Advanced Manufacturing Processes

The competitiveness of U.S. manufacturers depends on their ability to create new product concepts and to speed the translation from concept to market while decreasing product cost. This is equally true for well-established "commodity" industries, such as automotive and aerospace, and rapidly growing or emerging industries, such as biotechnology and nanotechnology. For existing products, manufacturing is a critical step in reducing product cycle time. Rapid, low-cost development of manufacturing processes is needed to incorporate new materials into complex product shapes with higher performance at equivalent or lower cost as the competing, established materials and methods. For innovative product concepts, new materials with increasing functionality are needed to translate these concepts to reality.

To realize such improvements in materials and manufacturing, MSEL is developing robust measurement methods, models, standards, and materials and process data needed for design, monitoring, and control of manufacturing processes. A growing challenge is being able to design, monitor, and control such materials and manufacturing processes at size scales from nanometers to meters. The Advanced Manufacturing Processes Program focuses on the following high-impact areas:

- Combinatorial, high-throughput methods for materials ranging from thin films and nanocomposites to micro- and macroscale material structures;

- Industry-targeted R&D centered on unique measurement facilities in forming of lightweight metals for automotive applications, polymer processing, and high-speed machining;

- Innovative testbeds for emerging materials, including carbon nanotubes and fuel cells;

- National traceable standards having a major impact on trade, such as hardness standards for metals and process standards for polymers; and

- Innovative, physics-based process modeling tools.

Our research is often conducted in close collaboration with industrial consortia and standards organizations. These collaborations not only ensure the relevance of our research, but also promote rapid transfer of our research to industry for implementation. Three projects focused on Advanced Manufacturing Processes are highlighted below.

NIST Combinatorial Methods Center (NCMC)

The NCMC develops novel high-throughput measurement techniques and combinatorial experimental strategies specifically geared towards materials research.

These tools enable rapid acquisition and analysis of physical and chemical data, thereby accelerating the pace of materials discovery and knowledge generation. By providing measurement infrastructure, standards, and protocols, and expanding existing capabilities relevant to combinatorial approaches, the NCMC lowers barriers to the widespread industrial implementation of this new R&D paradigm. MSEL uses a two-pronged strategy for accelerating the development and implementation of these approaches: an active intramural R&D program that demonstrates the ability of combinatorial methods to produce cutting-edge scientific research and an ambitious outreach activity; key to this effort is the validation of these approaches with respect to traditional "one at a time" experimental strategies.

Forming of Lightweight Metals

Automobile manufacturing is a materials intensive industry that involves about 10 % of the U.S. workforce. In spite of the use of the most advanced, cost-effective technologies, this globally competitive industry has major productivity issues related to measurement science and data. Chief among these is the difficulty of designing stamping dies for sheet metal forming. An ATP-sponsored workshop ("The Road Ahead," June 20–22, 2000) identified production of working die sets as the main obstacle to reducing the time between accepting a new design and actual production of parts. This is also the largest single cost (besides labor) in car production. To benefit from weight savings enabled by new high-strength steels and aluminum alloys, a whole new level of formability measurement methods, models, and data is needed, together with a better understanding of the physics behind metal deformation. MSEL is working with U.S. automakers and their suppliers to fill this need.

Polymer Processing

Polymers have become ubiquitous in the modern economy because of their processability, high functionality, and low cost. However, these materials can exhibit complex and sometimes catastrophic responses to the forces imposed during manufacturing, thereby limiting processing rates and the ability to predict ultimate properties. The focus of our polymer research is on microfluidics and microscale processing, modeling of processing instabilities, and on-line process monitoring of polymers. Our unique extrusion visualization facility combines in-line microscopy and light scattering for the study of polymer blends, extrusion instabilities, and the action of additives. These measurements are carried out in close collaboration with interested industrial partners.

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Advanced Manufacturing Processes

Synchrotron X-ray Measurements in Support of Solid Oxide Fuel Cell Development

Control of solid oxide fuel cell microstructure and electrochemistry close to the electrode–electrolyte-interconnect interfaces is important for optimizing fuel cell performance and lifetime. Quantifying the associated gradients and degradation effects during service life is needed to exploit fully the underlying phenomena governing the material properties. A combination of third-generation x-ray synchrotron measurements at the Advanced Photon Source seeks to address this need.

Andrew J. Allen

S olid oxide fuel cell (SOFC) systems are undergoing rapid development for large-scale power applications. We are addressing the long-term need to improve the control and integrity of the gradient microstructures within the cathode and anode close to, and at, the interfaces with the dense electrolyte layer. At the typical SOFC operating temperatures of 600 °C to 800 °C, this issue can influence the in-service performance degradation and SOFC lifetime during successive thermal cycles. The operative electrochemistry at the electrolyte–electrode interfaces is, itself, ultimately affected by these changes. A combination of third-generation x-ray synchrotron measurements at the Advanced Photon Source seeks to quantify the microstructure and electrochemistry, and establish the relationships between them.
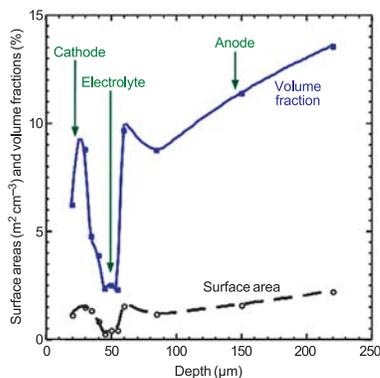
Figure 1: USAXS.

Figure 1 presents spatial variations in the absolute void volume fraction and surface area within a SOFC, with respect to the electrolyte membrane position. The data were obtained by ultrasmall-angle x-ray scattering (USAXS), as were complete void size distributions. A dense yttria-stabilized zirconia (YSZ) electrolyte layer clearly separates the porous cathode (lanthanum strontium manganate or LSM) and anode (Ni/YSZ cermet) layers. An x-ray vertical beam dimension of less than 10 μm

was achieved to provide the needed spatial resolution. Degradation or changes in the measured void variations, as a function of fabrication process or service cycling, would affect both the SOFC electrochemical performance and structural integrity.
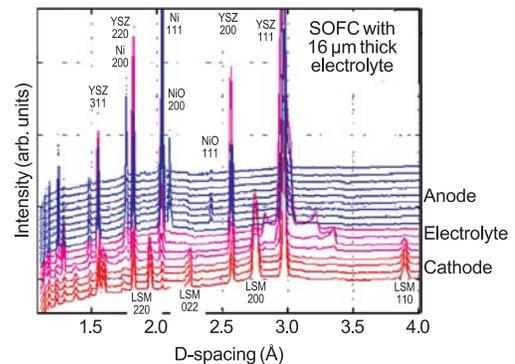
Figure 2: HE-WAXS.

Figure 2 shows high-energy wide angle x-ray scattering (HE-WAXS) measurements of the complete x-ray diffraction pattern at successive positions with respect to the SOFC electrolyte layer. HE-WAXS and corresponding high-energy small-angle x-ray scattering (HE-SAXS) studies of the void surface area variation (calibrated by cross-reference to USAXS) have been made with a 5 μm x-ray beam size. At the 80 keV x-ray energy, both WAXS and SAXS data can be obtained with similar measurement geometries and at identical sample positions. Thus, the spatial variations in void microstructure and phase can be cross-referenced to infer the electrochemical behavior of the electrode microstructures close to the interface with the YSZ electrolyte.

Recently, the electrochemical issues have been explored more directly through measurement of x-ray fluorescent yield (FY) spectra. We have used an *in-situ* heating chamber to study SOFC cathode layers under controlled atmosphere conditions at temperatures close to those encountered in an operating SOFC. By combining the electrochemical data obtained for specific interfaces with knowledge of the SOFC microstructure and phase information above, we seek to facilitate improved SOFC design.

Contributors and Collaborators

Data, Reference Materials, and Measurement Methods

The Ceramics Division has been a vigorous participant in support of NIST's core mission as a Measurement Standards Institute. The Division has made significant contributions to all aspects of standard reference databases, standard reference materials, and standard measurement methods and practices. As may be observed here, the products established by the Division provide a substantial resource spanning a considerable sector of materials metrology.

DATABASES

Crystallography

**NIST principal investigator:
V.L. Karen**

NIST Standard Reference Database 15

NIST/Sandia/ICDD Electron Diffraction Database. Chemical, physical, and crystallographic information for more than 81,500 materials, including minerals, metals, intermetallics, and general inorganic compounds; the database and associated software enable highly selective identification procedures for microscopic and macroscopic crystalline materials. Available for purchase at **http://www.nist.gov/srd/nist15.htm**.

NIST Standard Reference Database 83

NIST Structural Database. Crystallographic and atomic position information for metallic crystalline substances, including alloys, intermetallics and minerals; the database is distributed in an ASCII format, convenient for reading into a variety of database management systems or processing by independent software routines. Available for purchase at **http://www.nist.gov/srd/nist83.htm**.

NIST Standard Reference Database 84

FIZ/NIST Inorganic Crystal Structure Database, Release 2004/1 (February 2004); produced cooperatively by the Fachinformationszentrum Karlsruhe (FIZ) and NIST; a comprehensive collection of full structural crystallography data of inorganic compounds; contains more than 70,000 entries. Available for purchase at **http://www.nist.gov/srd/nist84.htm**.

Phase Equilibria Diagrams

**NIST principal investigator:
T.A. Vanderah**

NIST Standard Reference Database 31

NIST/ACerS Phase Equilibria Diagrams. Produced jointly by NIST and the American Ceramic Society; thirteen regular book volumes, four topical volumes, three annual volumes, and a computerized database on CD ROM; more than 53,000 units have been sold; the current CD contains approximately 20,000 critically evaluated diagrams and 15,000 expert commentaries. (Free demo CD available from NIST.) Available for purchase at **http://www.nist.gov/srd/nist31.htm**.

Materials Properties

**NIST principal investigator:
R.G. Munro**

NIST Standard Reference Database 30

Structural Ceramics Database. Physical, mechanical, and thermal properties; more than 38,000 numeric values. Available online at **http://www.ceramics.nist.gov/srd/scd/scdquery.htm**.

NIST Standard Reference Database 62

High Temperature Superconductors. Physical, mechanical, thermal, and superconducting properties; more than 30,000 numeric values. Available online at **http://www.ceramics.nist.gov/srd/hts/htsquery.htm**.

NIST Property Data Summaries

Focused studies with comprehensive property sets for specific materials and topical studies focused on one property for a wide range of materials. Available as follows:

- Alumina, **http://www.ceramics.nist.gov/srd/summary/scdaos.htm**
- Silicon Carbide, **http://www.ceramics.nist.gov/srd/summary/scdscs.htm**
- Titanium Diboride, **http://www.ceramics.nist.gov/srd/summary/scdtib2.htm**
- Yttrium Barium Copper Oxide, **http://www.ceramics.nist.gov/srd/summary/htsy123.htm**
- Elastic Moduli Data, **http://www.ceramics.nist.gov/srd/summary/emodox00.htm**
- Fracture Toughness Data, **http://www.ceramics.nist.gov/srd/summary/ftmain.htm**
- Fracture Data for Oxide Glasses, **http://www.ceramics.nist.gov/srd/summary/glsmain.htm**

Fractography montage
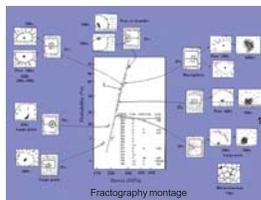
Fractography

NIST principal investigator: G.D. Quinn

Characterization of Fracture Origins

Provides an efficient and consistent methodology to locate and characterize fracture origins in advanced ceramics. May be used in conjunction with ASTM standard C-1322. Available online at **http://www.ceramics.nist.gov/webbook/fracture/fracture.htm**.

STANDARD REFERENCE MATERIALS

SRMs produced by the Ceramics Division are available for purchase at **http://ts.nist.gov/ts/htdocs/230/232/232.htm**.
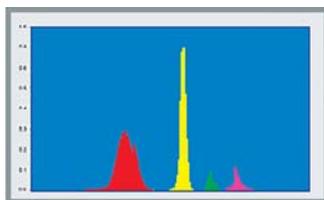
Particle Size Metrology SRMs

NIST principal investigator: J. Kelly

Standard Reference Material 1021

Glass Beads — Particle Size Distribution, a particle size standard for size range 2 μm to 12 μm.

Standard Reference Material 1003c

Glass Beads — Particle Size Distribution, a particle size standard for size range 20 μm to 50 μm.

Standard Reference Material 1004b

Glass Beads — Particle Size Distribution, a particle size standard for size range 40 μm to 150 μm.

Standard Reference Material 1017b

Glass Beads — Particle Size Distribution, a particle size standard for size range 100 μm to 400 μm.

Standard Reference Material 1018b

Glass Beads — Particle Size Distribution, a particle size standard for size range 220 μm to 750 μm.

Standard Reference Material 1019b

Glass Beads — Particle Size Distribution, a particle size standard for size range 750 μm to 2450 μm.

Standard Reference Material 659

Particle Size Distribution for Sedigraph Calibration, a particle size standard for size range 0.2 μm to 10 μm.

Standard Reference Material 8010

Sand for Sieve Analysis.

Standard Reference Material 1982

Zirconia Thermal Spray Powder — Particle Size Distribution, a particle size standard for size range 10 μm to 150 μm.

Standard Reference Material 1984

Thermal Spray Powder — Particle Size Distribution, Tungsten Carbide/Cobalt (Acicular), a particle size standard for size range 9 μm to 30 μm.

Standard Reference Material 1985

Thermal Spray Powder — Particle Size Distribution, Tungsten Carbide/Cobalt (Spheroidal), a particle size standard for size range 18 μm to 55 μm.

Mechanical Properties SRMs

NIST principal investigator: G.D. Quinn

Standard Reference Material 2830
Knoop Hardness of Ceramics.

Standard Reference Material 2831
Vickers Hardness of Ceramics and Hardmetals.

Standard Reference Material 2100
Fracture Toughness of Ceramics.
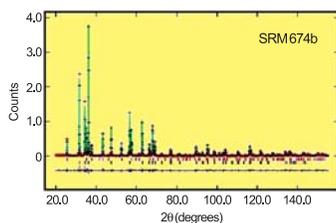
X-Ray Metrology SRMs

NIST principal investigator: J. Cline

Standard Reference Material 640c
Silicon Powder Line Position/Profile SRM, silicon powder, used for calibration of line position and characterization of the instrument profile function, certified with respect to lattice parameter.

Standard Reference Material 660a
LaB_6 Powder Line Position/Profile SRM, LaB_6 powder, used to characterize the instrument profile function and calibrate line position, certified with respect to lattice parameter.

Standard Reference Material 675
Mica Powder Line Position (Low Angle) SRM, synthetic fluorophlogopite mica powder, used to characterize the instrument line position at low two-theta angle, certified with respect to lattice parameter.

Standard Reference Material 1976a
Instrument Response, a sintered alumina plate, certified with respect to lattice parameter and diffraction intensity as a function of two-theta angle (texture), used for general calibration of diffraction equipment, with respect to line position and intensity, via conventional data analysis methods.

Standard Reference Material 676
Alumina Powder for Quantitative Analysis, high purity alumina powder for general quantitative analyses via powder diffraction methods, certified with respect to lattice parameter.

Standard Reference Material 1878a
Quantification of Alpha Quartz, respirable (5 µm) powders, certified with respect to amorphous content, used primarily by the industrial hygiene community for quantification of quartz in airborne dust.

Standard Reference Material 1879a
Quantification of Cristobalite, respirable (5 µm) powders, certified with respect to amorphous content, used primarily by the industrial hygiene community for quantification of cristobalite in airborne dust.

Standard Reference Material 674b
Quantitative Analyses, four powders, Cr_2O_3, CeO_2, TiO_2 and ZnO, allows the user to match the linear attenuation of the standard to that of the unknown, certified for phase purity using neutron time-of-flight diffraction. Supplemental information will include the reference intensity ratio (RIR) or I/Ic value and the lattice parameters as determined with conventional x-ray diffraction.

Standard Reference Material 656
Si_3N_4 Powder for Quantitative Analysis, two samples of high purity silicon nitride powder, one high in the alpha phase while the other is high in the beta phase, for quantitative analyses via powder diffraction methods, certified with respect to phase purity and the alpha to beta phase ratio.

Standard Reference Material 2910
Calcium Hydroxyapatite, calcium hydroxyapatite powder for use in evaluating calcium apatites, primarily in the field of biological research, certified with respect to lattice parameters and phase purity.

Standard Reference Material 1979
Crystallite Size/Line Broadening, CeO_2 and ZnO powder which exhibits diffraction line profile broadening due to crystallite size effects, certified with respect to particle size via XRD line profile analysis, applicable to a range of materials research and industrial interests concerned with crystallite size determination via powder diffraction techniques.

STANDARD TEST METHODS
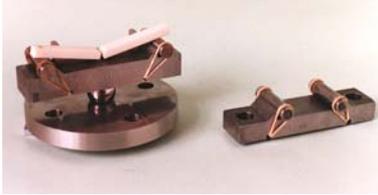
Mechanical Property Test Methods

NIST principal investigator: G.D. Quinn

ASTM C 1161 (2002)
Standard Test Method for Flexural Strength of Advanced Ceramics at Ambient Temperature.

ASTM C 1322 (2002)
Standard Practice for Fractography and Characterization of Fracture Origins in Advanced Ceramics.

ASTM C 1326 (2003)
Standard Practice for Knoop Hardness of Advanced Ceramics.

ASTM C 1327 (2003)
Standard Practice for Vickers Hardness of Advanced Ceramics.

ASTM F 2094 (2001)
Standard Specification for Silicon Nitride Bearing Balls. This standard addresses the basic quality, physical and mechanical properties, and test requirements for silicon nitride balls used for ball bearings and other specialty applications.

ASTM C 1211 (2002)
Standard Test Method for Flexural Strength of Advanced Ceramics at Ambient Temperature.

ISO Standard 14704 (2000)
Fine Ceramics (Advanced Ceramics, Advanced Technical Ceramics) — Test Method for Flexural Strength of Monolithic Ceramics at Room Temperature.

ISO Standard 18756 (2003)
Fine Ceramics (Advanced Ceramics, Advanced Technical Ceramics) — Determination of Fracture Toughness of Monolithic Ceramics at Room Temperature by the Surface Crack in Flexure (SCF) Method.

ISO Standard 17565 (2004)
Fine Ceramics (Advanced Ceramics, Advanced Technical Ceramics) — Test Method for Flexural Strength of Monolithic Ceramics at Elevated Temperature.

Sheet Metal Forming for Automotive Applications: Anelasticity and Springback Prediction

Increased computing power coupled with finite element modeling methods (FEM) has brought springback-compensated die design within reach of the automotive industry. In developing this technology, industry has determined that better measurement methods and an improved understanding of the influence of large plastic strains on the properties and behavior of materials during springback is required. This project seeks to develop the understanding, measurements, and data to meet this need.

Richard E. Ricker

A U.S. Council for Automotive Research (USCAR) Consortium on Springback Prediction has developed finite element springback prediction models to reduce die design and tryout costs. However, these models consistently underpredict springback. Three alloy properties could vary with plastic strain and contribute to prediction errors: (1) elastic modulus, (2) anelastic modulus, and (3) strain-dependent anelastic behavior (reverse creep or plastic hysteresis). Currently, FEM modelers compensate for these errors with arbitrary constants estimated from trials or prior experience. The objectives of this study are to determine the origin of these errors, evaluate relevant measurement methods, and provide materials data that improves FEM springback prediction codes.

In FY 2003, we demonstrated that the large biaxial strains typical of forming can significantly reduce the elastic modulus of Al alloys (18 %) and that texture changes cannot explain this behavior. In FY 2004, finite element models were used to analyze the results of NIST 3-point bend springback measurements. Combining these results with modulus data obtained in FY 2003, it was determined that the strain and elastic modulus variations are too small to measure in these experiments. During FY 2004 these results were
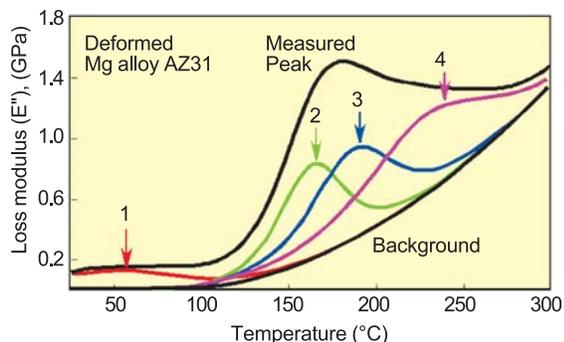
Figure 1: *DMA peak in deformed Mg alloy AZ31.*

presented at industry workshops (USCAR Consortium, Deep Drawing Research Group) and at metallurgy and physics conferences (ASM, TMS, APS).

Also in FY 2004, Mg and Mg alloys were studied to determine how widespread this anomalous modulus behavior is and to gain additional clues as to its origin. Mg is an extremely lightweight HCP metal that would be a prime candidate for automotive applications if not for its poor formability and high chemical reactivity. Biaxial strain experiments did not produce a significant change in the elastic modulus, but the limited ductility prevented measurements at the high strains required to unambiguously reduce the modulus in Al alloys. Dynamic modulus analysis (DMA) found that plastic strain produced a broad peak in the imaginary component of the complex modulus. Previous researchers attributed this peak to grain boundary sliding, but plastic strain and twinning were found to be responsible for this peak which analysis indicated contains 4 subpeaks (Figure 1).
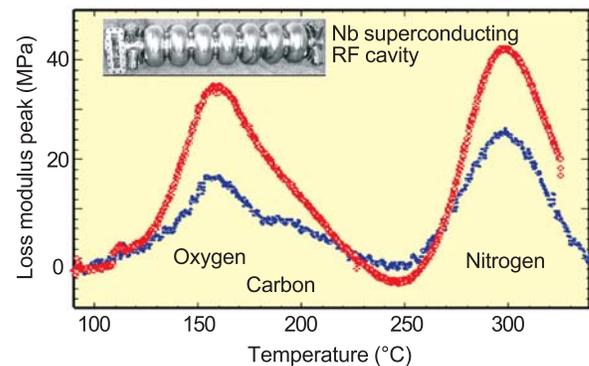
Figure 2: *DMA peaks from two lots of Nb compared to the calculated locations for O, C, and N.*

In a separate study, niobium is a BCC metal that DOE's Jefferson Laboratory (JL) uses to fabricate superconducting structures by stamping and forming operations similar to those used by the automotive industry to form BCC steel. The Jefferson Laboratory has funded NIST to investigate the catastrophic effect of impurities on the forming behavior of high purity Nb. DMA experiments detected variations in the interstitial impurity content of this high purity metal (Figure 2), which will now be correlated with forming behavior.

Contributors and Collaborators

S.W. Banovic, R.J. Fields, L. Ma, D.J. Pitchure (Metallurgy Division, NIST); D. Dayan, A. Munitz (NRC-Negev); V. Luzin (NCNR); G. Myneni (JL); E. Chu (Alcoa); USCAR Springback Consortium (Alcoa, DaimlerChrysler, Ford, GM, LSTC, U.S. Steel)

Microstructural Origins of Surface Roughening and Strain Localizations

The existing data, measurement methods, and basic understanding of metallurgical factors that influence friction, tearing, and surface finish during sheet metal fabrication are insufficient to meet the predictive modeling requirements of the automotive industry. This project addresses these needs by exploring the microstructural origins of the distribution of slip, surface roughening, and strain localization during plastic straining. The primary focus of these investigations is the relationships between the initial material characteristics and the deformation behavior of Al and Fe base sheet materials.

Mark R. Stoudt and Stephen W. Banovic

Replacement of conventional steel sheet by aluminum alloys and high-strength low-alloy steels would significantly reduce automobile weight and increase fuel efficiency. However, wide spread application of these materials by the automotive industry is limited primarily due to formability issues and deficiencies in material databases/constitutive laws affecting finite element modeling. This project examines the underlying structure property relationships associated with formability in an attempt to improve the numerical simulations that predict deformation behavior of materials.
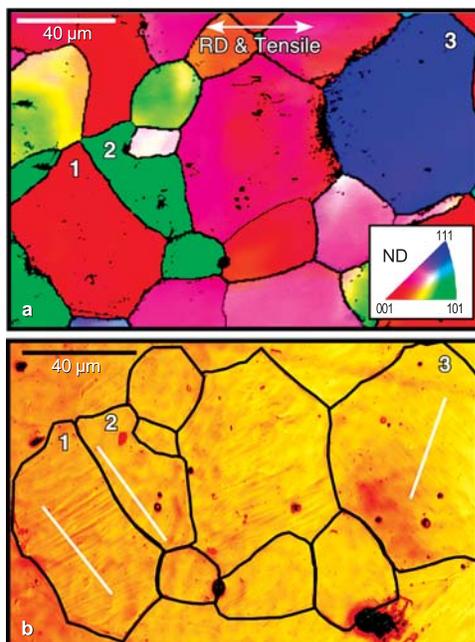
Figure 1: Surface Characterization of 6xxx series aluminum deformed to 0.08 uniaxial strain. a) EBSD generated grain orientation map; b) SLCM surface topograph of same region.

In FY 2004, several experimental techniques were used together to explore the relationships between strain, local crystallographic texture and surface roughening of aluminum alloys. Figure 1a is an electron backscattered diffraction (EBSD) map showing the variations in surface grain orientation on a 6xxx series aluminum sample after applying a uniaxial strain of 0.08. As reflected in the figure inset, the surfaces of grains 1, 2 and 3 have <001>, <101> and <111> orientations, respectively. A 3D topograph of the same region obtained with a scanning laser confocal microscope (SLCM) is shown directly below Figure 1a in Figure 1b. The labels indicate the same grains in both figures. There are clear differences in the slip band structures of the grains. The roughness profiles shown in Figure 2 were acquired from the SLCM data along the white lines in Figure 1b. The different crystallographic orientations in the three grains produced distinctly different roughness characters for the same level of macroscopic uniaxial strain. New statistical analysis techniques are currently being developed to investigate correlations in these data.
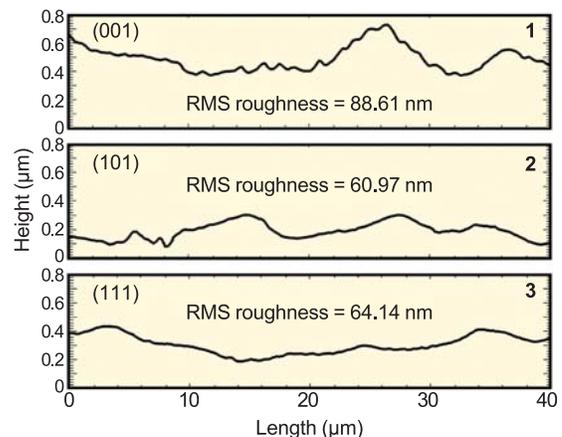
Figure 2: Roughness profiles obtained from the three individual grain orientations shown in Figure 1.

Other topics explored during this fiscal year include: 1) statistical analyses of surface roughness data aimed at determining what roughness measures would be most useful for industry; 2) EBSD/SLCM studies of AlMg binary alloys as a function of strain; and 3) exploratory work on new methods for measuring friction under conditions designed to emulate actual forming operations.

Contributors and Collaborators

Plasticity, Fabrication Processes, and Performance

Predicting the final shape of a part produced using a complex fabrication process can be extremely challenging. This is particularly true when microstructure and residual stresses play significant roles. Understanding the interplay of these factors in industrially important test cases is the goal of this project. Work on this project was completed this fiscal year.

Lyle E. Levine and Hank Prask (856)

Figure 1: *Aluminum parts machined to test shape changes caused by relaxation of residual stresses.*

Diffraction provides a powerful means of very accurately measuring both microstructure and mechanical behavior in a way that provides insight simultaneously into both, and offers particular opportunities for understanding plasticity. This project collaborated with the developers of the NIST Object Oriented Finite Element (OOF) program to implement a plasticity model into OOF and devise critical experimental and computational benchmarks to validate OOF using the NCNR neutron diffractometer to measure residual stress, texture and elastic properties. Conventional X-ray sources were also used where stress states measured at or near surfaces were important for understanding the behavior of materials or to compare with predictions. Synchrotron X-rays were used to deal with subsurface residual stresses in the thin, highly textured samples that result from simulated forming operations. Specifically, the following tasks were part of this project:

- Experimentally validate calculation of the important role played by residual stresses on high-precision machining and forming operations (includes collaborative contributions from MEL, ALCOA and Boeing Corporation);

- Provide technical assistance and validation testing to CTCMS staff engaged in adding 3D plasticity to OOF;

- Develop the ability to characterize near-surface residual stresses; and

- Further develop neutron and synchrotron radiation sources to provide high-resolution data needed to relate microstructure, residual stresses, and their effect on springback.

Overall Project Accomplishments

- **Validation of Distortion Prediction Method:** In 2002, we validated residual stress measurement and prediction methods used by industry. In 2003 and 2004, we used the NCNR to measure residual stress distributions within 7000 series aluminum bars and used high-speed machining to produce test parts. The shapes of the final parts were measured using a contact measuring machine and ALCOA will compare these shapes to their model predictions.

- **Test of OOF:** In FY 2003, textured polycrystalline samples were tested for elastic modulus dependence on texture. These results were compared with predictions using Electron Backscatter Diffraction and OOF.

- **Measurement of residual stresses in standard springback cups in FY 2002:** Measurements were provided for the project on Standard Tests and Data for Sheet Metal Formability. In addition, analyses were done to understand the origin of these stresses.

- **Incorporation of plasticity:** Project personnel worked with CTCMS staff to provide algorithms and techniques for incorporating plasticity into OOF.

Although this project is ending this fiscal year, outgrowths of the work on residual stress measurements of deformed sheet metal and plasticity modeling for OOF continue in other projects.

Contributors and Collaborators

R. Fields, R. deWit (Metallurgy Division, NIST); T. Gnäupel–Herold, V. Luzin (NIST Center for Neutron Research); R. Ivester, R. Polvani (Manufacturing Metrology Division, NIST); D. Bowden (Boeing); E. Chu (ALCOA); R. Reno (University of Maryland)

Standard Tests and Data for Sheet Metal Formability

To meet the PNGV goals for fuel efficiency, the U.S. automotive industry is moving to lighter, high-strength materials for auto bodies. NIST has surveyed industry and found that providing designers with accurate material properties, and methods to incorporate them into finite element models of sheet metal forming dies, is a critical need for the US auto industry. This project seeks to develop new standard tests and metrology to accurately determine sheet metal mechanical response under forming conditions.

Tim Foecke and Mark Iadicola

For the U.S. automotive industry to transition to new materials for formed sheet metal parts, they must be able to mechanically characterize the starting materials under realistic forming conditions, and input this information into die design models. The Metallurgy Division is conducting research to develop two sheet metal formability tests, along with associated metrology, that can be standardized and used by industry.

Springback is the elastic shape change to a part associated with the residual stresses that develop during the stamping process. This shape change complicates assembly and accurate fit-up; thus, the automotive industry has a strong desire to be able to either avoid it, or at least be able to predict its magnitude and design dies to account for it. The proposed test for springback consists of splitting open a ring cut from the sidewall of a deep drawn cup.
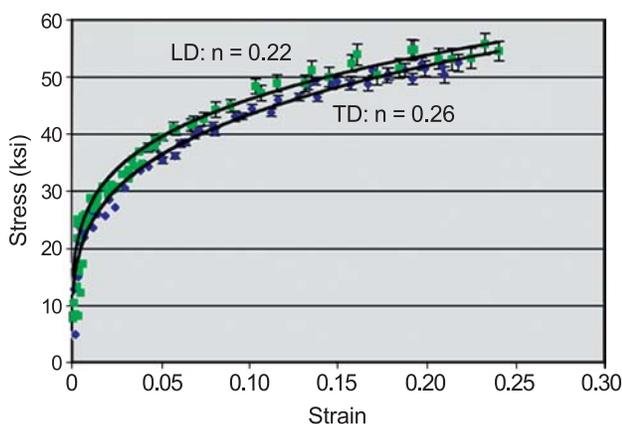
This year, the springback cup test was introduced to ASTM at its national meeting in Florida, leading to industry's proposal to form a new ASTM committee to explore standardization of this test. A crucial step in this process has been taken by identifying several industrial partners that are willing to participate. Additional participants from both the producer and end-user sides of the sheet metal industry are now being sought for this new committee. The initial robustness data set generated at NIST last year forms a solid basis for the design of a round-robin testing matrix to be implemented as part of the standardization process.

Last year, an x-ray stress measuring system was installed on the sheet metal formability station. This unique instrumentation allows for the direct, *in situ* measurement of the stress in a given direction while the sample is under multiaxial load. This year we made significant progress in mapping the multiaxial stress–strain surface for three aluminum sheet alloys of interest to the automotive industry: 5182, 6111 and 6022. Typical data is shown in the Figure 1, where for the first time the biaxial hardening exponent has been measured. In addition, both the flow stress and the hardening exponent, n, were found to differ in the transverse and rolling directions of the sheet. These data will be used by industry to eliminate several assumptions in place that extrapolate estimated biaxial flow behavior based on a series of uniaxial tensile tests. This should lead to more accurate designs and cost savings.

This year, NIST was asked to generate materials property data for simulations of prototype parts as part of the NUMISHEET 2005 conference. In addition, taking advantage of our unique capabilities to measure stress in a forming part, another layer of complexity of the prototype part simulation will require reproducing the measured stresses at points of the part under the forming load.

Plans for FY 2005 involve completing measurement of the multiaxial stress–strain surfaces for the three above-mentioned aluminum alloys, as well as for a series of steel alloys. This new project, in collaboration with modelers at GM, will involve studying how the flow surface evolves with different types and amounts of multiaxial prestrain.

Figure 1: *Balanced biaxial flow stress for 5182 Al alloy in transverse (TD) and rolling (LD) directions.*

Contributors and Collaborators

T. Gnäupel–Herold (NIST Center for Neutron Research); M. Shi (USS); E. Chu (ALCOA); C. Xia (Ford); T. Stoughton, M. Wenner, C.T. Wang (GM); A. Andersson (Volvo); E. Schedin (Avestapolarit)

The NIST Center for Theoretical and Computational Materials Science

The NIST Center for Theoretical and Computational Materials Science was founded in 1994 in order to fulfill its three-fold mission: to investigate important problems in materials theory and modeling with novel computational approaches; to create opportunities for collaboration where CTCMS can make a positive difference by virtue of its structure, focus, and people; and to develop powerful new tools for materials theory and modeling and accelerate their integration into industrial research. The CTCMS supports numerous materials theory and modeling projects both within and externally to the Materials Science and Engineering Laboratory.

James A. Warren and Benjamin P. Burton

The NIST Center for Theoretical and Computational Materials Science (CTCMS) is a research program addressing industry needs for theory and modeling tools for materials design and processing. The CTCMS is a center of expertise in computational materials research that develops tools and techniques and fosters collaborations.

CTCMS integrates ongoing research at various institutions by forming temporary multidisciplinary and multi-institutional research teams as required to attack key materials issues of national importance. The CTCMS has three principal activities, all operating interactively: planning, research, and technology transfer. Workshops are held as the first step in defining technical research areas with significant technological impact, identifying team members, and building the infrastructure for collaborative research. The CTCMS provides infrastructure and support for its members, including an interactive World Wide Web server (**www.ctcms.nist.gov**) and modern computing and workshop facilities.

Current research areas include theory and simulation of a wide range of materials behavior, including phase transformation kinetics and morphology, micromagnetics, composite materials, foams, microstructure and dynamics of disordered and partially ordered materials, complex fluids, materials reliability, reactive wetting, pattern formation, crystal growth, sintering, phase transitions in biological systems, and solidification. Current CTCMS working groups include the following:

- **High-Throughput Analysis of Multicomponent Multiphase Diffusion Data.**

- **Phase Field Modeling Tools:** The phase field method has become one of the most flexible and powerful methods for predicting the evolution of materials microstructure. This effort focuses on the development of both new applications for this method and tools enabling the solution of the complex equations which emerge from these models.

- **Effective Hamiltonian Methods:** Use of fundamental, quantum-mechanical descriptions to derive the properties of matter is the ultimate goal of materials modeling. This effort uses electronic structure calculations to derive the phase stability of alloys.

- **WWW Tools for Scientific Collaboration:** CTCMS is working with information science specialists to develop web-based tools for scientific collaboration.

- **Tools for Neutron Scattering Measurements:** While neutron scattering has become a critical tool for the probing of material structure and properties, interpretation of the results of experiments presents a host of challenges for the scientist. This effort attempts to develop a better theoretical framework for the interpretation of such experiments.

- **Object-oriented finite element modeling of composite materials:** This team of researchers is developing a set of object-oriented finite element modeling tools to improve the characterization and property prediction of composite materials. Public domain software tools are available at **www.ctcms.nist.gov**.

The CTCMS also hosts web pages with resources and tools in the following areas: an interactive, electronic library of Green's function and boundary element solution; accurate, standardized micromagnetics modeling tools; software tools to improve electronic packaging processes; and a tool to compute equilibrium crystal shapes. More detail can be found at **www.ctcms.nist.gov**.

Mechanisms for Collaboration with CTCMS

The CTCMS facilitates numerous interactions between industry, academia, NIST, and other government and national labs to apply materials theory and modeling to solve U.S. industrial problems in materials design and processing. Researchers interested in joining existing efforts or starting new ones are encouraged to contact the CTCMS. The CTCMS participates in the National Research Council postdoctoral fellowship program and hosts short-term and long-term visitors.

Underlying Processes of Plastic Deformation in Metal Alloys

A substantial increase in the use of aluminum alloys and high-strength steels in automobiles would greatly increase fuel efficiency. The primary reason why this has not yet occurred is a lack of accurate deformation models for use in designing the stamping dies. This project is developing a physically based model of plastic deformation using a combination of statistical physics approaches, atomistic modeling and advanced measurement techniques.

Lyle E. Levine

Plastic deformation of metals (as in cold rolling, stamping, drawing, and metal fatigue) is of great importance to industries worldwide, and improvements in the basic technology would have a significant effect on the U.S. economy. Unfortunately, existing constitutive equations cannot accurately predict the material behavior, and many tryout and redesign steps are required. Another related difficulty is in the design of new alloys with improved formability characteristics. Currently, alloy design is done empirically with little understanding of how the various constituents affect the mechanical properties.

Addressing both of these issues, this project is focused on developing constitutive laws based upon the underlying physical processes that produce the observed mechanical behaviors in metal alloys. Such constitutive laws are inherently multi-scale since they must describe phenomena on length scales ranging from the atomistic all the way to the macroscopic stress–strain behavior of bulk material.
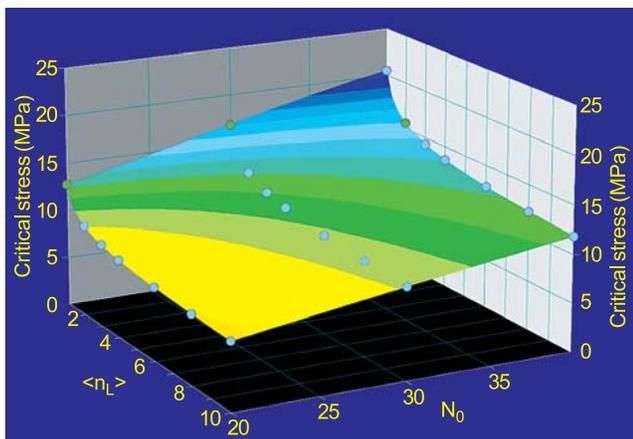
Figure 1: *Universal flow surface (critical surface) for Al alloys at ≈ 15 % strain.*

Since the underlying processes are extremely complex, most of our theory, modeling and experimental efforts over the past several years were concentrated on single-crystal pure Al as a model system. This work culminated in the development of the segment length distribution (SLD) model, that describes how macroscopic deformation arises from the statistical behavior of large numbers of dislocations. The model correctly predicts the flow stress (Figure 1), the linear behavior of stage II hardening, the non-linear hardening in stage III and the development of slip lines and slip bands. The statistical variables, $<n_L>$ and N_0, represent the density of primary dislocations and pinning points, respectively, in the sample. Alloying the Al changes the mechanical properties by affecting these statistical variables. Thus, this critical surface is a *universal* surface for all Al alloys. The next step is to connect the evolution of the statistical variables to the underlying physics for Al alloys using atomistic simulations that accurately incorporate the effects of alloy chemistry.

Quantum-mechanics based (*ab initio*) modeling is required to adequately describe the effects of chemistry in atomistic simulations. Unfortunately, such simulations are extremely CPU intensive and thereby limited to a few hundred atoms. Atomistic modeling using classical potentials can handle much larger systems but fails for large bond distortions and chemistry effects. A ground-breaking approach for directly coupling the two methods has been developed that allows the use of large-scale atomistic simulations with simple classical potentials while limiting the more accurate *ab initio* approaches to critical regions. Preliminary calculations of vacancy energies near dislocations are now underway.

Washington State University (WSU) is conducting experimental validation tests of the SLD model using chemi- and photo-emission techniques to study the time dependence of new surface production during deformation. NIST researchers designed the UHV tensile stage and single-crystal growth facilities, and WSU paid for the fabrication with funding from DOE.

Finally, NIST researchers are supporting the development of supporting science by serving on the executive committee of the international conference "Dislocations 2004" and coorganizing symposia at the Fall 2004 MRS meeting and at "Plasticity 2005."

Contributors and Collaborators

High Speed Machining

U.S. industry annually spends $200 billion on the machining of metal parts, and potential cost savings are a driver towards high-speed machining. Traditional knowledge-based approaches have not been effective in improving the efficiency of this rapidly developing field: One recent study showed that industry chose the correct machining parameters less than half of the time. Through this project, NIST will provide measurement capabilities, materials data, and assessment of constitutive laws and deformation models, which will provide users with a capability of producing a first part correct.

Carelyn E. Campbell

To improve the efficiency of high-speed machining and tooling, industry has employed finite element modeling (FEM) to predict correct tooling and machining parameters. However, FEM has had limited success as much of the needed material property data for high speed machining processes, which involve large strains (>>1), high-strain rates (up to 10^6 s^{-1}), and high-heating rates (greater than 10^5 °C/s), is insufficient. This project emphasizes two complementary areas: (1) the development of fundamental data on dynamic material behavior at high strain and heating rates and the assessment of the constitutive laws used to model this behavior; (2) the modeling and characterization of the microstructural changes that occur during the rapid deformation and rapid heating in real machining operations. Residual stresses, responsible for part distortion after machining, are being measured at the NIST Center for Neutron Research.

The first research effort is focused on obtaining the materials data and assessing whether currently used constitutive laws are appropriate. A dynamic material testing facility using a pulse-heated Kolsky bar has been developed at NIST and is being used to measure dynamic stress–strain data at high-strain rates (approximately 500 s^{-1} to 10^5 s^{-1}) with heating rates ranging from 10^3 Ks^{-1} to 1 Ks^{-1}. Measurements on 1045 steel showed significant differences in the stress–strain behavior depending on the heating and strain rates (Figure 1). The two microstructures shown in Figure 1 demonstrate the observed microstructural differences resulting from different heating rates. Test 504 was rapidly heated and quenched, leaving no time for the pearlite to dissolve and reform. In contrast, test 509 was heated, held at temperature for 1.4 s, then quenched, leaving enough

time for the pearlite to dissolve and then re-crystallize during quenching, producing a finer grain size.

These results demonstrated that the non-time dependent constitutive relationships used by industry to describe the stress–strain data for machining simulations are not correct. A time-dependence must be included in the constitutive relationship to correctly model the material behavior during high-speed machining. Using the dynamic material property data collected using the pulse-heated Kolsky bar, time-dependent constitutive laws will be developed and then tested in machining simulations.
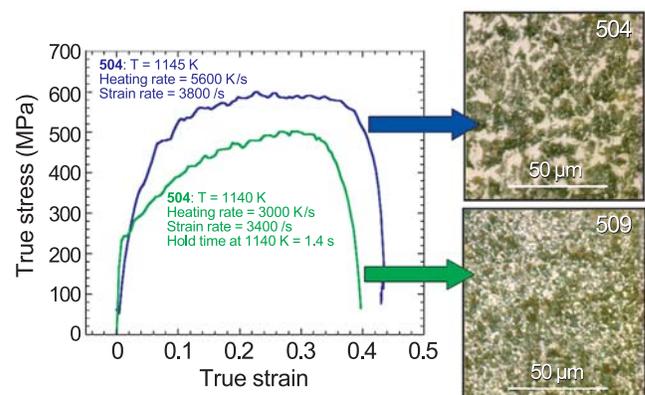
Figure 1: The effect of various heating and strain rates on both the stress–strain behavior and the microstructure of 1045 steel.

The second area of research focuses on characterizing and modeling microstructural changes in the deformation/hot zone of aluminum alloys during machining. Transmission electron microscopy (TEM) correlated with optical microscopy of the chip has revealed bands of re-crystallized grains. The work surface is being characterized using microhardness measurements, TEM, optical microscopy and residual stress measurements. A model based on these microstructural characterizations and temperature *vs.* time data from thermal images will be used as input to a microstructure model. The microstructure model, along with the time-dependent constitutive relationship, will be implemented into a finite element code for machining simulation.

Contributors and Collaborators

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Mechanisms for Delivery of Thermodynamic and Kinetic Data

The availability of reliable materials data is the key to successful design of new materials and manufacturing processes. Many commercial processes are controlled by the thermodynamic and diffusion properties of the material. Thermodynamic and diffusion mobility databases provide an efficient method of storing the wealth of these data, and software tools allow the user to efficiently retrieve the needed information.

Ursula R. Kattner and Carelyn E. Campbell

The complexity of traditional thermodynamics and diffusion kinetics prevented their direct application to the design of complex materials and processes in the past. By the same token, graphical representation of multicomponent systems is too complex, and storage of every single datum is inefficient due to the enormous amount of data. However, mathematical functions that represent thermodynamic and diffusion properties of the phases permit efficient storage. Since these functions are based on physical models, they further provide the power of extrapolation of binary and ternary systems to higher order systems. Software then allows calculation of the desired quantities. This approach is called the CALPHAD methodology. Unfortunately, previous software was tailored to be efficient for expert users and was difficult for the occasional, less-experienced user.

The databases and software developed in this project are designed to provide users with simple tools to retrieve and disseminate information needed for efficient materials and process design.
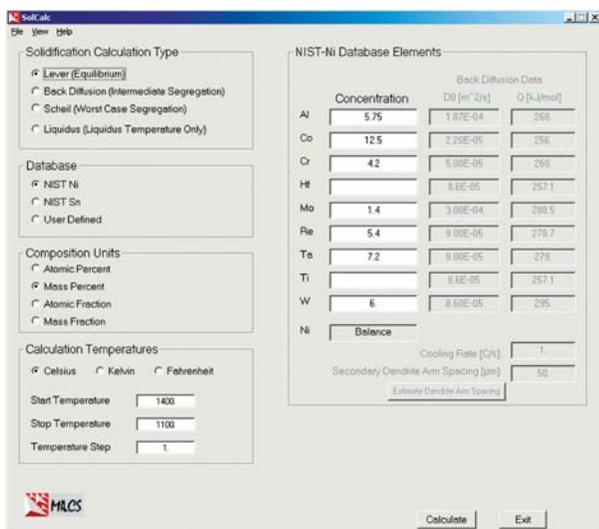
Figure 1: Graphical user interface for solidification calculations.

A modern, user-friendly front end for user input has been developed for solidification calculations (Figure 1). The results of the calculation are delivered to the user in graphical as well as in tabular form. This program is bundled with the NIST superalloy and solder thermodynamic databases, but has the capability to work with user-supplied databases as well. Results can be used with a Mathematica script for DTA analysis simulation. The software, databases and scripts are available on the Metallurgy Division website (**www.metallurgy.nist.gov**).
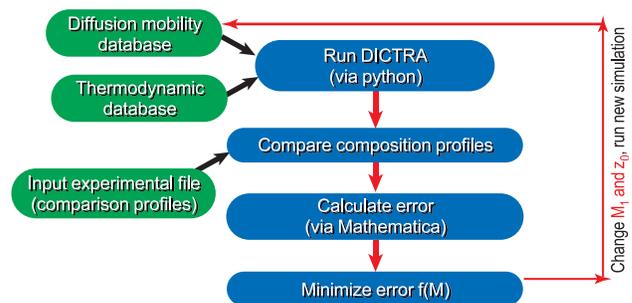
Figure 2: Schematic of an optimization scheme to allow direct input of diffusion couple composition profiles.

Multicomponent, multiphase diffusion couples can be simulated using NIST thermodynamic and diffusion mobility databases, and experimental and calculated composition profiles can be compared. However, the complexity of such couples prevents experimental diffusion coefficients from being easily extracted. Current work focuses on methods to allow experimental composition profiles to be directly inputted into a data assessment process, so the composition profiles can be directly related to the diffusion mobility parameters stored in the database (Figure 2).

Interactions developed through the "High Throughput Analysis of Multicomponent Multiphase Diffusion" workshop series have led to several software codes aimed to improve the analysis of multicomponent diffusion couples based on combinatorial libraries. These codes and other resources are listed on the group's website (**www.ctcms.nist.gov**).

Work continues to convert the NIST Diffusion Data Center into an electronic searchable form. A preliminary version should be available by December 2004.

Contributors and Collaborators

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Phase Field Modeling of Materials Systems: Simulation of Polycrystalline Growth

Many properties of structural and functional materials depend on the distribution of composition, phases, grain orientations, internal surface stresses, and microstructure. These structures span length scales from nanometers to meters. Predictive models are needed to reduce the enormous costs and development times involved in designing and inserting new materials into products. Phase field models of solidification, coupled to stress, grain orientation, and solute and vacancy dynamics are being developed to address these needs.

James A. Warren

Modeling of microstructures produced by solidification, grain evolution, and stress, as well as other processes, involves mathematical solution of equations for heat flow, fluid flow, current flow and/or solute diffusion. Boundary conditions on external surfaces reflect the macroscopic processing conditions, while boundary conditions at internal interfaces correspond to the liquid crystal (grain) or grain–grain interfaces. These internal interfaces are moving boundaries and require boundary conditions with thermodynamic and kinetic character.

To deal with the complex interfacial shapes that develop during solidification, grain growth, and the application of external stress or pressures, the phase field method has become the technique of choice for computational materials scientists. This approach often requires numerical techniques to solve the model equations but readily deals with complex interface shapes and topological changes. The research, conducted in collaboration with the Polymers Division, is also supported by the NIST Center for Theoretical and Computational Materials Science.

This year, significant advances were made in the understanding of the formation of multi-grained (polycrystalline) materials. Polycrystals often arise by either the impingement and growth of grains nucleated in a liquid (equiaxed grains), or via the nucleation of columnar grains on a surface. In collaboration with researchers in Japan and Hungary, we developed a phase field model to study such growth. In a surprising development, this same model has now elucidated a third mechanism of polycrystalline growth: growth front nucleation. This mode of growth is manifested when new orientations nucleate on the front of a growing crystal, yielding a densely branched morphology in which the structural symmetries that arise due to effects of surface energy anisotropy are disrupted by the nucleation process, yielding

an isotropic pattern. This model demonstrated that this type of growth can be initiated by either static or dynamic heterogeneities in the solidifying system, solving a riddle that has been of substantial interest to materials scientists. This work, published in *Nature Materials*, has attracted extensive academic and industrial interest.
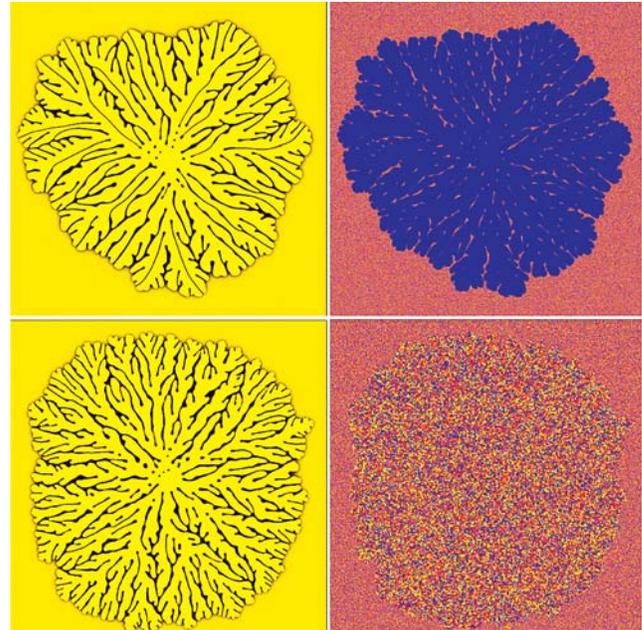
Figure 1: *Two simulations of seaweed-like growth of an alloy. The left column shows the solute profile while the right column shows grain orientation. The upper row is a single crystal while the lower is polycrystalline. Using such techniques, the potential for polycrystalline growth to disrupt the influence of surface energy anisotropy (which gives dendritic growth) is demonstrated.*

Although a remarkable amount of progress has been made, there are still physical phenomena that need to be properly included in phase field models if engineering impact is desired. With this in mind, much effort has been devoted to account for the effects of stress and vacancies on both solidification and interdiffusion. It is also believed that our model for polycrystalline growth may explain spherulitic growth as well as provide insight into the observations of Bendersky and NIST coworkers of a stable glass phase in highly supercooled alloys.

Contributors and Collaborators

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Hardness Standardization: Rockwell, Vickers, Knoop

Hardness is the primary test measurement used to determine and specify the mechanical properties of metal products. The Metallurgy Division is engaged in all levels of standards activities to assist U.S. industry in making hardness measurements compatible with other countries around the world. These activities include the standardization of the national hardness scales, development of primary reference transfer standards, leadership in national and international standards writing organizations, and interactions and comparisons with U.S. laboratories and the National Metrology Institutes of other countries.

Carlos Beauchamp and Sam Low

Figure 1: *Prototype of new steel microhardness SRM.*

At the international level, we are leading the Working Group on Hardness (WGH) under the International Committee for Weights and Measures (CIPM). The primary goal is to standardize hardness measurements worldwide. As secretary of the WGH, we have led an effort this year to better define the Rockwell hardness test procedure used by National Metrology Institutes (NMIs). Other activities include chairing the ASTM-International committee on Indentation Hardness Testing and heading the U.S. delegation to the ISO committee on hardness testing of metals, which oversees the development of the respective hardness test method standards published by those organizations; and as the Secretariat for the International Organization of Legal Metrology (OIML) committee on hardness, we have revised the international requirements for regulating Rockwell hardness machines.

The primary task at the national level is to standardize the U.S. national hardness scales and to provide a means of transferring these scale values to industry. Currently, we are producing test block Standard Reference Materials® (SRMs) for the Rockwell, Vickers, and Knoop hardness scales, as well as developing new reference standards. Twelve different microhardness SRMs for Vickers and Knoop hardness are now available. Fifteen units of a new steel SRM are in the process of being certified at a nominal hardness of 760 kgf/mm^2 for each of the Vickers and Knoop hardness scales. These SRMs are being certified at loads of 2.943 N, 4.905 N, and 9.81 N. In addition, renewal of low inventory of two of the Knoop Scale SRMs is underway. Ten units of each of the copper and nickel SRMs are being certified with nominal hardness levels of 125 kgf/mm^2 and 600 kgf/mm^2, respectively, at loads of 0.245 N, 0.490 N, and 0.981 N.

We also introduced two new SRMs for the Rockwell B scale (HRB) to complement the three SRM Rockwell C scale blocks currently available. The HRB scale is used for testing softer metals, such as aluminum, copper and brass. Work is also continuing to produce a new Rockwell hardness diamond indenter SRM, which has become feasible due to the successful completion of a Small Business Innovative Research (SBIR) Phase-2 project with Gilmore Diamond Tools to develop an improved method for manufacturing geometrically correct Rockwell diamond indenters.

Other activities at the national level occurring this year included: the assessment of commercial secondary hardness calibration laboratories for the NIST National Voluntary Laboratory Accreditation Program (NVLAP) providing direct linkage to the use of the NIST SRMs; the development of a NVLAP proficiency testing program for hardness calibration laboratories; and the development of indentation Finite Element Analysis models that have been used to analyze the effect of using different indenter materials for Rockwell hardness tests in support of proposed revisions to international test standards.

Contributors and Collaborators

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NIST Combinatorial Methods Center (NCMC)
Pioneer and Partner in Accelerated Materials Research

Combinatorial and high-throughput (C&HT) techniques hold great potential for making materials research more productive, more thorough, and less wasteful. However, significant barriers prevent the widespread adoption of these revolutionary methods. Through creative, cost-effective measurement solutions, and with an eye towards fruitful collaboration, the NIST Combinatorial Methods Center (NCMC) strives to ease the acquisition of C&HT techniques by the materials research community.

Cher H. Davis and Michael J. Fasolka

Now in its third year, the NIST Combinatorial Methods Center continues to be a sought after partner among industry, government laboratories, and academics interested in acquiring C&HT research capabilities for materials research. Indeed, the NCMC consortium currently includes 22 member institutions (see table) representing a broad cross-section of the materials research sector.

The NCMC is successful because it serves the combinatorial materials research community on several levels. Our foundation is the extensive suite of NCMC technologies, which provide measurement solutions to parties interested in acquiring C&HT capabilities. Many of these methods are described elsewhere in this report, as identified by the NCMC symbol (see top right corner).

Technology transfer efforts complement our methods foundation, as evidenced by the many institutions that have adopted NCMC techniques. For example, Air Products, Rhodia, National Starch (ICI), Dow, Procter and Gamble, and Eastman, plus many universities, have replicated NCMC devices in their laboratories. In this respect, NCMC *Focused Projects* are a new paradigm for NIST/industry partnership, which are extremely effective for both methods development and technology transfer.

> *"The focused project approach is particularly effective since it allows active collaboration with industry, allowing real needs to be addressed, and resulting technology transferred. The [NCMC] is at the leading edge of combi-based material science discovery, and this reflects both the quality of the research program and of the people."*
> — Dr. J. Carroll, ICI/National Starch, Strategic Technology Group

Under a Focused Project, NIST scientists and 2–3 member companies collaborate to develop a particular C&HT measurement solution. While the research is co-funded by industry members, we avoid the study of proprietary materials and all results are published; this allows the research to have the broadest impact. Currently, there are two Focused Projects. In the first, NIST is working with Procter and Gamble and National Starch (ICI) to produce HT microfluidic measurements of interfacial tension. The second Focused Project, sponsored by Intel and National Starch (ICI), will produce C&HT methods that gauge the performance of epoxy adhesives for flip chip electronics applications. Several other Focused Projects are in development.

New scientific endeavors (such as C&HT materials research) gain momentum when stake-holding parties are brought together. Accordingly, to advance the field, the NCMC invests itself in *community forming* activities aimed at information transfer and goal consolidation among institutions interested in C&HT research. Industry workshops play a major role in this endeavor, and in FY04 we hosted the 4th and 5th additions to the NCMC workshop series, focused on *Polymer Formulations* and *Processing and Characterization,* respectively.

> *"The NCMC provides a unique platform to exchange information and ideas with other member companies who form a part of this consortium."*
> — D. Bhattacharya, Global Coatings Application Development, Eastman Chemical Co.

Moreover, we have been very active in organizing symposia at national conferences. In FY04 alone, NCMC staff developed and organized multi-day symposia on C&HT methods for the Materials Research Society, the American Chemical Society, the Adhesion Society, and the Knowledge Foundation.

> *"I have heard nothing but praise from all who attended the recent NCMC conference...NIST did a superb job organizing the symposia, selecting thought-provoking topics, and leading good general discussions."*
> — Personal observation of J. Dias, ExxonMobil; Chair ACS PMSE

For more information on the NCMC, C&HT technologies, or post-doctoral research opportunities, see our website at **http://www.nist.gov/combi**.

NCMC Members (*New in FY2004):	
3M	Honeywell International
Accelrys*	Hysitron International*
Air Force Research Lab	Intel*
Air Products & Chemicals	ICI/National Starch & Chemicals
Akzo Nobel	Michelin
Atofina Chemicals*	PPG Industries
BP*	Procter & Gamble
BASF	Rhodia
Bayer Polymers	Sealed Air Corp*
Dow Chemical Company	Symyx*
Eastman Chemical*	Univ. of Southern Mississippi
ExxonMobil Research	Veeco/Digital Instruments*

Contributors and Collaborators

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Polymer Formulations: Rapid Prototyping Technology for Polymeric Materials Development

Industrial development of complex mixtures of materials known as "formulations" has traditionally relied upon empirical data and technical intuition, resulting from years of trial and error studies. We accelerate product discovery and optimization by providing new testing platforms that use high-throughput and combinatorial methods to rationally explore formulations variable space. These techniques, which have proven powerfully effective in drug and catalyst discovery, are now adapted to the myriad of materials measurements to which complex mixtures are typically submitted.

Kathryn L. Beers and João T. Cabral

Commercially available combinatorial and high-throughput (C&HT) fluid handling and measurement capabilities have enabled tremendous progress in industrial product development; however, the platforms are often costly and time-consuming to implement. The approach adopted by most manufacturers has been to build these automated platforms that mimic the development process for a specific material in a narrow application. This greatly increases data acquisition rates, but it is challenging to adapt this system-specific infrastructure to changing R&D needs. In response, our research aims to develop new methods for the manipulation and measurement of complex polymeric fluids, thereby providing flexible and inexpensive alternatives to robotics-driven instrumentation.

To improve the versatility of high-throughput formulations testing, we employ microfluidic technology to build a toolset of complementary library fabrication and test methods. The preparation of devices is fast and modular, allowing for rapid prototype development

and increased flexibility. Our fabrication method is an adaptation of existing procedures that uses an optical resin with good solvent resistance and obeys a frontal polymerization mechanism, which enables us to prepare quasi-three-dimensional channel structures (Figure 1).

This year, we have built and demonstrated several methods of preparing polymer libraries in microfluidic devices (see Technical Highlights: Polymer Library Fabrication Techniques Using Microfluidic Technology). The libraries produced are designed to feed directly into the thin film gradient tools previously developed in the NCMC as well as the fluid measurement capabilities currently being built in our lab.
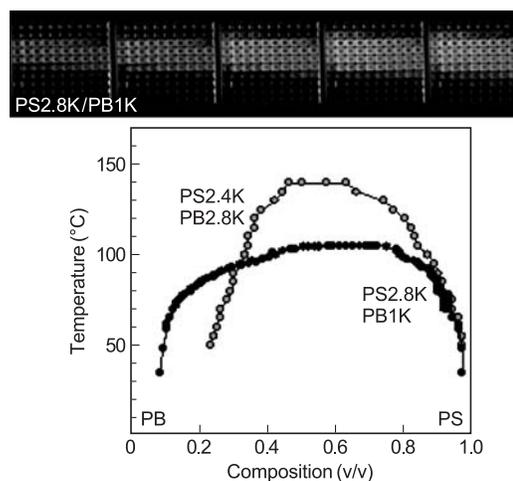
Figure 2: High-throughput cloud point curves (graph) determined from uniform temperature sweeps of an array of blend compositions in a prototyped sample plate (top images).

Complex fluid capabilities developed this year to complement our library fabrication include a high throughput microfluidic device for measuring interfacial tension (see related article in this report), a combinatorial magneto-driven rheometer, and a small angle light scattering (SALS) instrument for high throughput screening of polymer blends and solutions. The SALS instrument builds upon our work demonstrating high throughput cloud point mapping of polymer blends using sample libraries prepared in prototyped arrays (Figure 2).

Figure 1: Profilometry image of a fluidics device master prepared by patterning an optical resin. 3-D channel structure is possible due to the frontal polymerization mechanism of the resin.

Contributors and Collaborators

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Carbon Nanotube Processing

We are developing new metrologies for quantifying the dispersion and orientation of carbon nanotubes in polymer melts and solutions. This will open the door to innovative processes and in-line characterization methods that will, in turn, empower novel approaches in materials science and engineering, creating a pathway toward the realization of a modern generation of materials and applications for carbon nanotubes.

Erik K. Hobbie and Barry J. Bauer

Carbon nanotubes exhibit remarkable physical properties, and there is considerable interest in using them as nanoscale building blocks for a new generation of novel materials. Despite this promise, fundamental issues related to the dispersion, fractionation, and orientation of individual carbon nanotubes remain unresolved, and bulk processing schemes do not yet exist. In fact, techniques for measuring these parameters in nanotubes are primitive. In light of these issues, we have established a program to enable proficient nanotube processing by quantifying the response of carbon nanotube suspensions and melts to changes in such parameters as composition, aspect ratio, shear stress, and dispersant.

The manufacture of nanotube-based devices and composites typically entails suspending them in an aqueous or molten polymeric media and subjecting them to shearing stresses. We have completed a comprehensive set of measurements detailing the response of nanotube suspensions to imposed flows. These experiments have been conducted over a wide range of shear rates, concentrations, and tube type (single or multi-wall). By combining optical methodologies with neutron scattering, the influence of flow on nanotube clustering, orientation, and dispersion has been elucidated.

Typical optical measurements are shown in Figure 1a, which shows scaled birefringence as a function of a scaled shear rate (Peclet number), where the left inset (red scale bar) is a SEM image of the multi-wall nanotubes (MWNT), and the right inset (blue scale bar) is an AFM image of a single-wall nanotube (SWNT) bundle (scale bar = 50 nm). The measured order parameter has been scaled onto the data, and the line is a power-law fit. Figure 1b shows an analogous plot of the birefringence, where the left inset is an optical micrograph of a MWNT (scale bar = 5 μm), and the right inset is a SANS pattern for a SWNT suspension (scale bar = 0.06 nm^{-1}). The scaling shown in Figure 1 confirms theoretical predictions of the importance of hydrodynamic interactions in the semi-dilute regime. One intriguing result is a segregation by tube length in
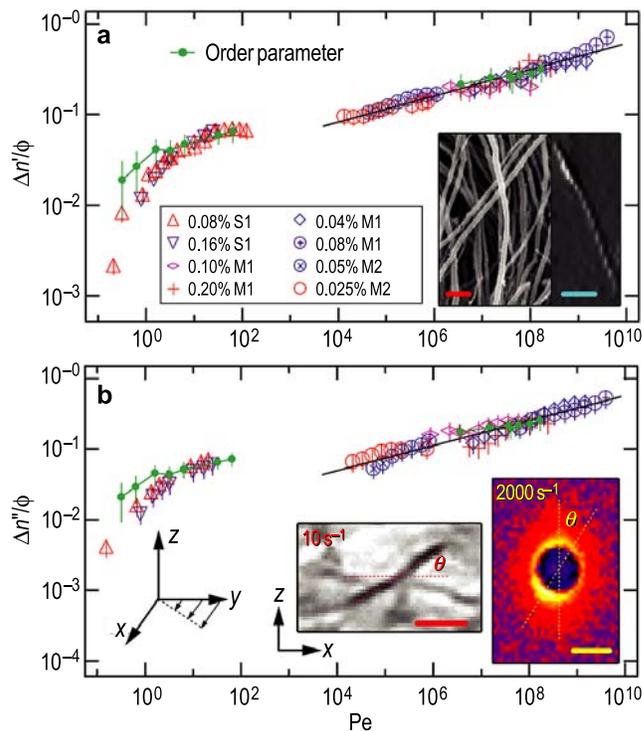
Figure 1: *Scaled birefringence (Δn′) and dichroism (Δn″) as a function of Peclet number for a variety of carbon nanotube suspensions. (φ is the volume fraction.)*

the shear cell; this suggests a path towards the goal of the production of monodisperse nanotubes.

A "grand challenge" in nanotube research is to break up the clusters and "ropes" that naturally form so that isolated single-wall tubes are realized, which can be utilized in applications. Numerous recipes for dispersing the nanotubes have been proposed, but there is little quantification of the resulting suspensions and no powerful method for comparing different techniques.

We are employing neutron scattering to establish base-line standards for nanotube dispersion and orientation using a variety of functionalization and dispersion methods. These measurements will resolve a number of controversial and outstanding questions regarding form and structure in single-walled carbon nanotube suspensions, including persistence length and phase behavior.

Contributors and Collaborators

D. Fry (Polymers Division, NIST); H. Wang (Michigan Tech)

Processing Flows and Instabilities

As polymer processing is carried out under highly non-equilibrium conditions, it is difficult to assess the state of the polymer without in-situ real-time measurements. Our program develops and applies in-situ measurement technology to problems chosen on the basis of input from our industrial partners. This year's focus has been on the state of dispersion of nanoclay-polymer composites, as well as on additives to control the extrusion process.

Anthony Bur and Kalman Migler

In the marketplace of commodity polymers, much of the value added is due to processing operations. Indeed, the ability to precisely control product quality often determines the economic viability of a product. Due to the highly non-linear and non-equilibrium processes that occur during large-scale processing operations, it is generally not feasible to obtain accurate determinations of the relevant process state that would allow precision control. Thus, most of the quality control is engineered into the manufacturing process during the R&D stage.

Our program has built numerous collaborative relationships with the upstream industries, such as materials producers, additive suppliers, and instrument manufacturers to further industry's ability to monitor processing parameters. We have developed a variety of on-line instruments which can characterize critical parameters of the polymer during processing such as its temperature, velocity field, molecular orientation and morphology of dispersed components. This year we focused on two projects: the behavior of polymer additives during processing; and techniques to assess the state of dispersion of clay in polymer nanocomposites.

Additives are frequently mixed into polymeric materials in minute quantities in order to make them processable into the typical products well known to consumers, such as plastic sheets, pipes, and wire insulation. However, the basis for the effectiveness of these additives remained unknown because the existing tools available to measure their behavior in the manufacturing process were rather crude. We utilized the optical phenomena of Frustrated Total Internal Reflection (Frus-TIR) to directly visualize the behavior of fluoropolymer additives in polyethylene melts.

From visualization of the additive coating process, we developed a semi-quantitative model which predicts the coating efficiency as a function of additive droplet size and shear rate. A collaboration between NIST, DuPont Dow Elastomers, The University of Minnesota, and The University of Maryland is now using this Frus-TIR technique to test for the critical factors that influence the coating efficiency.
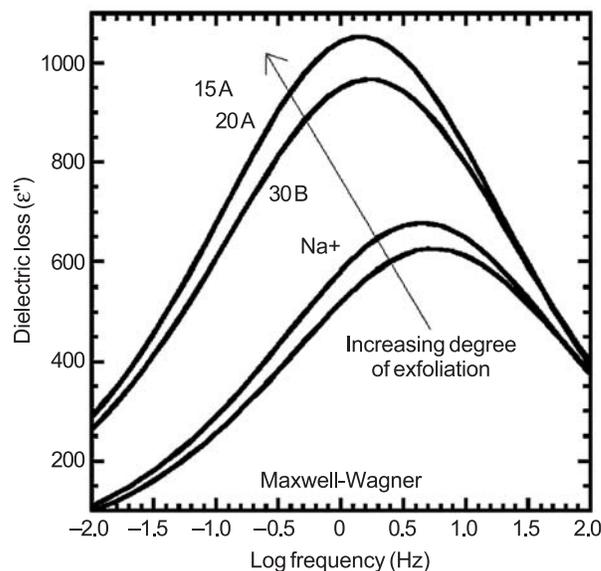
Figure 1: *Use of dielectric spectroscopy to assess the state of dispersion of a nanoclay composite. Nylon 11 compounded with four different clays.*

The second focus was to measure the dispersion of nanoclay additives using an on-line dielectric cell. This cell is effectively a slit die with interdigitated electrodes glazed onto one wall. Past work has shown that it can also be used to carry out rheological and optical measurements. The program achieved its goal of finding the signature of exfoliation in the spectra of the dielectric measurements (see Figure 1). Further, the state of exfoliation was measured from two complementary methods: the changes in the optical fluorescence when certain dyes were incorporated into the clay; and changes in the transparency of the material as a function of exfoliation. This last method is particularly inexpensive and may be of use to end-users. These measurements correlated well with the traditional laborious off-line techniques (transmission electron microscopy and x-ray).

Contributors and Collaborators

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Quantitative Polymer Mass Spectrometry

Traditional measures of molecular mass (and the standards derived from them) provide either absolute values for only one moment of the distribution or relative values for the entire distribution. As we discovered from our two recent industry workshops, producers and users of synthetic polymers, analytical laboratories, and standards developing organizations, need a method (and standards derived from it) for absolute molecular mass distribution determination. Mass spectrometry is being developed as such a method. Both Type A ("random") and Type B ("systematic") uncertainties must be included in determining the uncertainty budget for mass spectrometry.

William E. Wallace

In mass spectrometry, methods exist to calibrate the mass axis with high precision and accuracy. In contrast, the ion-intensity axis is extremely difficult to calibrate. This leads to large uncertainties in quantifying the content of mixtures. This is true whether the mixture is composed of different oligomeric species of the same polymer (*i.e.*, the molecular mass distribution), of polymers with the same repeat unit but having different end groups (*e.g.*, pre-polymers), or polymers having different repeat units (*i.e.*, copolymers). The aim of this project is to calibrate the ion intensity axis. This task has been divided into three parts: sample preparation/ion production, instrument optimization, and data analysis.

Matrix-assisted laser desorption/ionization (MALDI) is used to create intact gaseous macromolecular ions. We have begun to study the MALDI ion-creation process using two-dimensional combinatorial libraries where the analyte:matrix ratio is varied in one dimension and the analyte:salt ratio is varied in the other. We add a factorial design methodology to optimize the instrument parameters at each composition using the signal-to-noise ratio. Instrument parameters to be optimized included laser energy, several critical ion optics voltages, detector voltage, as well as analyte:matrix ratio and matrix material. From this, it was discovered that the detector voltage was the single most important factor, followed by the laser energy. Additionally, we continue to develop the MassSpectator computer code to perform unbiased processing of the data.

To gain greater insight into the complex mechanisms of ion creation, the MALDI process was studied as a function of sample temperature. The common MALDI matrix 2,5-dihydroxybenzoic acid (2,5-DHB) was used due to the extensive literature on its physical properties. Due to the high vapor pressure of 2,5-DHB, single crystals were necessary to minimize the surface-to-volume ratio and thereby decrease the sublimation rate.
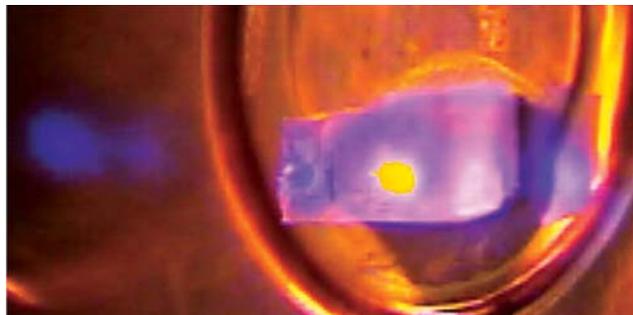
Figure 1: A 2,5 DHB single crystal on the sample stage. The bright yellow feature is the near UV laser spot. Notice the light pipe effect as visible radiation escapes from the ends of the sample. The sample is approximately 3 mm long.

It was observed that a steep rise in ion production occurs at 90 ºC, achieved a maximum between 120 ºC to 130 ºC, then decreased sharply to a minimum at 130 ºC to 140 ºC, and returned to a second maximum value at 150 ºC. Above 150 ºC, useful information could not be obtained because of rapid volatilization of the sample into the vacuum. The overall trend in ion production is well described by a recent two-step theory of the laser desorption/ionization process, which takes into account the temperature-dependent effects of plume expansion. It was observed that thermal dehydration, condensation, and decarboxylation reactions increase the volume of gas released under laser ablation at high temperatures. The resultant higher local pressure at the crystal surface was found to have a profound effect on gas-phase ion formation with higher pressures leading to lower ion production.

Contributors and Collaborators

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Polymer Standards

Producers, processors, and users of synthetic polymers use polymer standards for calibration of instruments, assessment of laboratory proficiency, test method development, and materials improvement. NIST assists in the standards process by providing standard reference materials (SRM®), reference materials (RM), and reference data. Activities include recertifying SRM®s and RMs as stock is depleted, determining opportunities for production of new SRM®s and RMs, producing new SRM®s and RMs and building databases of relevant data pertaining to SRM®s and RMs.

Bruno Fanconi, Charles Guttman, and John Tesk

Recertification of SRM® 1476

SRM® 1476, a branched polyethylene, was originally issued as a melt flow rate standard. It was discontinued because insufficient material remained for recertification as a melt flow rate standard. During its availability, SRM® 1476 was also used in studies of branching in polyethylene, a desirable molecular characteristic for certain types of products. Although chemists now have methods to produce a variety of branch structures, measurement methods to quantify the critical aspects of the branch architecture are lacking. Owing to the available molecular data on SRM® 1476, manufacturers of chromatographs include small quantities of the original SRM® 1476 with purchases of their instruments for comparative measurements. NIST has received inquiries from manufacturers, researchers and resin producers about making the remaining supply of SRM® 1476 resin available, not as a melt flow rate standard, but as an aid in chromatographic measurements. The remaining supply of SRM® 1476 resin was sufficient for this purpose. Hence, recertification of SRM® 1476 resin for chromatographic measurements was completed in FY 2004. Although the new SRM is not intended as a melt flow rate standard, it remains certified for this purpose to assure continuity with the original material.

Reference Scaffolds for Tissue Engineering

At the November 19, 2003 meeting of ASTM International Committee F04.42 — Tissue Engineered Biomaterials, a task force was initiated for the development of reference scaffolds for tissue-engineered medical products (TEMPs). Reference scaffolds had been identified at a NIST workshop as the most needed reference material for TEMPs. The task force will conduct measurements to characterize test scaffolds that will be supplied to its members; the results will be used to determine the most useful characterizations to employ when

the reference scaffolds are produced. Scaffolds of known porosity, interconnectivity, surface and bulk chemistry, physical and mechanical properties, and cellular reactivity are needed. Initially, the focus will be on characterizing porosity (pore volume and pore size distribution), connectivity, and interconnectivity of pores and work toward consistent, unambiguous understanding of terminology. Scaffolds that consist of a regular array of cubic pores, such as with 600 µm pore-edge dimensions and consistent interconnections, were identified for the task force's initial study. Micro-x-ray Computed Tomography (µ-CT) was used for preliminary evaluation of scaffold designs manufactured by different processes, materials, dimensions, and pore size. On this basis, two designs were chosen for distribution to the 17 laboratories participating in the ASTM activity. Laboratory evaluations of these designs will ensure that the characteristics needed for the reference scaffolds will be well defined and that their measurements will produce consistent results when the reference scaffolds are produced. The reference scaffolds will be available for distribution to researchers and developers of scaffolds for tissue engineering applications. Initial measurements by NIST showed that µ-CT would be an important measurement method for distinguishing scaffolds with acceptably consistent features.
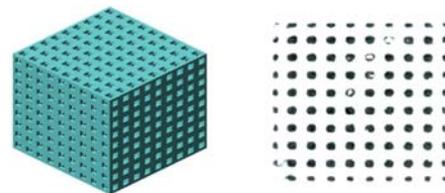
Figure 1: *Cubic scaffold with cubic pores (left) and µ-CT scaffold slice (right).*
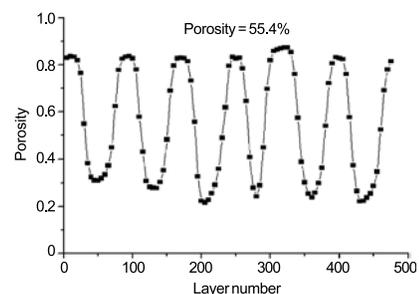
Figure 2: *Porosity as a function of depth of µ-CT slice (layer).*

Contributors and Collaborators

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