phases with favorable dielectric properties. CT and CAN have similar perovskite-related crystal structures but very different room temperature dielectric constants: e = 170 for CT; e = 27 for CAN. With lattice parameters and space groups as the only experimental inputs, the researchers used density-functional theory methods to compute e for CT and CAN as a function of temperature, and obtained room temperature values of 140 and 25, respectively, in good agreement with experiment. Low-frequency phonons dominate the dielectric properties, and their calculations predict important differences between the properties of the low-frequency phonons in CT and CAN. In CT, frequencies are lower and all cations move in opposition to the oxide ions; in CAN however, frequencies are higher and Al and Nb move with the oxide ions. Their calculations of phonon properties have been verified experimentally by infrared reflectivity measurements. Ultimately, determination of the microscopic origin of dielectric behavior will permit the rational, efficient discovery and development of advanced ceramics needed for next-generation applications.

Materials for Magnetic Data Storage

Pinning Magnetization by a Special Thin-Film Deposition Technique (January 2001)

When materials are deposited onto substrates to make thin films, the usual goal is to produce a smooth deposit. However, recent work in MSEL's Metallurgy Division has shown that rough deposits can have some special advantages. In particular, when the incoming flux of atoms strikes the substrate at an oblique angle, a deposit is formed with a strongly textured surface consisting of parallel ridges and valleys. This structure has some special advantages for the fabrication of magnetic thin-film devices.

In the MSEL work, it was found that a thin layer of tantalum, obliquely deposited, has a textured roughness that can have a strong effect on a magnetic layer deposited on top of it. The textured surface pins the magnetization direction in the magnetic material, producing a magnetic anisotropy. Such pinning of the magnetic direction is needed for the functioning of a special structure known as a spin valve, which is used in modern read heads of computer hard disks. The pinning is strong enough to prevent reversal of the magnetization direction of the magnetic film, and the pinning remains strong at the elevated temperatures that may be encountered during use.

The anisotropy produced by obliquely deposited tantalum thin films has a number of desirable properties: it is strong, it is uniform, and it has good thermal stability. In addition, the system has good corrosion resistance and chemical compatibility. These properties are advantageous, as the increased demand for sensitivity in read heads has led to higher current densities and hotter operating temperatures, and as read heads become smaller to accommodate narrower recorded tracks.

Non-destructive Measurement of Magnetostriction in Thin Films (June 2001)

Thin films of magnetic materials deposited on various substrates are of fundamental importance to the magnetic recording industry as well to the operation of microscale actuators. Their magnetostrictive properties must be tailored to the application and are usually measured by depositing the film on one side of a slender, non-magnetic reed. When an external magnetic field is applied, the bending of the reed yields values for the magnetic field dependence of the magnetostriction coefficient of the film. Drawbacks of this common procedure are that (1) it is destructive in that the reed must be fabricated with specific dimensions, (2) the results are characteristic of the entire film, and (3) the material of the substrate may not be the same as that used in the final application. An ultrasonic technique that can be applied to a local region of the film on any substrate is being developed for application to Combinatorial Libraries of magnetostrictive films. This method employs an ultrasonic wave in the substrate to apply an elastic strain of known wave length and frequency to the film. Since the film is magnetostrictive, it generated a magnetic field above the surface that can be detected by a non-contacting coil held above the film. The magnitude of this field and hence the amplitude of the electrical signal from the coil measures the magnetostrictive coefficient of the film under the coil. An external source of a DC biasing magnetic field allows the magnetic field dependence of the magnetostrictive coefficient to be measured. At present, the ultrasonic wave is introduced by a piezoelectric transducer attached to an edge of the substrate some distance from the sensor coil. In the future, this transducer will be replaced by a coil that uses the film's magnetostriction to generate the ultrasonic wave. Thus, a probe that can be scanned over the surface of a magnetic film on any substrate can be constructed and used to measure local magnetostrictive properties of films on devices.

New Absolute Magnetic Moment Standard Reference Material for the Recording Industry (June 2001)

A new Standard Reference Material for use in calibrating the magnetometers used in the recording industry and research laboratories has been issued. Industry should find this SRM (SRM 762) more useful than the existing SRM (SRM 772a) because its geometry is similar to the sample shapes used for recording tape or hard disk samples, and it will eliminate the need for applying shape corrections for accurate measurements. Because the magnetic properties of metals depend on thermomechanical processing history and geometry as well as purity, the properties of the nickel disks used for this SRM were certified using the absolute magnetometer developed by NIST. The saturation moment of the new SRM (1.75 mAm^2 or 1.75 emu) is about half that of the old SRM which may be advantageous for some magnetometers. The new SRM is certified for applied fields between 280 kA/m and 4000 kA/m (3500 Oe and 50,000 OE) and for temperatures between 280 K and 310 K.

Domain Walls in AF/FM Magnetic Bilayers (November 2001)

The exchange coupling between a ferromagnet (FM) and an antiferromagnet (AF) creates a magnetic bias field on the ferromagnet and thereby controls its magnetization characteristics. Discovered more than 40 years ago, this perplexing phenomenon has been intensely studied in recent years, and has been incorporated in the new high sensitivity computer disk read heads that have enabled multiple-gigabyte hard disks.

Using the NIST-developed magneto-optical indicator film technique, MSEL researchers have observed directly for the first time the antiferromagnet domain walls and the evolution of a special type of hybrid domain wall in exchange-coupled FM/AF bilayers. We accomplished this using special samples demagnetized at high temperature and cooled to room temperature in zero field. In such samples, we discovered the presence of a hybrid domain wall consisting of coincident ferromagnet and antiferromagnet sections. Under an applied magnetic field, the ferromagnet domain wall moves while the antiferromagnet wall remains stationary. In the process, an exchange spring develops that connects the moving ferromagnetic and the stationary antiferromagnetic domain walls.

As a consequence of the winding and unwinding of the exchange spring during the backward and forward magnetization reversals, a shifted hysteresis loop is observed. These results should enable magnetic recording disc manufacturers to prepare more reliable and controlled devices since now they know what magnetic features to control and how to examine them.

Interlayer Magnetic Coupling In Ferromagnetic Semiconductors For Spintronic Applications (January 2002)

Advancements in semiconductor circuitry have revolutionized data processing in recent decades. Simultaneously, developments in magnetic-based media have expanded capabilities for permanent data storage. An emerging technology called spintronics integrates magnetic components with semiconductor devices and has the potential to increase processing power by many orders of magnitude. In the ongoing search for materials combining properties of ferromagnets and semiconductors, researchers have discovered a promising new class of dilute ferromagnetic semiconductors that includes $Ga_xMn_{1-x}As$.

MSEL researchers at the NIST Center for Neutron Research (NCNR) have begun to probe these structures with polarized neutron reflectometry and small-angle neutron scattering to determine the nature and relevant length scales of cooperative magnetic behavior in these materials. Polarized neutron reflectometry is ideally suited to the study of these structures because it provides depth-dependent magnetic profilometry of buried magnetic layers with sub-nanometer resolution. Since the equilibrium Mn solubility in GaAs is low (less than seven percent), the ferromagnetic transition temperature of the homogeneous alloy is limited to 110 K, far below feasible temperatures for device operations.

To stabilize a higher concentration of Mn, researchers at University of California Santa Barbara fabricated digital GaAs/Mn superlattices by molecular beam epitaxy techniques. NCNR and University of Utah researchers have probed digital structures with polarized neutron reflectometry to determine how the interaction between the Mn layers changes as a function of their separation distance. The experiments show that the Mn layers spontaneously align parallel to each other after cooling in zero magnetic field. These early polarized neutron reflectometry measurements provide guidance for fine-tuning the structure to maximize the ferromagnetic order ing temperature as well as to establish other fundamental spintronic properties of these innovative semiconducting materials.

Interface of Materials with Biology

Reference Biomaterial for Orthopedic Research (November 2000)

Reference Material (RM) 8456, an orthopedic grade Ultra High Molecular Weight Polyethylene (UHMWPE), became available in October 2000. RM 8456 is intended primarily for use in mechanical characterization of material properties and laboratory-simulated performance of orthopedic joint replacement implants. The availability of this reference polyethylene is expected to aid in development of improved test methods and materials by providing a benchmark for comparisons. The need for this reference biomaterial was identified at a workshop on reference biomaterials held at NIST and its development was the result of collaboration among a materials supplier, the orthopedic research community, and NIST.

The material used to prepare RM 8456 was donated by Poly Hi Solidur, Inc., MediTECH Division, Fort Wayne, Ind., in a form similar to that from which many orthopedic components are machined: a cylindrical bar with nominal dimensions of 7.62 cm (3 in) in diameter. Reference properties, reported as mean values with their expanded uncertainties, are Young’s modulus, tensile yield strength, tensile ultimate strength, and tensile elongation-to-failure. These properties characterize the bar across the center 5.62 cm (2.21 in) of its diameter and down the entire bar length. Material beyond the central 5.62 cm was found to differ significantly from that within.

Analysis of Dental Composites by Near Infrared Spectroscopy (June 2001)

Collaborative research among the American Dental Association, the University of Colorado, and NIST led to an improved method to analyze dental composites. Vinyl resin based composites are increasingly being used as alternatives to amalgam fillings. The durability and biocompatibility of dental restoratives materials, however, may be affected by the thoroughness to which they polymerize and how much water they will absorb in the oral environment. The collaborative work exploited near infrared (NIR) spectroscopy, which uses clinically relevant sized specimens, to provide information on both vinyl group conversion and water uptake on the same composite specimen. Owing to the nondestructive nature of this analytical technique, these properties can be monitored versus time and aqueous exposure. With NIR spectroscopy, it now becomes possible to assess the influence of the type and amount of filler phase of the composite on conversion and water absorption. In contrast to conventional gravimetric water absorption studies, NIR spectroscopy allows differentiation between free or unbound water and hydrogen-bonded water, thereby aiding in elucidating how water interacted with the polymer network.

Recent studies have extended the use of NIR spectroscopy to monitor the conversion of the oxirane group in new types composites utilizing epoxy resin binders.

Recognition

<u>November 2000</u>

MSEL Metallurgist Elected Fellow of the American Physical Society

Sam Coriell, who retired at the beginning of November 2000, after 38 years at NIST, has for a long time been a national leader in the theoretical analysis of crystal growth and solidification processes. Working with numerous collaborators, Sam studied the factors, including fluid flow, which determine the shape and stability of shape in growing crystals. He was recently elected to fellowship in the American Physical Society. The citation was "For Fundamental contributions to the theory of the interaction between hydrodynamics and morphological instabilities during solidification." The announcement will be published in the March 2001 issue of *APS News*.

NCNR Director Becomes AAAS Fellow

J. Michael Rowe, director of the NIST Center for Neutron Research, has been elected a Fellow of the American Association for the Advancement of Science. Each year since 1874, the Council of the AAAS elects members whose efforts on behalf of the advancement of science or its applications are scientifically or socially distinguished. Rowe is being honored for outstanding leadership of the nation's premier neutron facility for research in physics, chemistry, materials, and biology. Rowe will be formally inducted in San Francisco on Feb. 17, 2001, during the AAAS Fellows Forum, a part of the Association's annual meeting.

<u>January 2001</u>

Wong-Ng Elected a Fellow of the International Centre for Diffraction Data

Winnie Wong-Ng, a staff scientist in the Ceramics Division of MSEL, was recently elected as a Fellow of the International Centre for Diffraction Data. Wong-Ng was honored based upon her long-term, significant contributions to the X-ray powder diffraction data files. Wong-Ng has an international reputation in the field of X-ray diffraction and phase equilibria. She is currently involved in the determination of complex phase diagrams pertinent to high Tc superconducting materials.

Vigliotti Receives Award of Appreciation

Dan Vigliotti of MSEL's Materials Reliability Division has received an Award of Appreciation from Committee E28 (Mechanical Testing) of the American Society for Testing and Materials. This award was given for outstanding service and participation in the development for standards for impact testing within ASTM. He also serves as the chairman of ASTM Task Group E28.07.02 on Oversight of Standard E 23, the Standard Test Method for Notched Bar Impact Testing of Metallic Materials. Notched bar impact testing uses a swinging hammer to assess the resistance of a material to brittle fracture. The low cost and simple configuration of the test have made it a common requirement in codes for critical structures such as pressure vessels and bridges. NIST provides standard reference materials (SRMs) to machine owners and to independent calibration services, then evaluates the results of tests of these specimens on their impact machines. Using the test results, Dan Vigliotti, as coordinator of the NIST Charpy Impact Verification Program, works with the machine owners to bring their machines into compliance with ASTM Standard E 23. This activity requires interaction with over 1000 customers each year.

April 2001

MSEL Researchers Win Award for Paper

Chris McCowan and Tom Siewert of MSEL's Materials Reliability Division have received the 2001 Wasserman Memorial Award from the American Welding Society. This award consists of a certificate and an honorarium. It is given annually for the best paper published during the past year in the *Welding Journal* on the subject of welding, brazing, or thermal spraying for maintenance and repair. The award was given for their paper describing development of innovative repair procedures for the castings that cover the dome of the U.S. Capitol. The paper, *Preserving a National Landmark*, published in the November 2000 issue of the *Welding Journal*, describes a procedure to reattach pieces of the outer casting that had fractured due to corrosion damage. The repair was complicated by the very high levels of phosphorus (about 0.15 mass percent) in the castings, leading to cracking when conventional repair techniques were attempted. The team worked with welding experts from Alloy Rods Corp. and the Office of the Architect of the Capitol

July 2001

Award Recipients in the Ceramics Division

Three of MSEL's Ceramics Division staff members have recently been honored by scientific societies. Winnie Wong-Ng and George Quinn were honored as fellows of the American Ceramic Society. Dr. Wong-Ng, with an extensive record in X-ray diffraction and phase equilibria of ceramic materials was recognized for her "notable contributions to the ceramic arts and sciences." Quinn was recognized for his "notable contributions to the understanding of mechanical properties and leadership in the development of standards for advanced ceramics." Said Jahanmir was selected by the ASME as the 2001 recipient of the Mayo D. Hersey Award for "distinguished and widely recognized research contributions in the field of tribology, particularly in wear mechanisms, boundary lubrication and ceramic machining."

December 2001

Robert Roth Receives Wilhelm R. Buessem Award

On Oct. 16, Robert Roth, retired MSEL scientist, received the Wilhelm R. Buessem Award from the Center for Dielectric Studies at Pennsylvania State University. Roth received the award in recognition of the significant impact of his long and distinguished career in the field of ferroelectric and dielectric ceramics. Roth, trained as a geologist at Coe College and the University of Illinois, and joined the National Bureau of Standards in 1951.

His second publication (out of some two hundred), co-authored with B. Jaffe and S. Marzullo in 1954, was entitled “Piezoelectric Properties of Lead Zirconate-Lead Titanate Solid Solution Ceramics.” The ceramic system described in this paper, now known as “PZT,” is one of the most important advanced electronic ceramic materials known to this day, with applications as diverse as providing the spark in charcoal grills and gas stoves to positioning mirrors in giant telescopes.

For this technical achievement, Roth received the U.S. Department of Commerce Silver Medal in 1962. He is the recipient of numerous other awards including the Department of Commerce Gold Medal, and the Sosman Award from the American Ceramic Society. Roth retired in 1991 after 40 years of federal service.

January 2002

Researcher Wins Award For Metallography

Chris McCowan of the Materials Reliability Division in MSEL has received an award for his study of impact induced annealing. A poster summarizing the work (coauthored by C.R. Brooks of the University of Tennessee) won first place in the color microscopy category in the 2001 poster competition of the International Metallographic Society. This annual competition includes metallography from around the world, and is organized into 12 classes based on microscopy and other factors. The work is judged primarily on technical content and sample preparation, within a format that allows the micrographs to tell the story.

January 2002

Eric K. Lin Receives Presidential Early Career Award for Scientists and Engineers

The White House has named Eric K. Lin of the Materials Science and Engineering Laboratory as one of this year's recipients of the Presidential Early Career Award for Scientists and Engineers (PECASE). These prestigious awards recognize some of the finest scientists and engineers who, while early in their research careers, show exceptional potential for leadership at the frontiers of science and engineering. The Presidential Award is the highest honor bestowed by the U.S. government to its scientists and engineers. The award to Dr. Lin was given for his work in chain mobility of polymer molecules near solid interfaces and his contributions to the development of a new methodology to characterize the structure and properties of nanoporous thin films for use in next-generation integrated circuits.

Eric Lin joined NIST in 1996 as an NRC postdoctoral fellow in the Polymers Division, after receiving his Ph.D. in Chemical Engineering from Stanford University. He is now leading a research team working with US industry in the area of lithographic polymers, enabling materials for the fabrication of faster and cheaper computer chips. Dr. Lin is a member of the American Physical Society, American Institute of Chemical Engineers, and the Materials Research Society.

Interactions and Workshops Featured in NIST Highlights

<u>October 2000</u>

Workshop Concludes That Reference Data and Reference Materials Are Needed for Biomaterials

Needs for reference data and biomaterials were identified at a NIST organized workshop held July 27, 2000. The 65 registrants from industry, National Institutes of Health, Food and Drug Administration, and academia joined with NIST staff in six concurrent breakout sessions that considered reference data needs in orthopaedic, cardiovascular, ophthalmologic, tissue-engineered, dental, and general biomaterials. Although the workshop was organized with the focus on reference data for biomaterials, an over-arching conclusion from participants was the complementary role of reference data and reference biomaterials in facilitating deployment of new health-care delivery devices and for the development of national and international standards. Owing to the rapid pace of innovation, the timely availability of reference data and reference biomaterials was deemed more critical to progress than completeness in most situations. In general, data on properties of interest included mechanical properties, surface and bulk physical and chemical properties, as well as biological and clinical responses to materials.

In addition to reference data, reference biomaterials for polymers, monomers, alloys, composites and ceramics were identified. The participants agreed that follow-up meetings should be held with the various constituencies for the purpose of exploring the formation of alliances to help meet the needs recognized in the workshop.

<u>February 2001</u>

NIST/FIZ-Karlsruhe Partnership to Improve the Inorganic Crystal Structure Database for Materials Research

The materials research community uses crystallographic data models on a daily basis to visualize, explain, and predict the behavior of chemicals and materials. Access to reliable information on the structure of crystalline materials helps researchers concentrate experimental work in directions that optimize the discovery process. Recently, the Fachinformationszentrum (FIZ) Karlsruhe and NIST have agreed to develop and enhance the Inorganic Crystal Structure Database (ICSD) on a continuing basis. The ICSD is a comprehensive collection of crystal structure data of inorganic compounds containing more than 50,000 entries and covering the literature from 1915 through the present. Work under the FIZ/NIST partnership has focused on modernizing and evaluating the ICSD. The database structure has been completely re-designed, the data converted and loaded into a relational database management system, and scientific application modules were created to analyze the results of database searches. A major effort has been made to create a Windows-based PC product for the ICSD, which is nearing completion. This product is tabular in design, allows for searching in five general categories of Chemistry, Crystal Data, Reduced Cell, Symmetry, and Reference Data, and includes enhanced features for the characterization of materials based on lattice and chemistry search modules, and three-dimensional visualization and powder pattern simulation of inorganic structures.

March 2001

Alliances Formed in Nanotribology for Magnetic Data Storage Technology

As the spacing (distance from the head to the middle of the magnetic layer) in magnetic hard disk storage systems decreases in order to increase the data storage density, head disk collisions become inevitable. Friction at the interface at the time of these collisions often controls the extent of damage to the disk. The measurement of friction and wear (nanotribology) of the head disk interface requires the development of new test procedures.

MSEL's Surface Properties Group has signed research agreements with the University of California at San Diego (UCSD) and Data Storage Institute in Singapore, and a cooperative research agreement with Pennzoil. These research alliances provide additional equipment, instrumentation, and expertise to allow NIST to achieve program objectives.

UCSD is providing the expertise and equipment in measuring contact forces at a head disk interface. UCSD also has extensive experience in conducting long-term durability simulation of disk coatings. The Data Storage Institute has commercial scale equipment housed in a clean room environment for film thickness measurement, micro-buffing, micro-polishing instrumentation of disks. Pennzoil has donated research equipment and support for postdoctoral fellows to explore the fundamentals of how a surface can be protected by a monomolecular layer in the face of increasingly severe impacts.

Working with these partners, NIST researchers have developed the fundamental guidelines of how a mono-layer film should be designed to achieve a certain level of shear resistance. Molecular weight, surface mobility, surface bonding characteristics have been shown to be important. Mixed molecular assemblies at a nanometer level have been shown to be feasible by controlling the deposition and surface reaction steps sequentially. This knowledge paves the way for using such monolayers to control surface properties of materials in MEMs, sensors, and actuators.

NIST Hosts Workshop on Thermal Spray Process Reliability

Thermal spray is used to deposit metals and ceramics onto substrates for a wide range of applications. Representatives from industry, universities, and national laboratories took part in a NIST workshop on Jan. 8-9, 2001, to discuss the role of sensors and diagnostics in improving the reliability of thermal spray processes.

In this workshop, scientists from MSEL's Metallurgy Division presented their work on process sensors, which had been carried out in response to needs identified in earlier workshops and conferences. The NIST work emphasizes issues of process stability, sensor calibration, and substrate characterization. Many process stability problems arise from long- and short-term variations in the temperature and velocity of particles in the thermal spray plume: sensors developed in the NIST work are revealing the magnitude and origin of some of these variations. Calibration of the non-contact sensors used to measure temperatures of particles and substrates requires knowledge of the material emissivity, and the NIST work showed how reliable emissivity data can eliminate a significant systematic error that results from the frequently-used "gray body" assumption. In the area of substrate characterization, non-contact sensors for surface topography and temperature are under development.

Speakers from the thermal spray community described some of the factors that make it difficult to obtain reliable and reproducible deposits and some of the sensor needs that would help to overcome these problems. Among the issues cited as important by workshop participants were the need for sensors to be simple, rugged, and reliable for use in industrial environments, the need for more reproducible powder feed stock and thus the need to combine NIST expertise in powder production with thermal spray expertise, the need to sense deposit and substrate characteristics, especially deposit thickness, and the need to correlate improved sensor performance to improved product performance.

The workshop results are being used to refine the direction of the NIST projects and to build working collaborations with the thermal spray industry.

May 2001

NIST Joins Industry Team to Accelerate Use of Lightweight Materials in Automobiles

The biggest bottleneck in bringing a new car to market is the time required to take the final design and make the first successful sheet metal stampings. The ATP Springback Predictability Project (SPP) was a successful project to develop software that accurately predicts the deformation of sheet metal, thus shortening this time and permitting the use of lightweight materials like high strength steel and aluminum. The SPP ended last autumn after 5 years of ATP support. The consortium of industries found the arrangement to be so effective that they have funded a continuation of the effort to solve related problems not addressed by the original ATP project. In an internal poll, these companies identified NIST involvement in large-scale metrology and metal plasticity research to be a key element in the new effort. Staff from MSEL's Metallurgy Division, the Center for Neutron Research, and MEL's Large-scale Coordinate Measurement Group have begun attending monthly meetings in Detroit to better address the industrial need. NIST staff are scheduled to make presentations at the first technical meeting of this project in June.

On a related theme, the Partnership for a New Generation of Vehicles (PNGV) recently started industrial projects on warm forming of aluminum and agile, flexible binders for metal stamping. The steering committees for these efforts have identified ongoing research in metal forming and plasticity in the Metallurgy Division as important to attaining their goals in a timely fashion. The details of NIST's collaboration are being worked out.

Centennial Celebration Sessions at the Spring Meeting of ASNT

Two special sessions of technical papers celebrating the NIST Centennial were organized by George Alers of MSEL's Materials Reliability Division at the request of the American Society for Nondestructive Testing (ASNT). They were presented at the annual spring meeting of the society held in Denver, Colo., March 26-29, 2001. Entitled "The NIST Contributions to NDE," the papers covered historical retrospectives as well as summaries of current research in the field of non-destructive evaluation.

At the beginning of the first session, the executive secretary of the society presented Leslie Smith, chairman of the NIST Centennial Committee, the ASNT Eagle Award "... in recognition of NIST's contributions in keeping US technology at the leading edge for 100 years—1901-2001." The award itself is a handsome trophy, which will be on display in the lobby of the NIST Boulder Laboratories, where much of the nondestructive testing research is being carried out.

Polymers Division Celebrates NIST Centennial with a Special Session at the American Chemical Society Meeting

A symposium entitled "Opportunities and Needs in Polymer Science for Measurement Techniques, Standards, and Future Technologies" was held at the 221st National Meeting of the American Chemical Society in San Diego April 1-5. Organized by MSEL's Polymers Division to celebrate the NIST Centennial, the symposium brought together past and present NIST scientists as well as other distinguished speakers in the field of polymer science. MSEL Director Les Smith gave the opening address on the history of polymer research at what was then the National Bureau of Standards. Early work focused on the processing and properties of natural polymers particularly leather and natural rubber. The first technical session was presided over by former Polymers Division chief Ron Eby and centered on the enduring relationship between neutron scattering and polymer science. The second technical session entitled "New Measurement Techniques" began with an overview of current areas of interest by the present Polymers Division Chief Eric Amis. The talks in this session covered areas of combinatorial methods, optical methods, and the growing field of polymer mass spectrometry as a means to determine a polymer's absolute molecular mass distribution as well as its molecular composition. The final session was entitled "Crystallization, Interfaces, and Aging" and was kicked off by Freddy Khoury of the Polymers Division. Khoury covered polymer crystallization with emphasis on crystal morphologies. This is a topic where NIST made a significant contribution to both the science and technological application of crystalline polymers. Talks in this session covered such diverse areas as polymer-matrix composites, polymer-polymer interfaces, and polymer degradation.

<u>July 2001</u>

NIST Collaborates With NEMI On Standards Project For Lead-Free Solders

Tin-lead (Sn-Pb) solder has been used extensively as an electrodeposited surface finish for component contacts/leads in the electronics industry because such coatings provide excellent solderability, ductility, electrical conductivity and corrosion resistance. The codeposition of Pb and Sn has been found to be effective in retarding Sn whisker growth and hence, has been the industry standard for over 20 years. In the absence of Pb, whiskers tend to grow spontaneously from electrodeposited Sn films, which can lead to electrical short circuits and device failure. Now that lead-free solder alloys have been introduced, electronic manufacturers are seeking a surface finish technology that will prevent Sn whisker growth without the use of Pb.

Researchers in MSEL are working to identify the basic mechanisms of Sn whisker growth by systematically studying correlations between deposit microstructure, whisker formation and electrodeposition parameters. For example, Sn-Cu solder has been mentioned as a possible replacement for Sn-Pb; however the NIST team has recently found that the addition of Cu^{2+} to the Sn plating bath actually increases the probability and the speed at which whiskers form. Gaining a fundamental understanding of the whisker growth mechanism is required to help eliminate the problem and to develop a reliable test method for predicting whisker growth which the microelectronics industry requires. Towards this end, NIST is participating in a new National Electronics Manufacturing Initiative standards development project to help develop a robust test method for predicting whisker growth for industrial surface finish systems.

August 2001

International Workshop on the Technical and Strategic Future of MatML

A workshop was held at NIST on June 26 and 27, 2001, to determine the next steps in the development of MatML, a Materials Markup Language, which will enable efficient transfer of materials data via the World Wide Web. The workshop was organized by Ed Begley, Ceramics Division, and Charles Sturrock, MSEL. Forty individuals from seven countries participated, representing testing machine and instrument manufacturers, materials software companies, auto manufacturers, materials-related professional societies, government agencies, and the academic community. Extensive discussions showed enthusiastic support for the project and strong interest in drawing new parties into the development and trial of MatML. In addition, the discussions inspired additional uses of the markup language, including quality assurance in medical materials. A steering committee was formed to prioritize the opportunities discussed and to identify organizations through which development and maintenance can be coordinated.

Summer School on Methods and Applications of Neutron Spectroscopy

A week-long summer school on Methods and Applications of Neutron Spectroscopy, jointly sponsored by the NIST Center for Neutron Research (NCNR) and the National Science Foundation, was held June 18-22 at the NCNR. The principal purpose of the school was to introduce research students and others to the uses and techniques of neutron spectroscopy. Most of the 32 participants from a variety of North American institutions were graduate and postdoctoral students; we also had an undergraduate student and a professor.

In a radical departure from the format of previous NCNR summer schools, plenary lectures were presented on the first morning only. After lunch the students were divided into four groups of eight, and each group performed an experiment using a different instrument (in one case a pair of instruments). Students learned the scientific motivation for the experiment, how the instrument works, and how to set up a set of measurements.

Students used the following instruments: the Spin Polarized Inelastic Neutron Spectrometer, the Disk Chopper Spectrometer, the High-Flux Backscattering Spectrometer, the Neutron Spin Echo Spectrometer, and the Filter Analyzer Neutron Spectrometer.

In evaluating the school more than 80 percent of the participants described it as “excellent,” and generally high ratings were received in all areas. The lectures and experiment handouts have been placed on the web. A short report about the summer school will appear in *Neutron News*.

September 2001

Monolayer Lubrication: Friction or Fiction?

As the size and spacing in devices shrink, the need to protect the surfaces against friction and adhesion increases. Monomolecular layer surface coatings are increasingly being examined for viability to protect the surface and control the friction between moving parts. This is evident in magnetic data storage technology, MEMs, digital micro-mirror displays, and accelerometers. The durability of such thin films is a key consideration.

Fluorocarbon molecules have been shown to be effective in providing such protection in many devices. As the moving contacts increase in severity, a better film is desired, i.e., one that can withstand higher contact pressures, faster moving speeds, and is capable of self-repairing after contacts. A monolayer with mixed molecules offers potentially many advantages in increasing the different capabilities such as shear resistance, bonding strength, friction control as different molecular structures within the film can impart different functions. However, many new issues such as molecular solubility, orientations on the surface, molecule-molecule compatibility arise. Initial experiments with fluorocarbons were not successful due to lack of solubility of fluorocarbons with other functionalized molecules.

In cooperation with a CRADA partner, Pennzoil Co., scientists in MSEL’s Surface Properties Group have been exploring the concept of mixed-molecule films using a family of novel multiple-alkylated cyclopentanes which have very low vapor pressure and high solubility. Results have shown that molecular weight, functional groups, and side chain length are important factors in organizing a homogeneous monolayer thin film. Mixed-molecule films of up to four molecular structures have been successfully demonstrated on silicon and diamond-like carbon surfaces using a successive vapor deposition and dip-coating technique. Friction and durability measurements results are encouraging.

Success in organizing mixed molecular monolayers opens up the way for different structures to come together for various specialized functions in protecting the surfaces. The scientific issues of how to define homogeneity, molecular compatibility, and solubility remain to be resolved.

November 2001

Cold Neutrons for Biology and Technology

NIST has joined a new NIH-funded bioengineering research partnership, Cold Neutrons for Biology and Technology (CNBT), consisting of investigators from five universities: University of California-Irvine; Pennsylvania State University; Rice University; Duke University; and Carnegie-Mellon University; along with the NIH. The CNBT partnership is committed to the development of advanced neutron scattering instrumentation devoted to basic and applied studies of membranes and macromolecules in membranes and to membrane-based technologies that include studies of protein complexes with relevance to bioengineering. A next-generation advanced neutron diffractometer/reflectometer, fully dedicated to biological membrane studies, has been designed and will be built at the NIST Center for Neutron Research (NCNR) within the next two years. In addition, 10 percent of a state-of-the-art small-angle neutron scattering (SANS) spectrometer, currently operating at the NCNR, will be dedicated to studies of biological membrane systems. New sample environments, optimized for membrane research, will be designed and built under the partnership.

Biological structure studies will be augmented by advanced molecular dynamics methods in order to produce three-dimensional structural models from the neutron diffraction or SANS data. A high-performance computer system will be put in place at the NCNR for this purpose. The CNBT instrumentation and computing facilities will provide new research capabilities not currently available in the United States, leading to important advances in the structural studies of membranes and membrane proteins. These advances are expected to have an impact on a number of bioengineering applications including pharmaceutical design and screening, tissue engineering, and biosensors.

January 2002

International Workshop on the Technical and Strategic Future of MatML

A workshop was held at NIST on June 26 and 27, to determine the next steps in the development of MatML, a Materials Markup Language, which will enable efficient transfer of materials data via the World Wide Web. The workshop was organized by Ed Begley and Charles Sturrock of MSEL. Forty individuals from seven countries participated. Extensive discussions showed enthusiastic support for the project and strong interest in both drawing new parties into the development and trial of MatML (testing machine and instrument manufacturers, for example), as well as additional uses (quality assurance in medical materials manufacture, for example). A steering committee was formed to prioritize the opportunities discussed and to identify organizations through which development and maintenance can be coordinated.

January 2002

Ceramics Division Expands Joint NIST/BAM SRM Collaboration

A new joint research project is now under way between the Ceramics Division and the Bundesanstalt Für Materialforschung und -prüfung (BAM) in Berlin to develop standard or certified reference materials (SRM's/CRM's) for nanomechanical property testing. The work is part of an MSEL/BAM agreement, signed in June, 2000, that lays the groundwork for co-development of reference materials by the two laboratories. Joint SRM/CRM's are already in development in the areas of ceramic powder surface area and ceramic porosity.

The new project focuses on the development and characterization of ceramic film/substrate systems for use in the verification of nanomechanical test instruments in general, and instrumented indentation and surface acoustic wave equipment in particular. Films will characterized by spectroscopic ellipsometry, surface acoustic wave spectroscopy and instrumented indentation testing, and the resulting SRM/CRM's will be certified for elastic modulus and indentation hardness. Both the films and the substrates will be amorphous and isotropic; film thickness will be in the range of 100 nm to 1 μm.