METALLURGY

1998 PROGRAMS

AND

ACCOMPLISHMENTS

MATERIALS

SCIENCE AND

ENGINEERING

LABORATORY

NISTIR 6250

UNITED STATES
DEPARTMENT OF
COMMERCE

TECHNOLOGY
ADMINISTRATION

NATIONAL
INSTITUTE OF
STANDARDS AND
TECHNOLOGY

New Materials Needed for Tomorrows Automobiles

Manufacturers can bring new, advanced materials into their products more quickly and at lower cost if they can predict exactly how the materials will behave during manufacturing and use. NIST collaborates with U.S. automobile manufacturers to measure the properties and behavior of new materials, including light-weight sheet metal for better fuel economy and high-temperature solders for more reliable performance. NIST also produces Standard Reference Materials, such as hardness test blocks, which will help U.S. products gain acceptance in international trade.

Certain companies and commercial products are mentioned in this report. They are used to either completely specify a procedure or describe an interaction with NIST. Such mention is not meant as an endorsement by NIST or to represent the best choice for that purpose.

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INTRODUCTION

Carol A. Handwerker, Chief

This report describes the major technical activities and accomplishments of the Metallurgy Division of the NIST Materials Science and Engineering Laboratory (MSEL) in 1998. The NIST Metallurgy Division mission is to provide critical leadership in developing measurement methods, standards, and fundamental understanding of materials behavior needed by US industry for the more effective production and use of both traditional and emerging materials. As part of this mission we are responsible not only for developing new measurement methodologies with broad applicability across materials classes and industries, but also for working with individual industry groups to develop and integrate measurements, standards, and evaluated data for specific, technologically important applications.

To that end we have established our research priorities thorough extensive consultation and collaboration with our customers in US industry. Industrial priorities are established by the Division's technical leaders through formal and informal means: industrial roadmapping activities, workshops, technical meetings, standards committee participation, and individual visits with our customers. However, industrial need and mission relevance are not enough. In order for us to undertake a new program or project within an existing program, the industrial and NIST resources must be sufficient to accomplish the goals and there must be a clear path for technology transfer of NIST results, whether the results are a fundamental understanding of materials behavior, measurement techniques, standards, evaluated data, software, or sensors for on-line process control.

In 1998 we have carried out major programs that focused on meeting specific, high priority measurement-related needs identified by the automotive, magnetic recording, microelectronics, aerospace, and stationary power generation industries. The Division is organized into groups that represent the Division's core expertise in Metallurgical Processing, Electrochemical Processing, Magnetic Materials, Materials Structure and Characterization, and Materials Performance. However, by virtue of the interdisciplinary nature of materials problems in these industrial sectors we serve, the Program teams cut across the Division's management groups and, in many cases, cut across MSEL Divisions and the NIST Laboratories in order to best meet the scientific and technical needs of our customers. The research accomplishments and industrial impacts of our programs in the following section provide an indication of the scope and quality of programs in the Metallurgy Division.

We hope that this report provides insight into how these research programs meet the objectives of our customers, how the capabilities of the Metallurgy Division are being used to solve problems important to the national economy and the measurements and standards infrastructure, and how we interact with our customers to establish new priorities and programs. We welcome feedback and suggestions from our customers on how we can better serve their needs.

In 1998 Metallurgy Division staff members were recognized for their outstanding contributions to measurement science and technology transfer in the areas of the modeling of aerospace casting processes, electrodeposition processing, and failure analysis of ship rivets and hull plate salvaged from the R.M.S. Titanic. The NIST Casting Consortium, led by Bob Schaefer and Bill Boettinger, was instrumental in developing measurement and modeling technologies which are now being used by the aerospace casting industry. Combining needed measurement and analysis expertise from across MSEL and NIST, and working closely with the Consortium's industrial and university members, the NIST program team included Bill Boettinger, Bob Schaefer, Ursula Kattner, Ralph Napolitano, and Ared Cezairliyan from the Metallurgy Division, Dale Fitting, Bill Dubé, and Tom Siewert from the MSEL Materials Reliability Division, and Bob Kelley from the NIST Chemical Science and Technology Laboratory (CSTL). For its achievements the Federal Laboratory Consortium recognized the NIST Casting Consortium through its award for excellence in technology transfer. Chris Johnson was awarded the American Electroplaters and Surface Finishers Society (AESF) Scientific Achievement Award for advancing the theory and practice of electroplating, metal finishing, and allied arts. For his failure analysis of rivets and hull plate from the R.M.S. Titanic, Tim Foecke was awarded the Captain Joseph Linnard Prize and the Cochrane Award by the Society of Naval Architects and Marine Engineers, and was named a "Hero of Public Service" by the Partnership for Trust in Government. In numerous presentations and media interviews, Dr. Foecke helped to make a nationwide audience aware of the critical role that materials behavior plays in large engineering systems, and of the ways that materials scientists can analyze this behavior. Jim Warren and three other MSEL scientists were awarded Commerce Department Bronze Medals for their contributions to the creation of the MSEL Center for Theoretical and Computational Materials Science, which has resulted in numerous highly productive interactions with industry and universities.

SIGNIFICANT ACCOMPLISHMENTS AND IMPACTS

Electronic Packaging, Interconnection and Assembly

- ***Solderability Measurements for Microelectronics*** - Several of the alloys investigated in the search for suitable Pb-free solder compositions suffer from a phenomenon known as fillet-lifting, in which the solder adjacent to through-hole joints breaks loose from contact with the printed circuit board. An analysis of the compositions which are subject to this phenomenon and of the microstructure in the vicinity of the fractures revealed that fillet-lifting is the result of hot tearing, in which residual stresses cause the solidifying material to tear apart along surfaces which are the last to solidify. This information has lead to strategies for minimizing such failures by proper design of printed wiring boards and soldering processes. The analysis of fillet-lifting and the complete results of the NCMS Lead-Free Solder Project were published this year on CDROM by NIST and NCMS.

- ***Precision Optoelectronics Assembly*** - Interconnection of optoelectronic devices by optical fibers requires precise alignment, and solder is used to hold the fibers parallel to the substrate for interfacing with surface-mounted electronics such as lasers or sensors. However, the positioning of the fiber is affected by capillary forces of the molten solder and by forces arising from shrinkage as the solder solidifies. NIST researchers have used the Surface Evolver software to calculate the shape of the solder drop and the elastic energy of the fiber as capillary forces bend it out of alignment. Working with collaborators at the University of Greenwich, a model was developed to describe the response of the fiber to forces developed during solidification of the solder. The NIST team worked to develop the needed modeling capabilities through close collaboration with the ATP-funded Precision Optoelectronics Consortium, in which the Boeing Company is the primary user of this technology.

- ***Metallurgy of the Electrical Contacts to Gallium Nitride Semiconductors*** - To take full advantage of the properties of gallium nitride for optoelectronics and high-temperature microelectronics, stable, low resistance metal-to-semiconductor contacts are needed. The performance of such contacts may be strongly affected by the formation of intermediate phases at the metal/GaN interface. NIST is collaborating with the University of Florida and North Carolina and Pennsylvania State Universities to examine the contact metallurgy and electrical characteristics in the Ti/GaN and (Ti,Al)/GaN systems. The interfacial reaction products in Ti_xAl_{1-x}/GaN thin films were identified and correlated with the Ti-Al-Ga-N phase diagram and diffusion paths. This approach allows prediction of how interfacial reactions in this system will depend on composition and temperature, so the performance of the metal/semiconductor contact can be optimized.

Magnetic Materials

- ***Processing and Micromagnetics of Thin Magnetic Films*** - A series of studies of ferromagnetic resonance in thin film systems revealed that better modeling of exchange biased films and better interpretation of measurement results could be obtained by inclusion of a rotatable anisotropy term in the model used to describe the systems. Computational micromagnetics continues as an active collaboration with numerous outside industrial and academic investigators, carried out through the MSEL Center for Theoretical and Computational Materials Science (CTCMS). Two workshops were held, and two new micromagnetic standard problems were developed to help the micromagnetics modeling community better quantify the accuracy of their modeling.

- ***Giant Magnetoresistance Materials*** - The investigation of Giant Magnetoresistance (GMR) materials has been expanded to include magnetic tunnel junctions (MTJs) which are under development as memory elements in nonvolatile computer memory chips. These materials contain a thin layer of Al_2O_3 between magnetic layers, and their performance increases as the thickness of the Al_2O_3 layer decreases. However, diffusion of the Al results in gaps in the Al_2O_3 layer which produce magnetic shorts. The NIST team is now investigating processing techniques, such as oxidation of the magnetic layer, to retard this diffusion. The GMR technology developed at NIST has been transferred to numerous corporations in the information storage industry through site visits, publications, and presentations.

Metals Data and Characterization

- ***Rockwell Hardness Standards*** - Hardness testing is the most widely used mechanical test for quality control and acceptance testing. This year calibrated Rockwell C scale test blocks at three different levels of hardness were offered for sale by NIST, and approximately half of them were sold within four months. These test blocks are a critical component of a system of national traceability of Rockwell hardness measurements in the U.S. Coincident with their sale, a Hardness Standardization Workshop was held at NIST to inform the hardness measurement community of the ramifications of having a national traceable hardness standard. Over two hundred persons attended the Workshop. To facilitate the acceptability of U.S. hardness measurements worldwide, NIST is taking an active leadership role in ASTM and ISO hardness committees as well as several other standardization organizations.

- ***Magneto-Optical Imaging*** - The Magneto-Optical Indicator Film (MOIF) technique has been applied with great success to the study of magnetization reversal in NiO/NiFe bilayers, revealing for the first time the influence of dislocations in this process. Magnetization reversal in one direction (parallel to the unidirectional anisotropy axis) was found to proceed by domain nucleation on dislocations and domain growth, while magnetization reversal in the opposite direction occurred by incoherent rotation. These bilayers are essential features of magnetic devices like GMR read heads, and the MOIF observations help explain why the hysterisis loops for such materials, although symmetric in shape, are displaced along the field axis.

- ***Metallurgy of the R.M.S. Titanic*** - NIST analysis of rivets and hull plates recovered from the wreck of the R.M.S. Titanic provided new insight into the type of damage that may have resulted from the ship's collision with an iceberg. In numerous presentations and media interviews, Dr. Timothy Foecke helped to make a nationwide audience aware of the critical role that materials behavior plays in large engineering systems, and of the ways that materials scientists can analyze this behavior.

Metals Processing

- ***Casting Consortium Work Completed*** - The Consortium on Casting of Aerospace Alloys held its final meeting at NIST on May 27-28, 1998. The Consortium's effort included several major projects, including the development of a thermodynamic phase equilibrium database and a solidification path analysis based on it, benchmark measurements of high-temperature thermophysical properties, analysis of conditions leading to defects in castings, and analysis of chemical interactions between titanium castings and the mold. These projects were all directed toward the aerospace casting industry objective of making better use of modeling to predict the design of casting processes. The Metallurgy Division also collaborated with the Chemical Science and Technology Laboratory in the development of a Standard Reference Material (SRM) requested by the industry, specifically a superalloy containing less than 1 ppm sulfur. The primary industrial collaborators were Howmet Corp., PCC Airfoils, Inc., GE Aircraft Engines, Pratt & Whitney, and UES, Inc., the last being a small business which produces the software used to model metal casting.

- ***Thermal Spray Sensors and Diagnostics*** - The NIST thermal spray system has been equipped with a full array of motion control systems to manipulate the plasma gun, the substrate, and the sensors which will be used to measure substrate and particle characteristics. Advanced sensor technology is being developed with the help of SBIR funding of several collaborators, including Stratonics, Inc., which has developed an imaging two-color pyrometer, and Cooke Corporation, which has provided a video camera with the necessary sensitivity. NIST is working with Praxair, Inc. to show how sensor technology can be used in the control of thermal spray processes and Ford Motor Company to develop improved alloys and processes for automotive body panel seam-filling.

- ***Nanoscale Electrochemical Processing*** - Techniques have been developed to electrodeposit Cu/Co multilayers from a single electrolyte onto a variety of substrates, including Si and GaAs. The magnetoresistive behavior of these films was found to be dependent on in-plane orientation due to the magnetocrystalline anisotropy of the epitaxial layer. In short wavelength multilayers, however, magnetoresistive behavior was absent, possibly because of the grooving of small-angle grain boundaries which were observed in TEM studies.

- ***Reactive Bonding in Metals*** - The thermodynamic and kinetic models needed to predict the time-dependent diffusion paths followed during transient liquid phase bonding are being developed, following some of the methodology used to analyze solidification paths in superalloy castings. By adding boron to the Ni-based superalloy database developed for the casting program, generating a mobility database, and developing a methodology to determine reaction paths, a model is being developed which will help users to select the correct filler material and thermal processing schedule for a given substrate alloy. The models have been tested by comparison to measured composition profiles, using Ni-Al substrates and Ni-B filler material.

Phase Equilibria

- ***Phase Structures in Complex Layered Ceramics*** - Advanced high-resolution transmission electron microscopy techniques have been used to determine the crystal structure of a series of complex phases in the BaO : TiO_2 : Fe_2O_3 system. Six phases were found in this system which belong to a new structural type built out of two alternating types of slabs, one of which is rich in iron. These can be considered as “self-assembled” magnetic multilayer systems with crystallographically flat interfaces. Measurement of the magnetic properties of these materials established a clear correlation between the magnetic and structural characteristics. The thermodynamic stability of these multilayer systems makes them attractive candidates for special wireless communications applications.

Dental and Medical Materials

- ***Silver-based Dental Restorative*** **-** Ductile, soft silver powder has been developed as an attractive candidate as a mercury-free direct restorative material. The powder can be consolidated by hand with the help of a fluoboric acid solution. Potentiometric measurements have been used to determine the concentration of H^+ required to remove the surface oxide from the powder and allow cold welding. Several of the mechanical properties of the hand-consolidated silver equal or exceed those of conventional silver amalgams. Biocompatibility testing has been carried out and the results encourage further development of this mercury-free silver restorative.

TECHNICAL ACTIVITIES

ELECTRONIC PACKAGING, INTERCONNECTION, AND ASSEMBLY

Today's U.S. microelectronics and supporting infrastructure industries are in fierce international competition to design and produce new smaller, lighter, faster, more functional electronics products more quickly and economically than ever before.

Recognizing this trend, in 1994 the NIST Materials Science and Engineering Laboratory (MSEL) began working very closely with the U.S. semiconductor packaging, electronic interconnection, assembly, and materials supply industries. These earlier efforts led to the development of an interdivisional MSEL program committed to addressing industry's most pressing materials measurement and standards issues central to the development and utilization of advanced materials and material processes within new product technologies, as outlined within leading industry roadmaps[1]. The vision that accompanies this program - to be the key resource within the Federal Government for materials metrology development for commercial microelectronics manufacturing - may be realized through the following objectives:

- develop and deliver standard measurements and data
- develop and apply *in situ* measurements on materials and material assemblies having micrometer- and submicrometer-scale dimensions
- quantify and record the divergence of material properties from their bulk values as dimensions are reduced and interfaces are approached
- develop fundamental understanding of materials needed for future packaging, interconnection and assembly schemes

With these objectives in mind, the program presently consists of nearly twenty separate projects that examine key materials-related issues, such as: electrical, thermal, and mechanical characteristics of polymer and metal thin films; solders, solderability and solder joint design[2]; interfaces and adhesion; electromigration and stress voidage; and built up stress and moisture in plastic packages. These projects are always conducted in concert with partners from industrial consortia, individual companies, academia, and other government agencies. The program is strongly coupled with other microelectronics programs within government and industry, including the National Semiconductor Metrology Program (NSMP)[3]. The NSMP is a national resource responsible for the development and dissemination of new semiconductor measurement technology.

More information about this program, and other NIST activities in electronic packaging, interconnection and assembly can be found at: (http://www.msel.nist.gov/research.html) or in *Electronics Packaging, Interconnection and Assembly at NIST: Guide and Resources*, NISTIR5817, copies of which may be obtained by contacting Frank Gayle at (301) 975-6161 or frank.gayle@nist.gov.

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[1] *National Technology Roadmap for Semiconductors*, Semiconductor Industry Association, San Jose, CA, 1994, 1997; *National Technology Roadmap for Electronic Interconnections*, Institute for Interconnecting and Packaging Electronic Circuits, Lincolnwood, IL, 1995, 1997; *National Electronics Manufacturing Technology Roadmap*, National Electronics Manufacturing Initiative, Inc., Herndon, VA, 1996, 1998 (in press).

[2] http://www.ctcms.nist.gov/programs/solder

[3] http://www.eeel.nist.gov/810.01/index.html

Project Title: **SOLDERABILITY MEASUREMENTS FOR MICROELECTRONICS**

Investigators: J. R. Manning, U. Bertocci, W. J. Boettinger, F. W. Gayle C. A. Handwerker, U. R. Kattner, K. Moon, R. E. Napolitano, L. C. Smith, G. R. Stafford, and M. E. Williams

Objectives:

To meet the electronic industry's need for improved manufacturing yield and solder joint reliability, NIST is developing test techniques and scientific guidelines that U.S. industry can use to evaluate solders and processes for creating reliable solder joints before committing them to the production line. NIST collaborates with industry groups which are pursuing projects in this area, including groups developing standard tests for solderability, identifying and testing environmentally friendly lead-free solders, and identifying and testing fatigue-resistant solders suitable for higher temperature automotive, telecommunications, and avionics applications.

Technical Description:

The decrease in dimensions of electronic devices has resulted in a dramatic increase in interconnection density. This trend has introduced increasingly stringent demands on solder and soldering processes and has produced a need for improved solderability measurements and standards. To aid industry, NIST is investigating the scientific reliability of tests being used to predict solderability and the resulting properties of solder joints. This work includes investigations of the effect of intermetallics on solderability and solder joint properties. Electrochemical tests are being applied to identify the chemical nature, structure, and thickness of oxide surface layers on copper substrates and the effectiveness of oxidation inhibitors in improving solderability. Through interactions with the Institute for Interconnecting and Packaging Electronic Circuits (IPC), NIST wetting balance results are being incorporated into national standards for wetting balance solderability tests.

NIST is collaborating with a consortium of industrial companies investigating a new class of fatigue resistant solders. This consortium, organized by the National Center for Manufacturing Sciences (NCMS), is evaluating a number of solder alloys for possible higher temperature microelectronic applications, such as those near the engine block in automobiles. NIST is applying its expertise in phase diagram and metallurgical science to provide information on solder alloys which are candidates for this application. In a continuation of work with companies involved in an earlier NCMS consortium project on lead-free alloys, failure mechanisms in solder joints made from lead-free alloys are being investigated. Cooperative work also has been done on solder joint failure mechanisms with the Interconnect Technology Research Institute (ITRI), a national association having microelectronic packaging companies as members.

Planned Outcome:

Improved solderability test methods will lead to increased manufacturability and reliability in microelectronic devices. Guidelines for identifying and testing lead-free and high-temperature fatigue-resistant solders will be established. Such solders are urgently needed to provide industry with improved flexibility in microelectronic applications. Improved understanding of failure mechanisms in solder joints will aid U.S. industry in reducing soldering defects and cost. Defect reduction is essential in surface mount and ball grid array interconnects, where small size scales and limits on visual inspection make rework of improperly soldered connection difficult or impossible. Electrochemical tests will allow evaluation of accelerated aging treatments as well as the effectiveness of protective coatings on microelectronic components.

External Collaborations:

NIST is working closely with the NCMS Consortium Project on High Temperature Fatigue Resistant Solders and with consortium members Delco Electronics, Ford, Allied-Signal, Indium Corporation of America, Heraeus Cermalloy, Johnson Manufacturing, Ames Laboratory and RPI, providing leadership in the consortium's Materials Task Group. On an industry-wide basis, collaborations are on-going with the IPC, its standards-writing committees, and ITRI research activities. NIST scientists serve as mentors for projects in universities funded by the industry-supported Semiconductor Research Corporation.

Accomplishments:

NIST led the Materials Task Group, which is responsible for one of the two technical aspects of the NCMS High Temperature Fatigue Resistant Solder Consortium Project. Metallographic examinations performed at NIST provided data for re-design of the consortium test assemblies, allowing major cost savings.

In situ observations and metallurgical analysis verified that fillet-lifting failures observed in Pb-free solder joints are due to hot tearing during solidification, pointing the way toward avoidance of such failures.

Oxidation effects which influence solderability on copper components were identified by electrochemical examination in boric acid-borate buffer. Three main constituents of electrochemically grown surface films have been identified: Cu_2O, CuO and $Cu(OH)_2$. The sequence of the oxidation and reduction reactions has been determined, and the amount of each constituent in the film can be measured by means of the electric charge passed.

Procedures were developed to obtain accurate intermetallic growth rate data in solder joints. These data provide predictions useful in solder joint design.

Impact:

NIST work on lead-free solders has been made publicly available through NCMS, providing technical information needed by industry and government bodies considering replacement of lead-containing solders. Recent verification of a hot-tearing failure mechanism occurring with some of these alloys is important for design of lead-free solder joints. Information developed at NIST has significantly aided U.S. companies in their search for higher temperature fatigue-resistant solders, needed especially for automotive applications. Results from NIST solderability measurements were incorporated into new IPC solderability test standard documents.

Outputs:

Publications:

Handwerker, C. A., Rosser, J., Napp, D., Whitten, G., Zhu, Y., Greaves, J. Pan, T-U., Artaki, I., Noctor, D., Mather, J., Schroeder, S., Vianco, P., Palmer, M., Felty, J., DeSantis, C., and Desaulnier, W., Lead-Free Solder Project - National Center for Manufacturing Sciences CD-ROM (NIST, Gaithersburg, MD)

Handwerker, C. A., et al., "Lead-Free Solder Project: Final Report," National Center for Manufacturing Sciences, Ann Arbor, MI, August, 1997.

Presentations:

Boettinger, W. J., "Metallurgical Aspects of Reactive Wetting," Dept. of Mechanical Engineering, SUNY-Binghamton, Binghamton, NY, November 1977.

Boettinger, W. J., "Fillet Lifting in Pb-free Solder: A Hot Tearing Problem?," Solder Interconnect Design Team Meeting, Center for Theoretical and Computational Materials Science (CTCMS), NIST, Gaithersburg, MD, February 1998.

Boettinger, W. J., "Direct Observation of Fillet Lifting in Pb-free Solder," Solder Interconnect Design Team Meeting, Center for Theoretical and Computational Materials Science (CTCMS), NIST, Gaithersburg, MD, August 1998.

Gayle, F. W., "Microstructural Evaluation Of Thermomechanical Fatigue Test Vehicle For Microelectronics," AlliedSignal Corporation, Kansas City Division, NCMS High Temperature Fatigue Resistant Solder Consortium Meeting, December 1997.

Poster/Extended Abstract

Moon, K. W., Boettinger, W. J., Williams, M.E., Josell, D., Murray, B., Carter, W. C., and Handwerker, C. A., "Dynamic Aspects of Wetting Balance Tests," International Conference on Characterization and Metrology for ULSI Technology, NIST, Gaithersburg MD, March 1998.

Patents Pending:

Lead-based Solders for High Temperature Applications, Frank W. Gayle (NIST) and James A. Slattery (Indium Corporation of America) US Patent Application No. 09/025,638, filed 2/18/98.

Project Title: **SOLDER INTERCONNECT DESIGN**

Investigators: J. A. Warren, C. A. Handwerker, and A. C. Powell, IV

Objectives:

The main objective of this program is to develop modeling tools for predicting the geometries of small-scale solder joints with a wide range of starting configurations of interest to industry. Implicit in the development of such tools is the necessity of developing the computational methods for importing solder geometries into other models of processing and reliability.

With these objectives in mind the Solder Interconnect Design Team (SIDT) seeks to establish and foster an industry-academia-national laboratory working group on solder joint design for the exchange of information and collaboration on topics of special importance. The SIDT acts as a forum for discussion of the calculations and models and, through the Center for Theoretical and Computational Materials Science, provides access to software through the Internet/WWW (http://www.ctcms.nist.gov/programs/profiles/solder.html). In addition, the SIDT also holds workshops and symposia to promote collaboration and bring the community toward a consensus on the features required for a useful solder modeling system.

Technical Description:

The NIST Solder Interconnect Design Team, with support from the NIST Center for Theoretical and Computational Materials Science, has been formed to address several pressing issues in the design and fabrication of circuit boards. This multibillion dollar industry is highly dependent on solder interconnects as the dominant method for attaching chips to a circuit board. Having met frequently over the past four years, in partnership with both academic and industrial researchers, the Team has established an agenda for solving modeling problems concerning equilibrium solder joint shape, and the consequential thermal and mechanical properties of the formed joint. Our ultimate goal is to provide the industrial community with a suite of useful software tools for solder interconnect design, and to provide solved test problems (available electronically on the World Wide Web). With this in mind we are actively supporting the development of software that will interface the public domain program Surface Evolver, which has been shown to be quite capable at computing equilibrium solder meniscus shapes.

Problems identified by groups members that are under current consideration include tombstoning (lifting of a small component off the circuit board), forces on the gull wing lead, solidification of the solder interconnect, reactive wetting (dissolution and the formation of intermetallics), and optoelectronic interconnects.

Planned Outcome:

This project will develop and provide improved software tools for the modeling of solder interconnects for use by industry and academic communities.

External Collaborations:

The SIDT is a industry-academia-government laboratory collaboration centered at NIST. Participants over the past few years have included many people and companies, including Edison Welding Institute, DEC, Motorola, BOC Gasses, Ford Motor Co., Lucent Technology, AMP, Rockwell, Delco, Texas Instruments (Raytheon), Susquehanna University, University of Colorado, University of Massachusetts, University of Wisconsin, University of Loughborough, Lehigh University, University of Greenwich, Marquette University, RPI, University of Minnesota, and Sandia. The CTCMS currently provides support to several SIDT members, including the author of the Surface Evolver, Ken Brakke (Susquehanna), and the University of Greenwich (Chris Bailey, PI).

Accomplishments:

This year saw two successful workshops from February 11-12, 1998 and August 19-20, 1998. Work on a variety of topics was presented spanning the industrial concerns of AMP, TI, Ford, Motorola, as well as new scientific work from many of our academic and government partners. Fundamental mathematical research was also presented at the workshop, which should have an industrial impact on the modeling of ball grid arrays.

Impact:

Most academic engineers who work in the area of solder interconnect issues in electronic packaging have now heard of the Surface Evolver. The infiltration of this solder modeling tool into the microelectronics solder interconnect community is nearly complete, and the SIDT is moving on to more fundamental research into the more complex, multi-physics, dynamic processes which occur during solder reflow. More material can be found at (http://www.ctcms.nist.gov/programs/solder)

Outputs:

Publications:

Powell, A., Warren, J. A., and Bailey, C., "Mechanism of Motion of an Optical Fiber Aligned by a Solder Droplet," MRS Symp. Proc. (Spring meeting 1998).

Lewis, D. J., Warren, J. A., and Josell, D., "Development of a New Solder Joint Modeling Tool for IC Package Designers," Proceedings of the 48th Electronic Components and Technology Conference (1998).

Presentations:

Powell, A., Warren, J. A., and Bailey, C., "Mechanism of Motion of an Optical Fiber Aligned by a Solder Droplet," San Francisco, CA, Spring meeting MRS 1998.

Lewis, D. J., Warren, J. A., and Josell, D., "Development of a New Solder Joint Modeling Tool for IC Package Designers," 48th Electronic Components and Technology Conference, Seattle, (1998).

Project Title: **PRECISION OPTOELECTRONICS ASSEMBLY**

Investigators: A. C. Powell, IV and J. A. Warren

Objectives:

Solder is used to join optical fibers parallel to substrates with surface-mounted electronics, e.g. lasers or sensors. In this process, the thin optical fiber is pulled out of alignment first by capillary forces during wetting of the solder on the fiber, and then by solder shrinkage during solidification and cooling. This research will provide users of this technology with modeling tools to predict the extent of fiber shift due to these two mechanisms and contribute to designs with reduced or more reproducible fiber shift.

Technical Description:

This project is divided into two parts: calculation of molten solder droplet shape and fiber shift due to capillary force; and simulation of heat transfer, solidification and solid mechanics to predict fiber motion due to solder shrinkage.

Solder droplet shape, capillary force, and fiber shift due to capillary force are calculated using the program Surface Evolver (available for free download from its author, Ken Brakke, at Susquehanna University). This software, which has been a mainstay of the NIST Solder Interconnect Design Team since its inception, calculates the surface shape which minimizes the total energy of the system, which in this case includes not only surface and interfacial energies of the solder droplet, but using a new algorithm in the input file, also incorporates the elastic energy of the fiber as it bends out of alignment in response to the capillary force.

The PHYSICA software package from the University of Greenwich is the foundation for a model which calculates the temperature field, time-dependent solidification front shape, and elastic/plastic deformation of the solder and fiber. This global model makes use of a relatively simple two-stage local plasticity model to describe solid solder deformation, involving linear elasticity to the von Mises yield stress criterion, followed by linear increase in stress with increasing strain. This type of model has been used by Christopher Bailey *et al.* (U. Greenwich) to calculate residual stresses in other solder joints, but the precision requirements of the current work will require an extension of their model to correctly account for solder flow around the fiber before the solidification front makes contact with it.

Planned Outcome:

Deliverables to our industrial partners include documentation of our findings using the model, and the parameterized input files to Surface Evolver and PHYSICA to allow use of the model beyond our participation in this field of study.

External Collaborations:

Much of the PHYSICA work in this project is based on that of Christopher Bailey and his colleagues of the University of Greenwich, with whom NIST researchers have been actively collaborating throughout this project. We have also worked closely with the ATP-funded NIST

Precision Optoelectronics Consortium, in which the Boeing Company is the primary user of this technology. Mark Beranek has led Boeing's experimentation in this area and works closely with us on this project, and Mostafa Rassaian is currently the primary user of models developed here.

Accomplishments:

A Surface Evolver input file was created which describes an initial geometry and gives surface and interfacial energies for the various components of the system. This input file includes a new algorithm for calculating the capillary force, a novel method for calculating motion of the fiber to balance elastic and capillary forces, and a script which allows start-to-finish running of the model with a single command. A proof-of-concept run of the PHYSICA model was made using an input file based on the model of Bailey *et al*., which will need to be extended as described above.

Impact:

By calculating the effect of geometric and other process parameters on the fiber shift, this research is expected to lead to more robust design of optoelectronics interconnects to meet the tighter tolerances required for use of higher bandwidth fiber in these devices, as described above. In addition, the algorithms for capillary force calculation, elastic body motion and robust operation introduced in the Surface Evolver input file are being made available to other members of the Solder Interconnect Design Team, allowing these techniques to be used for other electronics interconnect models.

Outputs:

Publications:

Powell, A. C., Warren, J. A., and Bailey, C., "Mechanism of Motion of an Optical Fiber Aligned by a Solder Droplet," MRS Symp. Proc. **531**, 95 (1998).

Presentations:

Powell, A. C., "Solder for Optical Fiber Alignment," NIST Solder Interconnect Design Team Workshop, Gaithersburg, MD, February 1998.

Powell, A. C., "Mechanism of Motion of an Optical Fiber Aligned by a Solder Droplet," Materials Research Society Spring Meeting, San Francisco, CA, April 1998.

Powell, A. C., "Modeling Fiber Alignment Shift During Wetting and Solidification", NIST Precision Optoelectronics Assembly Consortium Quarterly Meeting, Seattle, WA, July 1998.

Powell, A. C., "Modeling Fiber Alignment Shift During Wetting and Solidification," NIST Solder Interconnect Design Team Workshop, Gaithersburg, MD, August 1998.

Project Title: **STRESS MEASUREMENTS IN ELECTRONIC PACKAGING**

Investigator: Eva Drescher-Krasicka and G. J. McFadden (ITL)

Objectives:

This project develops techniques for the measurement of stresses in electronic packaging through scanning acoustic microscopy.

Technical Description:

A routine technique called phase inversion can be applied in acoustic microscopy reliability testing to detect delamination and other mechanical defects in electronic packaging. During this test the acoustic microscope lens is focused on the interface between the silicon die and mold compound. In this way a defocused longitudinal beam travels through the stressed material of the mold compound over the edges of the delamination. This existing phase inversion technique for delamination sizing works well for complete debonding between the die and plastic mold. However for the intermediate cases (when the die is not completely debonded), the phase inversion technique shows a gradual transition of phase shift which cannot be explained based on an ideal plane wave model. In response to this open question as to the cause of the intermediate phase shift in delaminated electronic packaging, our research has been directed toward creating the theoretical base to model the stress vs. received pulse dependence of the defocused longitudinal waves. A theoretical approach to the subject will allow us to model the value of the acoustic signal coming to the receiver from the unstressed and stressed areas and solve the problem of the effect of residual stresses on measuring the size of delaminated areas. Various attempts have been made to measure such internal stresses ultrasonically by exploiting the third order changes in elastic constants which accompany changes in internal stress. Until recently all of these approaches have employed measurements of the phase velocities of elastic waves. However, these velocities vary only weakly with changes in elastic constants, so that, except for idealized laboratory setups, attempts to use this approach to measure residual stresses have met with only limited success. A program has been underway at NIST to use other characteristics of ultrasonic waves, in particular longitudinal waves, which are more sensitive to changes in elastic constants than phase velocity, and which can be detected using an acoustic microscope. During the past year a theoretical basis for stress imaging using longitudinal waves was derived.

Planned Outcome:

A theoretical basis and experimental techniques to measure stress by scanning acoustic microscopy will be provided, with particular emphasis on applications in the electronics and microelectronics industries.

External Collaboration:

The theoretical research is done in close cooperation with Professor John Willis from Cambridge University, England. The experimental work has been conducted in close cooperation with Dr. Thomas Moore from Texas Instruments and Dr. James Sweet from Sandia National Laboratory.

Accomplishments:

A new way of approaching the detection and evaluation of the presence of residual stresses in materials was established. This new method is characterized by much higher sensitivity than previous (time of flight) stress measurements.

Outputs:

Publications:

Drescher-Krasicka, E., Moore, T. M., and Hartfield, C. D., "Scanning Acoustic Microscopy of Stress in Electronic Packaging," Proceedings of the 1998 International Conference on Characterization and Metrology for ULSI Technology, NIST, March 23- 27, 1998.

Presentations:

Drescher-Krasicka, E., Moore, T. M., and Hartfield, C. D., "Scanning Acoustic Microscopy of Stress in Electronic Packaging," 1998 International Conference on Characterization and Metrology for ULSI Technology, NIST, March 23- 27, 1998.

Project Title: **METALLURGY OF THE ELECTRICAL CONTACTS TO GALLIUM NITRIDE SEMICONDUCTORS**

Investigators: A. V. Davydov, F. S. Biancaniello, D. Josell, A. J. Shapiro, L. A. Bendersky, and W. J. Boettinger

Objectives:

The objective of this work is to show how phase equilibrium and diffusion data can be used to develop a metallization scheme that will enable the design of improved metal/ semiconductor interfaces for Group III nitride optoelectronic and electronic device fabrication.

Technical Description:

Gallium nitride, a wide band gap semiconductor, is an attractive material for optoelectronics and high-speed, high-temperature microelectronics. Development of GaN-based devices is hindered by a lack of thermal stability and an excessive voltage drop across the metal/GaN interface, causing poor device performance and reliability. In order to attain optimum electric behavior of the devices, it is crucial to develop thermally stable, low resistance ohmic metal-to-semiconductor contacts, as well as to design Schottky-type contacts to GaN with desirable energy barrier heights.

The thermal stability and electrical characteristics of metal contacts to gallium nitride can be affected to a great extent by the phase reactions occurring at the metal/GaN interface. Hence, information on phase equilibria and diffusion paths in potential metal-GaN systems is needed to understand the mechanism of contact formation.

This project examines the contact metallurgy and its effect on thermal stability and the electrical characteristics for the Ti/GaN and (Ti,Al)/GaN systems that show the best performance as ohmic contacts to n-type GaN.

Planned Outcome:

Improved understanding of metal-to-GaN contact formation and its thermal stability has been obtained, which will aid microelectronic design. Coupling fundamental phase diagram and thermodynamic data with interfacial metal/GaN reactions can be used to develop stable metal contacts with improved characteristics for electronic industry needs.

External Collaborations:

Throughout this project the Metallurgy Division is working closely with Profs. T. J. Anderson and P. H. Holloway of the University of Florida on GaN thin film deposition. Prof. R .F. Davis from the North Carolina State University was involved in designing and conducting contact lithography processes on GaN for the metal deposition and specific resistivity measurements. Project workers also interacted with Prof. S. E. Mohney from Pennsylvania State University and R. F. Karlicek from EMCORE Corporation on strategy development for using fundamental thermodynamic and phase diagram knowledge for designing ideal metal/semiconductor interfaces.

Accomplishments:
The experimental program and thermodynamic analysis of the thermal stability of the base semiconductor material, GaN, have been completed:

- The pressure-temperature-composition stability diagram of the Ga-N system has been assessed, which provides an estimate of thermal processing limits and boundary conditions in process models.

Key features of the Ti-Ga-N phase diagram have been established:

- A new ternary compound with a "Ti_3GaN" nominal composition was discovered; equilibrium tie-lines on the 800^{o}C isothermal section were determined.

Metallurgical reactions and diffusion paths for metallization of Ti and Ti-Al on GaN have been investigated:

- Interfacial reaction products in Ti_xAl_{1-x}/GaN (x=1; 0.15) thin films were identified and correlated with the Ti-Al-Ga-N phase diagram.

Outputs:

Presentations:

Davydov, A. V. and Anderson, T. J., "Thermodynamic Assessment of the Ga-N System Guiding Optimization of the Synthesis Parameters for the GaN Semiconductor," NATO Advanced Research Workshop, Moscow, Russia, March 1998.

Davydov, A. V., "Phase Equilibria in the III-N Systems," Pennsylvania State University, Seminar, June 1998.

Project Title: **ON-CHIP INTERCONNECT METROLOGY**

Investigator: J. E. Bonevich, R. R. Keller*, and C. E. Kalnas* (*Materials Reliability Division)

Objectives:

Studies of on-chip interconnect structure and chemistry at the nanometer scale are needed to explain the observed selectivity in local failure sites due to stress-voiding and electromigration. The project focusses analytical electron microscopy to probe local microstructural heterogeneities which are expected to be weak links in interconnects as linewidths become narrower. Knowledge of the microstructure and chemistry can provide insight on the controlling factors which determine overall interconnect reliability.

Technical Description:

Stress voiding and electromigration constitute major factors that jeopardize on-chip interconnect systems in both production and R&D, particularly with decreasing line cross sections, according to the 1997 Semiconductor Industry Association National Technology Roadmap for Semiconductors (NTRS). The NTRS indicates that improved characterization capabilities as well as an improved understanding of the mechanisms controlling these phenomena are now critically needed in order to develop successful, predictive reliability models. Gaining detailed understanding of the microstructure-based mechanisms controlling stress voiding and electromigration requires novel application of established characterization techniques to both copper- and aluminum-based metallizations. Such an understanding then allows for controlled variations in processing which can be introduced to directly build a more reliable interconnect structure.

In this new project, high resolution transmission electron microscopy (HRTEM) coupled with analytical electron microscopy (AEM) and compositional mapping will be used to determine the effects of local chemical heterogeneities on void nucleation and growth at the nanometer scale. HRTEM will also characterize, on a nanometer scale, effects such as segregation and/or precipitation of alloying elements to grain boundaries. Such measurements will then be correlated with both interconnect lifetimes and the selective propensity for void formation and growth in certain regions of the lines. Diffusion experiments in blanket films, with the goal of measuring grain boundary diffusivities, will be related to boundary structure. Such measurements will be used to further refine the statistically-based lifetime studies being conducted by NIST's Semiconductor Electronics Division (SED) to create standard test chips for interconnect reliability.

Planned Outcome:

Anticipated benefits of microstructural characterization of interconnects include: (i) complete, accurate data for input into reliability models, (ii) full correlations between different processing variables and the resulting effects on performance, (iii) development of characterization methods suitable for application to future generation interconnect systems, and

(iv) design and fabrication of standard test structures and analysis methods for interconnect reliability. These four benefits translate into the concept of building reliability directly into interconnects, for improved performance during and after fabrication. This ideally eliminates many quality check and failure analysis steps, resulting in a less expensive, more reliable product for the manufacturer and end user.

External Collaborations:

Electromigration test structures have been obtained from SEMATECH for evaluation. Prof. P. M. Ajayan and S. Murarka (Rensselaer Polytechnic Institute) and the Center for Advanced Interconnect Science and Technology (CAIST) at RPI are providing 180 to 250 nm copper interconnect specimens for evaluation and characterization.

Accomplishments:

In this project, initiated in mid-FY1998, collaborations with NIST and outside researchers, such as SEMATECH and the Center for Advanced Interconnect Science and Technology at RPI have been established. Procedures for the preparation of cross-section TEM specimens have been developed.

MAGNETIC MATERIALS

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

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

Areas of present study include the following:

- processing of magnetic multilayers for optimal giant magnetoresistance effect
- observation and micromagnetic modeling of magnetic domains for understanding magnetization statics and dynamics in advanced and conventional materials
- measurement and characterization of nanoscale magnetic interactions in multilayers, nanocomposites, and low-dimensional systems, needed for understanding and applying the physics of these materials
- measurement and modeling of the enhanced magnetocaloric effect in nanocomposites
- structure and magnetic characterization of new superconducting materials

- nanotribology of magnetic hard disks, measurement of stiction, friction, and wear at the nanometer scale

- measurement and understanding the origin of magnetic exchange bias in conventional and advanced magnetic structures and devices

- development of magnetic sensors of mechanical properties for incorporation as *in situ* controls in a steel mill

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

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

Project Title: **GIANT MAGNETORESISTANCE MATERIALS**

Investigators: W. F. Egelhoff, Jr., P. J. Chen (Guest Researcher), D. Parks (Guest Researcher), and G. Serpa (Guest Researcher)

Objectives:

The objective of this program is to provide assistance to U.S. companies manufacturing products based on the giant magnetoresistance (GMR) materials. These materials are used primarily in the computer hard-disk drive industry, but emerging markets include nonvolatile memory chips, magnetic field sensors, and ultrahigh speed isolators. We help these companies learn how to produce improved GMR materials so that they can operate successfully in the increasingly competitive world market. Our work provides U.S. companies with significant competitive help by investigating the science underlying the manufacturing process, something these companies cannot do on their own.

Technical Description:

Within a few years we will all be surrounded in our daily lives by consumer products that make use of GMR materials. As a result, GMR materials have become a matter of great economic importance. Not unexpectedly, a worldwide race is underway to develop the best GMR materials. A list of companies which have GMR-materials development programs underway is provided below:

U.S.	Japan	Europe
IBM	Toshiba	Philips
Hewlett-Packard	Hitachi	Siemens
Motorola	Sony	Thompson-CSF
Honeywell	NEC	Boesch
Kodak	Sanyo	
Nonvolatile Electronics	Alps	
Quantum	Toyota	
Applied Magnetics	Fujitsu	
Ford	Nisshin Steel	
Materials Innovation	TDK	
Seagate	Matsushita	
CDC Vacuum	Mitsubishi	
Read-Rite	Shimadzu	

Computer memory and hard-disk-drive products are a major force in today's economy, representing over $50B in annual sales, worldwide. The U.S. has a strong position in hard-disk-drives and is trying to make a comeback in memory products, but intense competition from overseas industries, especially Japan, has put the U.S. future at risk in these areas. Competition is forcing U.S. companies to rush GMR materials into products and onto the market. This rush-to-market comes at the expense of scientific research on how to improve GMR materials even at the largest companies. Japanese companies, however, do not follow this pattern, and most of the long-range research in GMR materials is presently being done in Japan. This situation puts the current U.S. lead in GMR products in jeopardy.

There are many applications for GMR materials beyond just computer products. GMR-based magnetic sensors, which can detect the presence and motion of magnets and other iron-containing objects, are better than existing sensors and have a host of applications. These include automation of factory production lines with position-sensing robots, antilock braking systems for cars, “smart” shock absorbers, vehicle-counting systems, currency sorting and counting based on magnetic inks, and on and on.

To assist U.S. industry, NIST set up a major new research program specifically aimed at providing the scientific understanding and measurement capability needed to allow U.S. industry to make the best GMR materials in the world. This program was centered on a new facility, known as the Magnetic Engineering Research Facility (MERF), which is the most elaborately instrumented magnetic thin-film production facility ever constructed. No comparable facility exists even in the R&D labs of major companies.

This unique facility puts NIST in an excellent position to assist not only the small companies in the GMR market but even the major ones. Over the past few years NIST researchers have developed the measurement techniques, clarified the scientific issues, and established the manufacturing processes needed to produce the highest quality GMR materials. NIST is presently capable of producing, albeit on a small scale, the best GMR materials in the world.

Planned Outcome:

Our work is anticipated to help U.S. companies overcome Japan’s advantage in GMR research and remain the world leader in this field of GMR materials. U.S. companies are eagerly working with us to transfer the improved manufacturing processes that we have developed into their production facilities. This process has begun in the form of visits by NIST staff to the affected companies to discuss implementation of the NIST ideas. Unfortunately, this implementation has turned out not to be a trivial matter because the companies are locked into their first-generation production facilities. However, we are already working with these companies and with the manufacturers of production equipment to get the NIST ideas incorporated into second-generation production facilities.

The Department of Defense is also very interested in GMR materials (again for a wide range of applications), and our work is presently being partially supported by the Defense Advanced Research Projects Agency (DARPA).

External Collaborations:

We have collaborated with a number of corporations in the area of GMR materials, including Motorola, IBM, Nonvolatile Electronics, Read-Rite, Honeywell, Integrated Microtransducer Electronics, and Advanced Research Corporation and with a number of university groups, including those of Prof. Falco, U. of Arizona, Prof. Gomez, U. of Maryland, Prof. Berkowitz, U. C., San Diego, Prof. Kryder, Carnegie Mellon, Prof. D. Smith, Arizona State, and Prof. Judy, U. of Minnesota, and with two Federal labs, G. Sandos, NRL and W. H. Butler, Oak Ridge. In all cases we have been making samples for these collaborators for them to analyze in their facilities or we have been examining their samples in our facilities.

Accomplishments:

The Magnetic Engineering Research Facility (MERF) at NIST was maintained at an operational status of approximately 90% of available time, meaning the facility was down only 10% of the time.

One of the important results of this year was an extension of our previous work on the use of surfactants during film deposition to improve GMR properties. We found that by using oxygen as a surfactant and depositing GMR films below room temperature, we could make GMR materials that exhibit an unusually small temperature coefficient. This means that the loss of GMR at high operating temperature is not as severe as in conventionally made materials.

This year we began investigating a variant of GMR materials in which Al_2O_3 is used in place of Cu as the spacer between magnetic layers. These promising new materials are known as magnetic tunnel junctions (MTJs) and are particularly well suited to being the memory element in nonvolatile computer memory chips. In studying MTJs we found what we believe is the key limitation on how thin the Al_2O_3 can be made, and thus on how large the magnetoresistance can be made. Metallic Al diffuses into the underlying magnetic metal at grain boundary sites (before the oxidation step to form Al_2O_3) and the resulting layer of Al_2O_3 has gaps that allow magnetic shorts. We are presently investigating the oxidation of the magnetic layer, prior to Al-deposition, as a remedy.

The new information produced in this work is being transferred to U.S. companies in the magnetic data storage industry through visits by NIST staff to those companies.

Impacts:

The information on our novel results has been transferred to our key collaborators at Motorola, IBM, Seagate, Nonvolatile Electronics, and Read-Rite. These collaborators are attempting to implement our findings in their production equipment. This advance knowledge together with our supporting consultations is giving U.S. companies a head start in developing the next generation of production facilities.

Outputs:

Publications:

McMichael, R. D., Chen, P. J., and Egelhoff, W. F., Jr., "Anomalous Properties of Spin Valves at Elevated Temperatures," IEEE Trans. Mag., **33**, 3589 (1997).

Egelhoff, W. F., Jr., Chen, P. J., Powell, C. J., Stiles, M. D., McMichael, R. D., Judy, J. H., Takano, K., Berkowitz, A. E., and Daughton, J. M., "Specular Electron Scattering in Giant Magnetoresistance Spin Valves," IEEE Trans. Mag., **33**, 3580 (1997).

Chopra, H. D., Hua, S. Z., Lashmore, D. S., Wuttig, M., Shull, R. D., Egelhoff , W. F., Jr., and Swartzendruber, L. J., "Magnetic Domains in Multilayers, Single Films, and Nanocomposites," Micro. Anal**.** **28**, 15 (1998).

Egelhoff, W. F., Jr., Chen, P. J., Powell, C. J., Stiles, M. D, McMichael, R. D., Judy, J. H., Takano, K., and Berkowitz, A. E., "Oxygen as a Surfactant in the Growth of GMR Spin Valves," J. Appl. Phys., **82**, 6142 (1997).

Chopra, H. D., Hockey, B. J., Chen, P. J., Egelhoff, W. F., Jr., Wuttig, M., and Hua, S. Z, "Nanostructural Considerations in Giant Magnetoresistive Co-Cu-based Symmetric Spin Valves," Phys. Rev. B, **55**, 8390 (1997).

Hua, S. Z., Lashmore, D. S., Chopra, H. D., Swartzendruber, L. J., and Egelhoff, W. F., Jr., "Observation of Domain Dynamics in GMR Co-Cu-based Polycrystalline CoNi/Cu Multilayer Films," J. Appl. Phys. 81, 4582 (1997).

Chopra, H. D., Hockey, B. J., Swartzendruber, L. J., Hua, S. Z., Chen, P. J., Raj, K., Lashmore, D. S., Wuttig, M., Lashmore, D., S., and Egelhoff, W. F., Jr., "GMR in Symmetric Spin Valves: Nanostructure and Domain Dynamics," Nanostructured Materials **9**, 451 (1997).

Egelhoff, W. F., Jr., "Fluorine as a Surfactant for a Monolayer of Iron on Cu(100)," Surface Sci **32**, 402, (1998).

McMichael, R. D., Chen, P. J., Stiles, M. D., and Egelhoff, W. F., Jr., "Ferromagnetic Resonance Linewidth in Thin Films Coupled to NiO," J. Appl. Phys. **83**, 7073 (1998).

McMichael, R. D., Chen, P. J., and Egelhoff, W. F., Jr., "Time and Temperature Dependence of High Thermal Stability in NiO\Co\Cu\Co\M Spin Valves," IEEE Trans. MAG, **34**, 897 (1998).
Egelhoff, W. F., Jr., Chen, P. J., Powell, C. J., Parks, D., McMichael, R. D., Judy, J. H., Martien, D., Berkowitz, A. E., and Daughton, J. M., "Optimizing GMR Spin Valves: The Outlook for Improved Properties," Proc. 1998 International Nonvolatile Memory Technology Conference, in press.

Chopra, H. D., Swartzendruber, L. J., Brown, H. J., and Egelhoff, W. F., Jr., "Magnetic Properties of GMR Spin Valves and Their Modification Using Surfactant Pb," Proc. MRS Fall '97 Symp. Proc., in press.

Fry, R. A., Bennett,. L. H, Della Torre, E. , Shull, R. D., Egelhoff, W. F., Jr., Farrow, R.F.C., and Lee, H., "Magneto-Optical Measurements of Ultrathin Co-Pt(111) Multilayers," JMMM in press.

Egelhoff, W. F., Jr., Chen, P. J., Powell, C. J., Parks, D., McMichael, R. D., Judy, J. H., Mariten, D., Berkowitz, A. E. and Daughton, J. M., "Surface Effects in the Growth of GMR Spin Valves" 1997 MRS Symp. Proc., in press.

Presentations:

Egelhoff, W. F., *"Surface Effects in the Growth of GMR Spin Valves," Dept. of Electrical Engineering, Univ. of Maryland, College Park, October 1997.

Egelhoff, W. F., *"Surface Effects in the Growth of GMR Spin Valves," Workshop on Antiferromagnetics, Univ. of Alabama, Tuscaloosa, November 1997.

Egelhoff, W. F., *"Surface Effects in the Growth of GMR Spin Valves," Surface Science Lunch Group, NIST, November 1997.

Egelhoff, W. F. *"Specular Electron Scattering in GMR Spin Valves," Joint MMM/Intermag Conf., San Francisco, January 1998

Egelhoff, W. F., *"Surface Effects in the Growth of GMR Spin Valves," Naval Research Labs, Washington D.C., January 1997.

Egelhoff, W. F., *"Optimizing the Growth of GMR Spin Valves," Commonwealth Scientific, Alexandria, VA, February 1998.

Egelhoff, W. F., *"Surface Effects in the Growth of GMR Spin Valves," Read-Rite Corp., Fremont, CA, February, 1998.

Egelhoff, W. F., *"Surface Effects in the Growth of GMR Spin Valves," CVC Vacuum Co., Milpitas, CA, February 1998.

Egelhoff, W. F., *"Specular Electron Scattering in GMR Spin Optimizing the Growth of GMR Spin Valves," MRS Conf., San Francisco, CA, April 1998

Egelhoff, W. F., *"Recent Studies of GMR Spin Valves at NIST" Motorola Labs, Tempe, AZ, April 1998.

Egelhoff, W. F., *"Optimizing the Growth of GMR Spin Valves: A Surface Science Perspective," Nonvolatile Electronics, Eden Prairie, MN, May 1998.

Egelhoff, W. F., *"Optimizing the Growth of GMR Spin Valves: A Surface Science Perspective," Honeywell Labs, Plymouth, MN, May 1998.

Egelhoff, W. F., *"Surface Effects in the Growth of GMR Spin Valves," 3rd International Conference on Magnetic Multilayers, Vancouver, BC, June 1997.

Egelhoff, W. F., *"Optimizing GMR Spin Valves: The Outlook for Improved Properties," International Nonvolatile Memory Technology Conference, Albuquerque, NM, June 1998.

Egelhoff, W. F., *"Surface Effects in the Growth of Spin Dependent Tunneling Devices," DARPA Workshop, Minneapolis, MN, July 1998.

Egelhoff, W. F., *"Recent Studies of the GMR Effect at NIST," DARPA Workshop, Minneapolis, MN, July, 1998.

Egelhoff, W. F., *"Surface Effects in the Growth of GMR Spin Valves," Workshop on Magnetic Heterostructures, Madison, WI, August 1998

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* Invited talks

Project Title: **PROCESSING AND MICROMAGNETICS OF THIN MAGNETIC FILMS**

Investigators: R. D. McMichael, H. J. Brown, D. E. Mathews, and G. Serpa (Guest Scientist)

Objectives:

This project seeks to provide measurement methods, computational methods and data on the thermal stability, exchange biasing and micromagnetics of thin magnetic films to the magnetic recording, magnetic sensor, and other magneto-electronic industries.

Technical Description:

The technical area addressed by this project includes the processing and micromagnetics of thin magnetic films. Specifically, this project is concerned with the thermal stability of "spin valve" multilayer films, the micromagnetics of thin films, including the ferromagnet/antiferromagnet interface in exchange biased layers, and dynamic measurements of thin magnetic films.

The thermal stability of multilayer structures exhibiting giant magnetoresistance is of concern to companies that manufacture recording heads for ultra-high-density magnetic data storage, other magnetic field sensors and non-volatile magnetic computer memory. The films of interest consist of magnetic and non-magnetic layers, each typically 2-5nm thick. The films must be able to withstand processing steps such as photoresist baking and must be able to serve reliably for many years at elevated temperatures.

The exchange biasing effect is technologically important for pinning the magnetization of thin films, and it depends on the micromagnetic spin configuration at and near the interface between the ferromagnetic film and an antiferromagnet. Measurement methods and meaningful characterization of the exchange biasing and associated effects are important for device design using currently available materials and materials with stronger exchange bias that will be needed in the future.

Micromagnetic modeling techniques are also developed and evaluated for predicting hysteretic behavior and magnetic domain configurations in small elements patterned from thin films and multilayers. Control of domain configuration is important to the design of linear, low-noise read heads and other sensors, and to the control of coercivity in memory elements.

Planned Outcome:

At the conclusion of this project, a collection of measurement methods, data, and models of thermally induced changes in magnetic multilayer performance will be available for industry to use in design of multilayers and for use in predicting device lifetime. Micromagnetic models and measurement methods will be available for exchange biasing materials selection, and micromagnetic computational methods and domain control methods will be available for device design.

External Collaboration:

The work on thermal stability is carried out in collaboration with Mark Stiles of Commonwealth Scientific Exchange Biased Materials

The work on micromagnetics is carried out through the MSEL Center for Theoretical and Computational Materials Science (CTCMS), with numerous collaborators including:

Ed Della Torre and Jason Eicke, George Washington University,
Wolfgang Rave, Alex Hubert and Karl Fabian, IFW, Dresden, Germany
Filipe Ribeiro, Paulo Freitas, and Jose Luis Martins, INESC, Lisbon, Portugal
Riccardo Hertel and Helmut Kronmuller, Max-Planck-Institut fur Metallforschung, Stuttgart, Germany
H. Neal Bertram, Alfred Liu, and Chris Seberino, Center for Magnetic Recording Research, University of California at San Diego.

Accomplishments:

In continuing work on the thermal stability of spin valve structures, we have begun to explore whether the thermal stability is sensitive to the method of deposition. We have compared results from an ion-beam deposited spin valve sample from Commonwealth Scientific with a sputtered sample deposited in the Magnetic Engineering Research Facility. We found that the samples made by these two methods did not exhibit significantly different behavior. We used a method developed in FY97 to characterize the rate at which irreversible changes take place in spin valves. In some samples, the resistance changes were found to fit an Arrhenius law model, and in these samples, the Arrhenius law parameters also predicted the temperature dependence of the magnetoresistance of the films, allowing predictions of sample lifetime at lower temperatures. This method, and results on several samples were presented in Jan '98 at the Joint MMM/INTERMAG conference and published.

Our investigations of exchange biased thin films (ferromagnetic films sharing an interface with antiferromagnetic material) resulted in the ability to separate the effects of reversible and hysteretic behavior in the antiferromagnet. In FY 97, we described an isotropic shift of ferromagnetic resonance (FMR) field in Permalloy films exchange biased by NiO using a phenomenological "rotatable anisotropy" energy having an easy axis that follows the equilibrium magnetization. In FY 98, in collaboration with Mark Stiles (PL), we worked out a model of ferromagnet/antiferromagnet interfacial interactions which included irreversible transitions in antiferromagnetic material. As a consequence, we were able to identify the isotropic resonance field shift as an effect of irreversible, or hysteretic, behavior in the antiferromagnet.

We measured the temperature dependence of NiO-biased Permalloy films using FMR, and compared the results with magnetoresistive hysteresis measurements. We found that the FMR yielded values of the exchange bias field that were consistently about 20% higher than the hysteresis loop results. We believe that the difference is due to false assumptions about hysteresis loop symmetry that do not affect FMR measurements.

The significance of this collection of results relating to FMR of exchange biased films is that a rotatable anisotropy term enables better modeling of exchange biased films and better interpretation of measurement results. These results were presented at the 3rd International Symposium on Magnetic Multilayers. The experimental results have been published in Phys. Rev. B, and a theory paper is in review for Phys. Rev. B.

In further work on the ferromagnetic resonance of exchange biased films, we derived dispersion relations for spinwaves in thin films and applied the results to a 2-magnon model of magnetization damping. The results gave a good description of the angular dependence of the damping observed in our FMR experiments. This work was presented at the MMM/ INTERMAG conference in January, and published in the J. Appl. Phys. We are in the initial stages of extending our capabilities in ferromagnetic resonance to cover a wide range of frequencies and to enable local measurements of magnetic thin film properties. In their Head Metrology Requirements Roadmap, the National Storage Industry Consortium states a need for characterization of anisotropy field strength and easy axis dispersion in thin films as one of the industry's metrology needs. To accomplish these goals, we will use non-resonant strip line/slotline waveguides. Major equipment purchases have been made and initial assembly is underway. In our work on computational micromagnetics, we hosted two workshops, and we have planned a third. The first micromagnetics workshop was piggy backed on the MMM/INTERMAG Conference, as an evening session. The main result of this workshop was a pair of proposals for two new micromagnetic standard problems. These proposals were posted on our web site (http://www.ctcms.nist.gov/~rdm/mumag.html) for comment and then made official. At another evening session to be held in conjunction with the MMM meeting in Nov. 98, several papers will be presented on our standard problems. We will present our results for standard problem #2. A paper has also been submitted for publication in J. Appl. Phys. The second workshop was held in Boulder, CO in Aug. '98, for the purpose of describing NIST work in micromagnetics including our work on standard problems, and micromagnetic computation software.

Impact:

In response to our micromagnetic standard problems, there will be a special session, "Standard Problems in Micromagnetics," at the 43rd Annual Conference on Magnetism and Magnetic Materials (MMM98). This session will include five presentations on standard problem solutions, including three from problem #2, posted this year. In addition, European workers have submitted three solutions to standard problem #3 for display on our web page.

Outputs:

Publications:

McMichael, R. D., Stiles, M. D., Chen, P. J., and Egelhoff, W. F., Jr., "Ferromagnetic resonance Studies of NiO-Coupled Thin Films of $Ni_{80}Fe_{20}$," Phys. Rev. B, **58,** 8605 (1998).

McMichael, R. D., Stiles, M. D., Chen, P. J., and Egelhoff, W. F., Jr., "Ferromagnetic resonance

Linewidth in Thin Films Coupled to NiO," J. Appl. Phys., **83**, 7037 (1998).

McMichael, R. D., Chen, P. J., and Egelhoff, W. F., Jr., "Time and Temperature Dependence of High Thermal Stability in NiO/Co/Cu/Co/M Spin Valves," IEEE Trans. MAG, **34**, 897 (1998).

McMichael, R. D. and Donahue, M. J., "Head to Head Domain Wall Structures in Thin Magnetic Strips," IEEE Trans. MAG, **33**, 4167, (1997).

McMichael, R. D., Chen, P. J., and Egelhoff, W. F., Jr., "Anomalous Properties of Spin Valves and Elevated Temperatures," IEEE Trans. MAG 3589 (1997).

Presentations:

McMichael, R. D., "Problems in Measurements of Exchange Bias," Surface Science Lunch Bunch, October 1997.

McMichael, R. D. ,"Magnetization Dynamics," Guest Lecture, George Washington University, November 1997.

McMichael, R. D., "Standards and Infrastructure for Computational Micromagnetics," 1998 Assessment Panel Poster Presentation.

McMichael, R. D., "Standard Problems in Micromagnetics,"µMAG Workshop, Boulder CO, August 1998.

McMichael, R. D., "Time and Temperature Dependence of High Thermal Stability in NiO/Co/Cu/Co/M Spin Valves," Seventh Joint MMM-INTERMAG Conference, January 1998.

McMichael, R. D., "Ferromagnetic Resonance Linewidth in Thin Films Coupled to NiO," Seventh Joint MMM-INTERMAG Conference, January 1998.

McMichael, R. D., "Ferromagnetic Resonance of NiFe/NiO: Rotatable Anisotropy and Comparison With Hysteresis Loops," MMML '98, Vancouver, BC, June 1998.

Project Title: **MAGNETIC PROPERTIES OF NANOMATERIALS**

Investigators: R. D. Shull, A. J. Shapiro, R. D. McMichael, L. J. Swartzendruber, H. J. Brown, R. V. Drew, D. E. Mathews

Objectives:

This program focuses on developing an understanding of the magnetic behavior of low dimensional systems, as in systems wherein one or more characteristic dimension has been reduced to nanometer sizes. For these new materials, it is not known whether their exciting novel behavior is due to new physics or to a logical extension of large-size behavior to small dimensions. Consequently, implementation of this new type of material into marketable products is significantly delayed. NIST is providing the measurement science to answer this critical unknown and to identify where standards may be required as the field becomes more mature.

Technical Description:

Since the magnetic behavior of nanomaterials is largely unknown, much of the focus in this effort is directed toward measuring the magnetic characteristics of this new class of materials and checking if they are consistent with present theories explaining the behavior in conventional materials. For instance, a characteristic feature of conventional ferromagnets is the presence and morphology of magnetic domains in the material. Magnetic anisotropy is required for such a domain structure to exist, and conventional wisdom would argue that the normal sources of magnetic anisotropy would average to zero in nanocrystalline and nanocomposite materials. Consequently, efforts are ongoing to image the domain structure in these new materials and their dynamics if they exist. Imaging by means of a ferrofluid decoration technique at domain walls as well as by means of a magneto-optic indicator film (the MOIF technique developed in our laboratory in collaboration with a group from Chernogolovka, Russia) on co-sputtered Ag-Co nanocomposites and electrodeposited nanocrystalline Ni are being pursued. In addition, domain kinetics are being investigated in nanometer-thick bilayer combinations of materials with dissimilar magnetic characters, like antiferromagnetism and ferromagnetism with various degrees of magnetic softness.

In conventional materials, the material will magnetize along the easy axis of magnetization, so that in a polycrystalline material the magnetization will fluctuate on a scale of the material's grain size. Small angle neutron scattering (SANS) is a useful method for determining such magnetic fluctuations, and this technique was applied for the first time to a single phase nanocrystalline material, electrodeposited nanocrystalline Ni, in order to observe anticipated nanometer-scale magnetic fluctuations. This material is uniquely suited for this examination because it possesses few pores, and therefore most scattering at small angles was predicted to be magnetic in origin.

In order to probe the effects of interaction between ferromagnetic species of varying small sizes, an effort has been in progress to study the magnetic behavior of such "nanomagnets" placed in a non-magnetic matrix. One new attractive way to controllably create such a nanocomposite is via the use of a class of materials called dendrimers. These materials, which grow from a solution by a dendritic process with each new growing branch developing its own side branches which repeatably develop their own side branches, possess only certain regions where there is sufficient space available for fitting in foreign atoms. Consequently, in a CRADA with the Michigan Molecular Institute an attempt was made this year to create a magnetic dendrimer by placing Fe, Co and Ni atoms into the unique spaces provided by the dendrimer matrix.

It has been found that in many of the compounds in the Ba-Fe-Ti-O system, the Fe is physically localized into nanometer-sized regions of the crystal structure. However the magnetic character of these various structurally-related compounds has been found to vary by great amounts, possibly due to size and interaction effects. In order to understand this extreme variability, in collaboration with T. Vanderah (Ceramics Division), several Ba-Fe-Ti-O compounds are being investigated using Mössbauer spectroscopy. This technique is particularly useful for detecting size effects in the magnetic character of the material, and to detect variations in magnetic moment for different Fe atoms in the structure.

In conventional ferromagnets, normally when a non-magnetic species is added to that material, the magnetic coercivity will increase due to retardation of magnetic domain wall motion. In order to assess whether that large-scale phenomenon still persists at small dimensions, the magnetic behavior of thin films of Fe and Co containing varying amounts of nanometer-sized C60 carbon was investigated using magnetometry, MOIF imaging, and electron microscopy. This was a collaborative effort with Rice University, experts at working with C60 complexes.

Magnetic nanocomposites possessing superparamagnetism were discovered at NIST to possess enhanced magnetocaloric effects, a finding which has opened up the possibility for magnetic refrigeration devices operating at much higher temperatures and at much lower magnetic fields than were previously possible. In order to assist industry to utilize this new understanding, a small business innovation research (SBIR) award was provided to a small company to build an operating magnetic refrigerator at 77K using a permanent magnet field source.

Planned Outcome:

It is anticipated that as a result of this program, one will possess an improved prediction capability of magnetic properties of magnetic nanomaterials in different morphologies. Success in this area will provide for an improved capability to engineer magnetic properties by design. In addition, it is anticipated that improved characterization techniques for magnetic nanomaterials will be developed, thereby leading to improved quality control by manufacturers. Furthermore, it is anticipated that one will be better able to exercise control over the flux dynamics in small magnetic devices. By exercising leadership roles in the scientific community, these improved capabilities would be transferred to industry, e.g. as by the organization of and participation in workshops and symposia in the area, and by publications and presentations at national and international meetings.

External Collaborations:

In collaboration with the University of Toronto (U. Erb) and the University of Saarlandes (J. Weissmueller), SANS measurements were performed on electrodeposited nanocrystalline Ni. In this collaboration U. Erb provided the samples and J. Weissmueller analyzed the SANS measurements. In a collaboration with the Russian Academy of Sciences at Chernogolovka, Russia (V. Nikitenko), a special magnetic domain imaging technique called MOIF has been developed. This technique has been used jointly to image several nanocrystalline and nanocomposite materials. In collaboration with Rice University (R. Barrera and A. Chang), the magnetic character of thin films of Fe and Co containing carbon in the C60 form prepared at Rice University were investigated. In collaboration with the Michigan Molecular Institute, MMI, (L. Balogh) the magnetic behavior of several magnetic dendrimers prepared at MMI were studied. R. Shull was elected as the Vice Chairman of the International Committee on Nanostructured Materials. An interagency group, comprised of NIST, NSF, ONR, DOC/TA, AFOSR, NIH, and NASA, and with R. Shull as one of the organizing members, sponsored a report assessing the status and trends in nanoparticles, nanostructured materials, and nanodevices.

Accomplishments:

For the first time dendrimers were prepared containing small pockets of ferromagnetic species. The magnetic characters of the "magnetic dendrimers" varied with processing conditions, and with the particular magnetic species. In addition, an attempt to prepare the magnetic dendrimer containing a magnetic compound was only partially successful.

The remagnetization behavior of an epitaxial antiferromagnet/ferromagnet bilayer (possessing magnetic exchange anisotropy) was shown to be accomplished by two completely different processes for remagnetization in the two different directions. This is the first time such a phenomenon has been observed in these materials, and may help answer the 40 year old question of why the coercivity of such materials is so low.

The magnetic coercivity of thin films of Fe containing nanometer-sized C60 complexes of carbon was found to increase with the C60 content as in conventional ferromagnets. However, the magnetic coercivity of thin films of Co containing the C60 complexes "decreased" with increased C60 content!

Magnetic domains were for the first time observed in a pure nanocrystalline material, 20 nm grain size Ni, using a ferrofluid decoration technique. Their walls were observed to be microns in length and unusually smooth in contrast to the very angular appearing domain walls in large-grained materials.

NIST was joined by NSF, ONR, DOC/TA, AFOSR, NIH, and NASA in sponsoring a world review of the status and trends in nanoparticles, nanostructured materials, and nanodevices. Following several foreign site visits and a U.S workshop, a concluding U.S. workshop was held and a report written. Several agencies are now using this report to reassess where to put their available research dollars.

Impacts and Technical Highlights:

NIST is now considered a pre-eminent organization on magnetic nanocomposite properties. As a result, NIST is consulted by industry and other national research organizations in assisting them to take advantage of properties discovered in the area and to help establish a national policy toward research in the area.

As a result of NIST research on magnetic nanocomposite refrigerants, many groups around the world have initiated research activities in the area, including in China, Germany, France, Great Britain, Japan, and the United States. A special invited-speaker session at the March meeting of the American Physical Society was devoted to magnetic refrigeration prospects, with NIST being one of the 5 invited speakers.

Outputs:

Publications:

Weissmueller, J., Michels, A., Barker, J., Shull, R. D., McMichael, R. D. and Erb, U., “Measuring Magnetic Microstructure by Spin-Polarized Small-Angle Neutron Scattering,” J. Nanostructured Materials, Proc. of the 4th International Conference on Nanostructured Materials, Stockholm, Sweden, 6/14-6/20/98.

Nikitenko, V. I., Gornakov, V. S., Dedukh, L. M., Kabanov, Yu. P., Khapikov, A .F., Shapiro, A. J., Shull, R. D., Chaiken, A. and Michel, R. P., "Asymmetry of Domain Nucleation and Enhanced Coercivity in Exchange-biased Epitaxial NiO/NiFe Bilayers," Phys. Rev. B, **57**, R8111 (1998).

Nikitenko, V. I., Gornakov, V. S., Dedukh, L. M., Kabanov, Yu. P., Khapikov, A. F., Shapiro, A. J., Shull, R. D., Chaiken, A. and Michel, R. P., "Direct Experimental Study of the Magnetization Reversal Process in Epitaxial and Polycrystalline Films with Unidirectional Anisotropy," J. Appl. Phys. **83**, 6828 (1998).

Nikitenko, V. I., Gornakov, V. S., Dedukh, L. M., Khapikov, A. F., Shapiro, A. J., Shull, R. D., and Chaiken, A., “Asymmetry of the Remagnetization Processes in Exchange-Biased NiFe/NiO Bilayers,” Journal of Magnetism and Magnetic Materials (in press).

Vanderah, T. A., Wong-Ng, W., Toby, B. H., Browning, V. M., Shull, R. D., Geyer, R. G., and Roth, R. S., “Characterization of Ternary Compounds in the $BaO:Fe_2O_3:TiO_2$ System: $Ba_6Fe_{45}Ti_{17}O_{106}$ and $BaFe_{11}Ti_3O_{23}$,” J. Solid State Chemistry (in press).

Chopra, H. D., Hua, S. Z., Lashmore, D. S., Wuttig, M., Shull, R. D., Egelhoff, Jr., W. F., and Swartzendruber, L. J., “Magnetic Domains in Multilayers, Single Films, and Nanocomposites,” European Microscopy and Analysis, January, 27 (1998).

Shapiro, A. J., Shull, R. D., Gorshkov, N., and Zachariah, M. R., “Mössbauer Study of NaCl-coated Fe Nanoparticles,” Proceedings of ICAME’97, Rio de Janeiro, Brazil, 9/97.

Nikitenko, V .I., Gornakov, V. S., Dedukh, L. M., Shapiro, A. J., Shull, R. D., Chaiken, A., "Influence of Crystal Lattice Defects on Domain Wall Nucleation and Motion in Exchange-biased Films," MRS Symposium Proceedings (1998).

Nikitenko, V. I., Gornakov, V. S., Dedukh, L. M., Kabanov, Yu. P., Khapikov, A. F., Moffat, T. P., Shapiro, A. J., Shull, R. D., Shima, M., and Salamanca-Riba, L., "Direct Experimental Study of Microscopic Remagnetization Mechanism in Co/Cu Magnetic Superlattices," J. Magn. Magn. Mater. (in press).

Presentations:

*Shull, R. D., “Magnetic Dendrimers and Other Nanocomposites,” American Chemical Society Annual Meeting, Boston, MA, August 1998.

*Shull, R. D. “Magnetic Nanocomposites,” SURF Seminar, NIST, Gaithersburg, MD, June 1998.

*Shull, R. D., “Best in the World: Magnetic Materials Group,” NIST Seminar, Gaithersburg, MD, June 1998.

*Shull, R. D., “Magnetic Domains in Nanocomposite and Nanocrystalline Materials,” Fourth International Conference on Nanostructured Materials, Stockholm, Sweden, June 1998.

*Shull, R. D., “The Enhanced Magnetocaloric Effect of Magnetic Nanocomposites,” Tenth Canadian Materials Science Conference, Ontario, Canada, June 1998.

*Shull, R. D., “The Enhanced Magnetocaloric Effect of Magnetic Nanocomposites,” American Physical Society March Meeting, Los Angeles, CA, March 1998.

*Shull, R. D., “Magnetic Properties of Nanostructured Materials,” Florida Advanced Materials Chemistry Conference, Palm Coast, FL, March 1998.

*Shull, R. D., “New Directions in Magnetism: Magnetic Nanocomposites,” Colloquium Speaker, Materials Science Department, Georgia Institute of Technology, Atlanta, GA, January 1998.

*Shull, R. D., “Magnetic Measurement Issues for Nano-Materials,” DOE Workshop on Instrumentation and Measurement Issues for Nanometer Particles, Minneapolis, MN, December 1997.

*Shull, R. D., “Magnetic Properties of Nanocrystalline and Nanocomposite Materials,” Metals Science Seminar Speaker, Pennsylvania State University, University Park, PA, November 1997.

*Shull, R. D., "Magnetic Properties of Nanomaterials," Institute for Computational Sciences and Informatics Colloquia Speaker, George Mason University, Fairfax, VA, October 1997.

*Shull, R. D., "Magnetic Properties of Nanomaterials," Physics Department Colloquia Speaker, University of Pittsburgh, Pittsburgh, PA, October 1997.

*Shull, R. D., "Magnetic Nanocomposites," Materials Science and Engineering Department Seminar speaker, Virginia Tech, Blacksburg, VA, September 1997.

Shull, R. D., “Investigation of Elementary Events of Magnetization Reversal Processes in Exchange-Biased Bilayers,” American Physical Society March Meeting, Los Angeles, CA, March 1998.

Shull, R. D., “Measurement of Absolute Magnetic Moment,” American Physical Society March Meeting, Los Angeles, CA, March 1998.

Shull, R. D., “Magnetization Reversal Processes in Exchange-Biased Bilayers,” Gordon Research Conference on Magnetic Nanostructures, Ventura, CA, January 1998.

Shull, R. D., “Nanocrystalline and Nanocomposite Magnets”, DARPA Workshop on Advanced Magnets for Power Systems, Arlington, VA, October 1997.

* denotes Invited Presentations

Project Title: **MAGNETICS FOR STEEL PROCESSING**

Investigators: G. E. Hicho, L. J. Swartzendruber, and F. Biancaniello

Objectives:

This project seeks to provide U.S. industry with a scientific basis for the development of magnetic sensors to monitor the uniformity of mechanical properties of sheet steels as they are processed and to serve as a quality control device for the user. Correlations between magnetic and mechanical properties of steels provide the basis for on-line, non-destructive sensors for the mechanical properties.

Technical Description:

In the steel industry, or for that matter any industry that requires the mechanical testing of the finished product, tensile tests are required to verify the mechanical properties, e.g. the yield and ultimate tensile strengths. The costs to industry for testing are quite high, and a rapid and nondestructive procedure for determining these mechanical properties would result in substantial savings. Past work for the American Iron and Steel Institute (AISI) showed that magnetic sensors have considerable potential for providing rapid and nondestructive measurement of the yield strength of sheet steels. In this work, methods for rapidly obtaining a large number of magnetic properties were developed. Using these findings, the relationship between yield strength and magnetic properties for a plastically deformed low carbon steel was examined. Results indicate that the magnetic and mechanical properties of steels are closely related because the same defects which pin magnetic domain walls also pin for example, glide planes. The yield strength of a low carbon steel was modified by plastic deformation and then a number of magnetic properties, including the Barkhausen signal emission, coercive force, and relative permeability were obtained. Both the yield strength and coercive field were found to be linearly related to the square root of the plastic strain. The widths of the Barkhausen signal emission curve and the permeability curved increased significantly as the strain, i.e., rolling deformation, were increased, showing that the dislocation density is non-uniform on a micro scale. Observations of the domain pattern using a high resolution colloidal contrast technique revealed a fine intra-grain magnetic domain structure with the walls more effectively pinned in the highly strained samples. In order to better characterize the contributions of dislocations to both the magnetic and mechanical properties, studies are currently underway using carbon-free high purity steel.

Planned Outcome:

Upon completion of the project, a relationship similar to that of the Hall/Petch relationship is to be developed. In place of the grain size parameter in the Hall/Petch equation, a combination of magnetic properties obtained from a surface coil detector will be used to obtain the yield strength without performing a mechanical property test. Of considerable importance is the fact that such a test could be rapidly applied to large sheets of steel to determine the uniformity of properties. Similar relationships could be developed to obtain the ultimate tensile strength, hardness, or grain size. Being able to determine the mechanical properties from the magnetic response will be advantageous to the steel producers and users because costly tensile testing will be eliminated and the amount of scrap steel will be considerably reduced, thereby producing savings in both costs and energy usage.

External Collaborations:

Professor Harsh D. Chopra of Dartmouth College is a co-investigator on this project. He has performed the domain size/dislocation determination on the strained low carbon steel. NIST has provided strained samples and Professor Chopra has used a high resolution interference colloidal contrast technique to reveal the fine intra-grain magnetic domain structure. We are also cooperating with G. Cohen and M. Melamud who have formed a company based in Israel for the production and sale of systems suitable for use on steel wire.

Accomplishments:

A large number of tensile samples, suitable for magnetic and mechanical measurements, of carbon-free pure steel were produced. These samples were subjected to various levels of strain in order to develop dislocation networks which will both change their magnetic and mechanical properties. The magnetic hysteresis, magnetic Barkhausen signal, dislocation structure and density, and domain dynamics were measured for three levels of plastic strain.

Impact:

Commercial magnetic property and Barkhausen systems are currently available for use in industry. The results of this project will aid in their improvement and application to a wider range of testing and processing of steel materials.

Project Title: **MAGNETIC PROPERTIES OF SUPERCONDUCTORS**

Investigators: L. J. Swartzendruber, L. H. Bennett, R. D. Shull, F. W. Gayle, A. J. Shapiro, M. J. Donahue, D. E. Mathews, H. J. Brown, R. V. Drew

Objectives:

This project is aimed at improving the usefulness of current magnetic measurements and developing new measurements for superconductors. Support is provided to the Ceramics Division in the determination of phase diagrams important for the processing of high temperature superconductors. Investigations are made of the magnetic properties of new superconducting materials and of materials prepared under varying processing conditions. Relationships between various microstructural features such as inclusions, compositional modulation, and precipitates, and the flux pinning in high temperature superconductors are sought.

Technical Description:

In collaboration with scientists from universities, industry, and other Divisions at NIST, superconducting materials are prepared and their microstructure and magnetic properties determined. The effects of impurities which are incorporated during processing of superconductors, or which are intentionally added to modify the properties, are also investigated. Measurements performed include ac and dc magnetization as a function of temperature and applied magnetic field, hysteresis loops, flux penetration and viscosity, critical fields, and critical temperatures. Microstructure studies are performed using scanning and transmission electron microscopy. Emphasis is on high temperature superconducting materials.

Planned Outcome:

The ability of manufacturers and researchers to interpret magnetic measurements in high-temperature superconductors will be improved. Manufacturers will be better able to characterize and control the characteristics and quality of material they produce resulting in improved material at a lower cost.

Accomplishments in FY 1998:

The magnetic properties of the so called brown phase (BaR_2CuO_5, R=La,Nd) used for flux pinning in BYCO high temperature superconductors were measured. A new superconducting phase in the ZrRh alloy system was discovered.

Impact:

Phase diagrams and relationships determined at NIST are being used by industry to fabricate improved high temperature superconducting materials. Commercial devices using high temperature superconductors are currently available. Many of these devices are being fabricated using laser ablation, a method which was developed by NIST in cooperation with the Johns Hopkins Applied Physics Laboratory. Our explanation of “inverse levitation” in terms of the effect of flux pinning on the magnetic properties of high temperature superconductors opens up many possibilities for the use of these materials in devices. An explanation of the reason for a measurement artifact, often referred to as a “positive Meissner effect,” and the effect of impurity compounds on magnetic measurements of superconductors enables better interpretation of magnetic measurements of high temperature superconductors.

METALS DATA AND CHARACTERIZATION

Predicting the performance of metals during use and their behavior during processing requires a detailed body of information on their physical properties and microstructure. The value of this information is greatly enhanced when it is developed within the context of models or theories which describe how the measured properties of a metal will vary with changes in composition, microstructure, temperature, geometry, or other parameters. The Metals Data and Characterization Program includes activities which refine the technology for measuring the properties and behavior of metallic materials, and which correlate these properties and behavior to alloy microstructures.

The large majority of metals are used in applications based on their mechanical properties, with other applications based on electronic, magnetic, optical, or other functional properties forming smaller but nonetheless critical markets. Whatever the application, satisfactory long term performance of metallic components demands microstructural and chemical stability, sometimes in the face of harsh environments. This program identifies those processing, microstructure, and properties characterizations which are critical to U.S. industry for both the processing and the performance of metals, and carries them out within the context of the NIST mission of providing data and standards. A significant part of the program is the development and use of advanced microscopy techniques to characterize the microstructures which form the basis of the measured properties.

Recent examples of the mechanical, thermophysical, and microstructural measurements carried out under this program include:

- Precision measurements of Rockwell Hardness, the primary parameter used to specify the mechanical properties of metals and alloys, are leading to the establishment of traceable national hardness standards. Calibrated test blocks have been issued, and together with national standards for measurement and calibration procedures, these will facilitate the acceptance of a wide range of US products in international markets, as well as minimizing product-acceptance disputes in domestic trade.

- Measurements and analysis of thermal transport through thin film and multilayer thermal barrier coatings are helping designers understand heat flow in systems ranging from integrated circuits to turbine engines. The measurements have extended from room temperature to 2000°C and have been applied to special multilayer materials fabricated at NIST as well as thermal barrier multilayer coatings fabricated by members of an industrial consortium.

- Special microscopy techniques, including high resolution transmission electron microscopy, electron holography, and scanning acoustic microscopy are being used to reveal the finest details of atomic structure, interface reactions, and residual stress in advanced materials. The systems under study include novel phases with potential microwave applications, electronic devices and interconnects, and nanolaminate multilayers.

Project Title: **HIGH-RESOLUTION THERMOPHYSICAL MEASUREMENTS DURING PULSE-HEATING**

Investigators: J. R. Manning, D. Basak, K. Boboridis, W. J. Boettinger, and J. L. McClure

Objectives:

The objective of this project is to develop and use millisecond- and microsecond-resolution techniques for the accurate measurement of thermophysical properties of high-temperature materials in their solid and liquid phases in the temperature range 1300K to 4000K.

Technical Description:

This project focuses on application of pulse-heating techniques to measure thermophysical properties of materials at high temperatures (1300K to 4000K). Properties to be measured are enthalpy, melting points of pure elements, melting ranges and melting behavior in alloys (liquidus, solidus and related quantities), specific heat capacity, heat of fusion, and electrical resistivity. Advances in high-speed temperature measurement and extension of measurement ranges well above the melting temperatures of high-melting-point metals and alloys are technical goals in this work.

Two separate pulse-heating systems are in operation. One uses electric current from a battery discharge to heat wires or tubular refractory metal specimens to their melting points in a fraction of a second and makes accurate thermophysical measurements with millisecond resolution during the pulse heating. A second more advanced system applies a capacitor discharge to heat metals up to and above their melting points in a fraction of a millisecond and makes measurements on a microsecond time scale during heating. Since the liquid in the melted wire maintains the original cylindrical configuration for ten to a hundred microseconds after melting, this ultra-fast system allows measurement of the liquid properties for hundreds of degrees above the melting point.

An essential feature of these systems is extremely fast electronic measurement and control, particularly very rapid temperature measurement. Advanced pyrometry is used to measure radiance temperature and polarimetry to measure emissivity. This combination allows very rapid measurement of true temperature even when black body conditions cannot be achieved.

Investigations are underway to apply this technique not only to pure metals but also to alloys. Whereas each pure elemental metal has a single sharply-defined melting point, alloys have a temperature range between the solidus and liquidus temperatures where melting takes place. Experiments and analyses are being done to define the ways in which this range influences the present experiments and determine the effect of heating rate, grain size and other features on the pulse heating results.

Planned Outcome:

Pulse-heating will be developed as an innovative rapid means of making accurate thermophysical measurements at high temperatures. Capabilities will be developed to measure liquid alloy thermophysical properties for hundreds of degrees above their melting points. The resulting systems will be applied to measure data on liquid superalloys needed for casting of aerospace alloys. Pyrometric and polarimetric systems will be combined to provide new capabilities in the measurement of true temperature at rapid rates, thus significantly advancing the science of temperature measurement, important in many dynamic processes. Accurate bench-mark thermophysical data on selected key materials will be generated, thus contributing to high temperature thermophysical standards and greater reliability in high temperature alloy phase diagrams needed for processing these alloys.

External Collaborations:

A laser polarimeter used for the measurement of normal spectral emissivity of specimens during pulse heating was developed in collaboration with Containerless Research, Inc. Collaboration is continuing in applying this technique to microsecond applications. Information was disseminated to members of the recently completed NIST/Industry Consortium Project on Casting of Aerospace Alloys, including General Electric, Pratt & Whitney and Howmet, on properties of alloys used in aircraft engines. Plans were made for continued collaboration with NASA and industrial members of the aerospace industry to provide needed metal and alloy property measurements.

Accomplishments:

The design and construction of a novel microsecond-resolution laser polarimeter for normal spectral emissivity measurements of liquid metals and alloys were completed in collaboration with Containerless Research, Inc. The polarimeter will permit the determination of true temperature from the measured radiance temperature. Preliminary tests successfully demonstrated the applicability of the laser-polarimetry technique to measurements in the liquid state.

A slow-heating system using a programmable power supply was developed. This permits application of slower heating rates, 0.1 to 1000 K/s, to study phase transformations and melting behavior in alloys.

The effect of heating rate and grain size on the melting behavior of the alloy 53Nb-47Ti was established. A diffusion-based model for melting was developed. The predictions of the model compared favorably with the experimental results.

Radiance temperatures (in the wavelength range 521 to 1500 nm) of iridium and rhenium at their melting points were measured. This work is needed for the establishment of high temperature reference points.

Specific heat, enthalpy, normal spectral emissivity, hemispherical total emissivity and electrical resistivity of the alloy 53Nb-47Ti were deterrmined in the temperature range 1600 to 2000 K.

Impacts:

A high-speed (millisecond resolution) laser polarimeter, developed jointly by NIST and

Containerless Research, Inc. (CRI) for this project, was commercialized by CRI and was successfully marketed internationally. This novel and unique instrument, which is capable of measuring accurately the normal spectral emissivity of a specimen surface, thus providing information on true temperature without the requirement of a black body configuration, significantly simplifies accurate measurements of high temperatures.

Thermophysical properties of alloys such as IN 718, measured earlier in this project, are now available to members of the NIST/Industry Consortium on Casting of Aerospace Alloys and have been used by them in their simulations.

Outputs:

Publications:

Matsumoto, T., and Cezairliyan, A., “A Combined Transient and Brief Steady-State Technique for Measuring Hemispherical Total Emissivity of Electrical Conductors at High Temperatures: Application to Tantalum,” *International Journal of Thermophysics*, **18**, 1539-1556, (November 1997).

Josell, D. and Cezairliyan, A., “Thermal Diffusion Through Multilayer Coatings: Theory and Experiment,” *International Journal of Thermophysics*, **19,** 525-535 (1998).

Cezairliyan, A., Krishnan, S., Basak, D., and McClure, J.L. “Measurement of the Specific Heat Capacity of Molybdenum in the Range 2000 to 2800 K by a Millisecond-Resolution Pulse Heating Technique,” *International Journal of Thermophysics*, **19**, 1267-1276 (1998).

McClure, J. L., Boboridis, K., and Cezairliyan, A., “Radiance Temperatures (in the Wavelength Range 521-1500 nm) of Iridium and Rhenium at their Melting Points by a Pulse-Heating Technique,” *International Journal of Thermophysics*, in press.

Oral Presentations:

Basak, D., “Thermophysical Properties Measurements,” Final Annual Meeting, Consortium of Casting of Aerospace Alloys, NIST, May 1998.

Boboridis, K., “Thermophysical Property Measurements on Pulse-Heated Materials: Application to Niobium,” 5th International Workshop on Subsecond Thermophysics, Aix-en-Provence, France, June 1998.

Basak, D., “Effect of Heating Rate on the Melting Behavior of the Alloy 53Nb-47Ti (mass%) in Rapid Pulse-heating Experiments,” 5th International Workshop on Subsecond Thermophysics, Aix-en-Provence, France, June 1998.

Manning, J. R. and Krishnan, S., “Thermophysical Properties at High Temperature Liquid Metals and Alloys,” Microgravity Materials Science Conference, Huntsville, AL, July 1998.

Posters:

McClure, J. L., Boboridis, K., and Cezairliyan, A., "Radiance Temperatures (in the Wavelength Range 521-1500 nm) of Iridium and Rhenium at Their Melting Points by a Pulse-Heating Technique," 5th International Workshop on Subsecond Thermophysics, Aix-en-Provence, France, June 1998.

Project Title: **MECHANICAL AND THERMAL PROPERTIES OF MULTILAYERED MATERIALS**

Investigators: D. Josell and T. Foecke

Objectives:

This project seeks to quantify the effect of high densities of interfaces on the thermal transport and mechanical properties of materials. In particular, evaluating the impact of interface thermal resistance on the conduction of heat through multilayer thermal barriers for the power generation industry is the major goal of NIST's thermal transport studies. Evaluating the effect of high interface densities on the stability, creep and yield behaviors of multilayer materials is the goal of the studies of mechanical properties.

Technical Description:

Thermal barrier coatings protect engine parts from the elevated temperatures of the combustion process and increase the efficiencies of turbine engines by raising their operating temperatures. It has been proposed that the presence of the numerous interfaces in multilayer thermal barrier coatings will decrease their thermal conductivity, making multilayer coatings more effective thermal barriers than the materials from which they are manufactured. We have been working to quantify the interface thermal resistance through measurements of a related property, the thermal diffusivity. Thermal diffusivity measurements of multilayer thermal barrier coatings are being made at elevated temperatures, to simulate turbine engine operating conditions, using a pulsed laser (< 100 ns) heating technique.

In a related effort, we have been studying mechanical properties of multilayer materials. This work is closely linked to the thermal transport studies because multilayer materials can only be practical if they are structurally sound and maintain their finely layered structures during use. Our work in this area includes tensile studies of free standing multilayer thin films to measure the relationship between layer thickness and yield stress. Additional efforts are geared toward modeling the mechanical properties of multilayer materials by both continuum and molecular dynamics methods. Finally, because capillary instabilities associated with the internal interfaces lead to degradation of the layered structure at the elevated temperatures where thermal barrier coatings are used, we are conducting creep studies to measure the capillary forces associated with the internal interfaces.

Planned Outcome:

The thermal transport studies will provide an upper bound for the contribution of internal interfaces to the thermal resistance of thermal barrier coatings. This information should assist our industrial partners in deciding whether they should continue to pursue the use of multilayer thermal barrier coatings. The modeling efforts will help to understand the critical factors for controlling the mechanical behavior of multilayer materials. The experimental data provided by the mechanical and stability studies will help to determine which models relating layer thickness and interface free energy to the mechanical properties and stability of multilayer materials are most accurate.

External Collaborations:

T. Foecke collaborates with Professor P. Anderson of Ohio State University, modeling the the results of in-situ transmission electron microscopy deformation experiments on multilayered materials using continuum techniques. He also collaborates with Professor D. Farkas of Virginia Technical University to model these results using molecular dynamics techniques.

D. Josell collaborates with Professor T. Weihs of The Johns Hopkins University (JHU) in Baltimore, Maryland studying interfacial free energies and the stability of multilayer materials. He also collaborates with Professor D. Shechtman of the Technion in Haifa, Israel studying the microstructures and mechanical properties of multilayer materials. This effort is funded by a jointly held grant from the U.S.-Israel Binational Science Foundation. D. Josell collaborates with Professor R. Cammarata of JHU to study the effect of interface stress in multilayers with extremely thin layers. As part of all of this study, multilayer specimens are fabricated at NIST for x-ray diffraction studies at JHU. D. Josell also collaborates with a consortium consisting of The Electric Power Research Institute, Battelle, Howmet and Solar Turbine. The consortium provides thermal barrier coatings; their thermal transport properties are evaluated by D. Josell using his pulsed laser heating system.

Accomplishments:

D. Josell fabricated specimens for the different studies of multilayer materials using his electron beam evaporator deposition system. Measurements were made of thermal conduction through multilayer thermal barrier coatings fabricated by D. Josell as well as provided by the industrial consortium.

A wafer curvature system was fabricated for the study of zero creep of multilayers at elevated temperatures. This system, fabricated by D. Josell with Professor T. Weihs and located at JHU, will be used to measure the interface free energy of different multilayer materials for comparison to the results of multilayer stability studies.

Impact:

The results of individual experiments to determine the thermal transport properties of multilayer thermal barrier coatings have been provided to our industrial consortium partners. These results will help them decide whether they should continue to pursue the study of these materials for use as thermal barrier coatings in engines.

Outputs:

Publications:

Josell, D., Gonzales, E. J., and White, G. S., “Correcting Errors in the Theory for Mirage-Effect Measurements,” J. Mat. Res. **13**, 1117 (1998).

Josell, D., Cezairliyan, A., and Bonevich, J. E., “Thermal Diffusion Through Multilayer Coatings: Theory and Experiment,” Intl. J. Thermophysics **19**, 525 (1998).

Josell, D., Carter, W. C., “Creep and the Stability of Multilayers,” Mat. Res. Soc. Symp. Proc. **505**, 157 (1998).

Tepper, T., Shechtman, D., van Heerden, D., and Josell, D., “Allotropic Phase Formation in Ti/Zr Multilayers,” Mat. Lett. **35**, 100 (1998).

Josell, D., van Heerden, D., Read, D., and Shechtman, D., “Tensile Testing Low Density Multilayers: Aluminum/Titanium,” J. Mat. Res., (in press).

Josell, D., van Heerden, D., Shechtman, D., and Read, D., “Mechanical Properties of Multilayer Materials,” J. Nanostr. Mat., (in press).

Josell, D., Carter, W. C., and Bonevich, J. E., “Stability of Multilayer Structures: Capillary Effects,” J. Nanostr. Mat., (in press).

Foecke, T., Kung, H., “MRS Bulletin,” Guest Editors (in press).

Gavens, A. J., van Heerden, D., Foecke, T., Weihs, T. P., “Evaluation of Vapor Deposited Nb/Nb_5Si_3 Microlaminates,” Mat. Sci. Eng. A, (in press).

Presentations:
Foecke, T., “Deformation Mechanisms in Metallic Nanolaminates,” invited talk at Carnegie Mellon University, Pittsburg, PA, February, 1998.
Foecke, T., “Hardness of Nanolaminates: A Dislocation Mobility Approach,” invited talk at APS March Meeting, Los Angeles, CA, March 1998.

Foecke, T., “Deformation Mechanisms in Metallic Nanolaminates,” invited talk at Virginia Polytechnic University, Blacksburg, VA, March, 1998.

Josell, D., “Creep and the Stability of Multilayers,” invited talk at Materials Research Society Fall Meeting, Boston, MA, December, 1997.

Josell, D., “Thermal Transport Through and The Mechanical Properties of Multilayer Materials,” invited talk at Harvard University, Cambridge, MA, March, 1998.

Josell, D., “Stability of Multilayer Structures: Capillary Effects,” talk at 4th International conference on Nanostructured Materials, Stockholm, Sweden, June, 1998.
Josell, D., “Mechanical Properties of Multilayer Materials,” poster at 4th International conference on Nanostructured Materials, Stockholm, Sweden, June, 1998.

Project Title: **ROCKWELL HARDNESS STANDARDS**

Investigators: S. R. Low, D. J. Pitchure, W. S. Liggett (ITL), J.-F. Song and T. V. Vorburger (MEL), R. J. Gettings (SRMP/TS), C. D. Faison (NVLAP/TS), C. D. Ehrlich (TS), and T. R. Shives (under contract to NVLAP)

Objectives:

The primary goals of this project are to provide U.S. industry with a means to make hardness measurements and calibrations with traceability to national standards, and to facilitate acceptability of American hardness measurements worldwide.

Technical Description:

In today's metal products and materials industries, hardness testing is the most widely used mechanical test for quality control and acceptance testing. Even so, worldwide unification and standardization of any hardness scale is yet to be accomplished. Furthermore, prior to the start of this project, no Standard Hardness Reference Scale within the United States was traceable to national standards. Historically, manufacturers of hardness equipment have established their own hardness calibration blocks and internal standard scales, assigning hardness values to each block based only on past performance of similar blocks without traceability to fundamental units of measure. Within the U.S., the consequence of this situation has been that the defined hardness scales of these different calibration laboratories have shown significant variability between laboratories and even within the same laboratory over time. This has led to frequent disputes between materials suppliers and customers and, in some instances, has made U.S. exports unacceptable in other countries.

The level of foreign market business at risk for the U.S. hardness industry alone is in the \$10 - \$20 M range. However, a much greater concern is that many regulatory agencies in foreign markets are now mandating that, for a product to be acceptable for importation, a well documented chain of measurements must exist from the point of use to the exporter's national measurement laboratory. For this reason, U.S. industries that require hardness testing as part of their acceptance criteria may soon experience artificial trade barriers to their products. The most significant impact will be for U.S. industries requiring hardness testing in their product specifications. These industries are essentially any metals manufacturing mill or heat treatment facility, or any manufacturer of products fabricated of a metallic materials, such as fasteners, automobiles, and aircraft. The value of goods affected could be in the billions of dollars.

Starting with the Rockwell hardness scales, the NIST Metallurgy Division in collaboration with the Manufacturing Engineering Laboratory (MEL), the Information Technology Laboratory (ITL), and the National Voluntary Laboratory Accreditation Program (NVLAP) and the Standard Reference Materials Program (SRMP) of Technology Services (TS) has undertaken to develop or assist in developing the components needed to establish a traceability system for Rockwell hardness measurements in this country. These essential components are: (1) standardized Rockwell hardness scales; (2) certified Rockwell hardness transfer standards; (3) a national laboratory accreditation program; and (4) internationally accepted national test method standards. The standardization of the Rockwell hardness scales and the development of transfer standards will be accomplished through the use of a precision, dead-weight hardness machine which was installed at NIST in 1992. The standardizing machine is essentially free from random and systematic errors in force, force application rate, and displacement, and is based on fundamental units of measurement traceable to NIST. The dead-weight tester also uses geometrically correct indenters certified by the Surface and Microform Metrology Group of MEL.

Standardization of the national Rockwell C hardness scale (HRC), identified as being in greatest demand by U.S. companies, has been accomplished in collaboration with MEL, and HRC transfer standards have been calibrated with the assistance of the statistical expertise of ITL. International HRC scale intercomparisons with countries in Europe and Asia have been made to ensure compatibility with the Rockwell C hardness scales of other countries. Certification of Rockwell hardness indenters as NIST Standard Reference Materials is also currently under development in cooperation with MEL.

A laboratory accreditation program for hardness calibration laboratories is being developed with the assistance of the NVLAP office, and with the cooperation and assistance of the American Society for Testing and Materials (ASTM). The hardness calibration laboratories include hardness machine manufacturers, indenter manufacturers, test block standardization laboratories, and companies that perform field calibrations of hardness machines.

NIST is assisting ASTM in revising their current Rockwell hardness Test Method to include requirements for obtaining traceability to the U.S. national hardness scales. This is being accomplished through leadership roles in ASTM and the International Organization for Standardization (ISO) hardness committees.

These efforts are expected to be expanded to the other Rockwell scales and other hardness tests in the coming years. The goal is to create a traceability system for all indentation hardness measurements used in the United States.

In addition to the effort to standardize the US hardness scales, NIST, as Secretariat of the International Organization of Legal Metrology (OIML) for hardness, is currently revising the OIML Recommendations for hardness testing. These test standards are currently not in wide use, but will provide a mechanism for legal metrology in the area of hardness testing for those countries requiring such a system. The revision of the Recommendations has begun starting with the Rockwell hardness test. This effort is being accomplished with the assistance of ASTM.

NIST is a member of an ad hoc working group on hardness (AHWGH) under an agreement with the International Committee of Weights and Measures (CIPM) to investigate the present state and needs for international comparison of hardness standards and to report to the Committee on the most appropriate platform for comparisons. This working group is in close communication with the hardness technical committees OIML/TC10/SC5, ISO/TC 164/SC3 and IMEKO/TC5.

Planned Outcome

It is anticipated that this program in developing hardness standards for the mechanical properties of commodity metals but will continue to evolve with the changing needs of U.S.

industry and technology. The short term goals are to standardize each of the Rockwell hardness scales, and provide a means to transfer the national hardness scales to industry through the production and sale of calibrated SRM hardness test blocks and certified indenters. An accreditation program for hardness calibration laboratories will be developed to be managed by NVLAP. ASTM hardness test method standards will be revised to reflect the use of the NIST SRMs and NVLAP programs. OIML recommendations will be revised for international use.

External Collaborations

The NIST Metallurgy Division collaborates extensively with the U.S. hardness industry and the manufacturing industries that use hardness testing in the production of their products. The collaboration is both direct, such as in the procurement of the uncalibrated hardness blocks for SRM production, and through ASTM, for example in their efforts to revise the test method standards. S. Low chairs three ASTM hardness task groups including Task Groups on Traceable Hardness Standards, and the Technical Advisory Group to ISO on Hardness. He is also the Head of the U.S. Delegation to ISO for Hardness Testing and chairs the National Working Group for OIML TC10/SC5 Hardness.

Accomplishments:

Approximately 100 test blocks at each of three levels of the Rockwell C scale (HRC) have been calibrated and delivered to the Standard Reference Materials Program and are available for purchase. Approximately half of the test blocks in stock were sold in the first four months.

A Hardness Standardization Workshop was held at NIST which included presentations by sixteen speakers from NIST, US industry, and international hardness standardizing laboratories. The purpose of the workshop was to inform and update U.S. industry on issues related to the standardization of indentation hardness testing. Two hundred persons attended the workshop including representatives of hardness equipment manufacturers, hardness calibration laboratories, users of hardness testing, and international hardness standardization laboratories.

The draft Technical Requirements were completed for use in the NVLAP accreditation program for hardness calibration laboratories.

Standardization of the Rockwell B scale was completed.

NIST was the first laboratory to participate in a worldwide intercomparison of Rockwell hardness scales that use diamond indenters.

Impact:

It is too soon to measure the impact from the release of the NIST SRMs for the Rockwell C Scale. However, the positive effect of NIST’s involvement in the standardization of the U.S. hardness scales can be evidenced by the many industry requests for information concerning the SRM test blocks, the movement of ASTM towards revising the Rockwell hardness test method standard, industry requests to have a hardness calibration laboratory accreditation program developed, and the introduction and expanding use of uncertainty in hardness measurements.

Outputs:

Publications:

Low, S. R., Liggett, W. S., and Pitchure, D. J, “A New Method of Certifying Standardized Rockwell Hardness Test Blocks,” Proceedings of HARDMEKO ’98 International Symposium on Advances in Hardness Measurement, June 1998.

Song, J., Low, S., Pitchure, D., and Vorburger, T., “Advances in NIST Standard Rockwell Diamond Indenters,” Proceedings of HARDMEKO ’98 International Symposium on Advances in Hardness Measurement, June 1998.

Presentations:

Low, S., “Standardization of Rockwell Hardness,” NIST Hardness Standardization Workshop, Gaithersburg, MD, June 1998.

Low, S., “The Use of Rockwell SRMs and Uncertainty in Hardness Measurements,” NIST Hardness Standardization Workshop, Gaithersburg, MD, June 1998.

Low, S., “A New Method of Certifying Standardized Rockwell Hardness Test Blocks,” HARDMEKO ’98 International Symposium on Advances in Hardness Measurement, Beijing, China, September 1998.

SRMs in Production:

SRM#2810	Rockwell C Scale Hardness - Low Range
SRM#2811	Rockwell C Scale Hardness - Mid Range
SRM#2812	Rockwell C Scale Hardness - High Range

SRMs Under Development:

SRM#2809	Rockwell Diamond Indenter
SRM#2814	Rockwell B Scale Hardness - Low Range
SRM#2815	Rockwell B Scale Hardness - Mid Range
SRM#2816	Rockwell B Scale Hardness - High Range

Rockwell N Scale Hardness

Rockwell T Scale Hardness

Project Title: **MAGNETIC PROPERTIES AND STANDARD REFERENCE MATERIALS**

Investigators: L. J. Swartzendruber, R. D. Shull, E. Della Torre, A. J. Shapiro, D. E. Mathews, R. V. Drew, and L. H. Bennett

Objectives:

The main objective of this project is to improve the understanding of the measurement process in magnetic materials in order to characterize these materials accurately and efficiently. This will enable industry to develop and produce better materials at a lower cost. This includes the development of standard reference materials where appropriate.

Technical Description:

Magnetic properties of materials important to the scientific and industrial community are determined and methods for improved measurements of these properties are developed. Standard reference materials for the calibration of instruments used in the measurement of magnetic properties are also developed and produced. In addition, methods are determined for characterizing the accommodation and "aftereffect" properties in materials used in magnetic recording and permanent magnets. In cooperation with industry, the magnetic properties of materials used in the control of flux in devices used for induction heating are also determined. Models are also developed for determining what parameters are necessary to fully characterize magnetic materials, including their magnetostriction and time dependence. These parameters can then be used in models which correctly predict the behavior of the magnetic material under actual operating conditions.

Planned Outcome:

The expected results of this activity are fourfold: (1) improved characterization of magnetic recording media resulting in lower overall net cost per unit of storage, (2) improved characterization of permanent magnets and other materials for magnetic devices resulting in more efficient use of such materials, (3) improved calibration of magnetic measurement instruments giving NIST traceability at lower costs, and (4) facilitation of commerce in magnetic materials through improved agreement between producer and consumer on the measurements of magnetic properties.

Accomplishments:

Improved models for the complex aftereffect behavior in magnetic recording materials were developed and experimentally tested in two types of media used by the recording industry. Improvements and extensions to the Preisach model were developed for use with magnetostrictive materials. Much of this work was the result of collaboration with E. Della Torre, George Washington University, during his sabbatical year at NIST. Equipment was collected and fixturing initiated to enable the sensitive measurement of magnetostriction. Computer programs were developed for use with the absolute moment measurement system.

Temperature control and magnetic shielding were also added to the electrobalance of this to improve measurement stability, and a set of high purity Ni balls suitable for issue as standard reference materials was fabricated. A series of these balls has been measured and statistical analysis of their properties is now under way.

External Collaborations:

We are collaborating with several companies which produce magnetic measurement equipment. We also collaborate with researchers at George Washington University.

Impacts:

A commercial instrument maker is developing software for commercial applications based on cooperative work between NIST and George Washington University.

Output:

Publications:

Swartzendruber, L.J, Bennett, L.H., Della Torre, E.,. Brown, H. J., and Judy, J. H., "Behavior of Magnetic Aftereffect Along a Magnetization Reversal Curve in a Metal Particle Recording Material," accepted for publication in Proceedings of the April 1998 meeting of the Materials Research Society.

Della Torre, E., Bennett, L. H., and Swartzendruber, L. J., "Modeling Complex Aftereffect Behavior in Recording Materials Using a Preisach-Arrhenius Approach," accepted for publication in Proceedings of the April 1998 meeting of the Materials Research Society.

Reimers, A. and Della Torre, E., "Fast Preisach Based Magnetostriction Model for Highly Magnetostrictive Materials," accepted for publication by the IEEE Transactions on Magnetics, 1998.

Hua, S. Z., Lashmore, D. S., Swartzendruber, L. J., Egelhoff, Jr., W. F., Raj, K., and Chopra, H. D., "Observation of Domain Dynamics in Giant Magnetoresistive Co-Cu Based Polycrystalline Multilayers," J. Appl. Phys. **81**, 4582 (1997).

Swartzendruber, L. J., Bennett, L.H., Vajda, F., and Della Torre, E. "Relationship Between the Measurement of Accommodation and After-Effect," Physica B. **223**, 324, (1997).

Swartzendruber, L. J., Hicho, G. E., Biancaniello, F. , Shull, R.D., and Shapiro, A.J., "Determination of Austenite/Ferrite Ratios in Stainless Steels Using the Moessbauer Effect," Proceedings of the International Conference on Applications of the Moessbauer Effect, September 1997.

Project Title: **PERFORMANCE OF STRUCTURAL MATERIALS**

Investigators: R. B. Clough, R. J. Fields, T. Foecke, D. A. Shepherd, and J. H. Smith

Objectives:

This project uses the expertise and facilities of the Materials Performance Group to provide assistance to U.S. industry and other Federal agencies in the broad area related to the performance of structural metals and alloys. Outputs include test methods and data.

Technical Description:

The cost to U.S. industry of failures of structural materials is extremely large. For example, a study by NIST and Battelle Columbus Laboratories estimated the cost of materials fracture in 1982 dollars to be $119B per year. Because metals are so heavily relied on for structural strength, their failures were found to contribute substantially larger costs than those of non-metals, and much of the cost was associated with the transportation and construction industries (motor vehicles, aircraft and the building of homes and non-residential construction).

In FY 98, work was conducted on five sub-projects:

Stress Rupture of Lead-Free Plumbing Solders

The 1986 amendments to the Safe Drinking Water Act prohibited the use of lead-containing solders in potable water systems. Although there are thirteen lead-free solder alloys contained in ASTM's Standard Specification for Solder Metal (B32), the current ASME Codes specify joint strengths for only one lead-free solder, Alloy Sb5 (95Sn-5Sb). The joint strength specified for this alloy is based on limited data reported by NIST in the early 1940s, so that unusually large safety factors are imposed. There has been a lack of data on which to base design codes made with the other lead free solders.

This work is being carried out in collaboration with the Copper Development Association (CDA) and with the B16 Committee of ASME, and is designed to establish permissible pressures for copper tubes joined by lead-free solders. In the NIST studies, stress rupture tests are being conducted on soldered sleeve joints in copper tube for times up to one year at temperatures in the range 100-250° F. In addition to Alloy Sb5, two other lead-free solders are being tested, namely Alloy E (4Cu-0.5Ag-bal.Sn) and Alloy HB (5Sb-0.3Ag-3.5Cu-1Ni-bal.Sn). The testing program is being supported by studies of the mechanism of failure to assist in statistical analysis of the data and in life prediction modeling.

A new statistical method was developed to obtain ermissible stresses from the stress rupture curves. The sets of data, in the form of stress rupture lifetime curves and permissible stresses extracted from these, were given to the Copper Development Association and accepted by ASME Sub-Committee B16. These data will serve as the basis for new potable water pipe fitting codes being drawn up by this subcommittee.

Structural Integrity of High Pressure Gas Cylinders

This work provides technical support for the U.S. Department of Transportation (DOT), which has the responsibility for developing and enforcing the regulations which cover the design, manufacture and testing of cylinders for the transportation of compressed gases. The focus in this activity is the development of design standards for advanced cylinders and of advanced testing procedures for high pressure cylinders. High pressure cylinders are currently constructed of high strength steel alloys, aluminum alloys and advanced composites.

Structural Integrity of Railroad Tank Cars

Since 1970, NIST (formerly NBS) has conducted an extensive series of metallurgical investigations on steels used in railroad tank cars used to transport hazardous materials. These investigations have included; (1) evaluation of steels taken from tank cars involved in accidents, (2) evaluation of steels taken from a tank car that was destroyed under simulated accident conditions, and (3) evaluation of new steels that are candidates for replacement of existing steels in new tank car construction. Microstructural evaluation and conventional mechanical properties tests, such as tensile tests, impact tests, and hardness tests were conducted on steels that had been exposed to temperatures that are experienced in fires and on steels at low (sub-zero) temperatures. Extensive testing was done to evaluate the fracture properties of tank car steels using Charpy-V-notch tests, dynamic tear test, nil-ductility test, drop weight tear tests, CTOD tests, K_{Ic} tests, K_{Ia} tests, J_{Ic} tests at normal operating temperatures and at the temperatures at which accidents occurred. Steels evaluated included the traditionally used A212 steel in the as-rolled condition, AAR TC 128 grade B steel in the as-rolled and normalized conditions, A515 grade 70 steel, and an experimental controlled-rolled steel designated A 8XX. From the the evaluation of steels taken from tank cars involved in accidents and of new candidate steels for tank car construction, a technical basis was provided for developing new requirements for steels used in tank car construction to reduce the fracture of tank cars that experience accident conditions.

Mechanical Properties of Orthorhombic Titanium Aluminides

Orthorhombic Ti-Al-Nb alloys are candidates for use as advanced propulsion and airframe components in future DoD and NASA aerospace programs. Small additions of Mo (less than 2 at %) have been found to significantly improve the tensile and creep properties of these alloys. This study was undertaken to determine whether the origin of this improvement is primarily microstructural (via phase stabilization) or substructural (via changes in dislocation structure and behavior). It is being conducted on two alloys, Ti-22Al-26Nb and Ti-22Al-24.5Nb-1.5Mo, prepared by both powder metallurgy and by conventional ingot metallurgy. Both alloys were heat treated by several different schedules. Samples have been characterized using scanning electron microscopy and electron probe microanalysis. Hot tensile and creep mechanical testing is being conducted. Resulting microstructural and compositional information will be correlated with mechanical properties.

Metallurgy of the R.M.S. Titanic

A forensic analysis of steel recovered from the wreck of the *RMS Titanic* was performed to help answer persistent questions as to why this "unsinkable" ship sank in less than 3 hours after a relatively minor collision with an iceberg. Mechanical property tests, including tensile and Charpy V-notch, were performed to establish mechanical properties. The hull steel and rivets were characterized both microstructurally and chemically, and deleterious components of the microstructure were identified. This information was examined in light of steel making practices common to turn-of-the-century Ireland.

Planned Outcomes:

The work on lead-free solders will generate permissible pressure ratings for the applicable ASME Codes for solder joints in copper plumbing tube for use in potable plumbing systems. Ratings will initially be generated for three solder alloys. Ratings on additional alloys are expected to be required in the future.

New national (DOT and CGA) and international (ISO) technical standards will be developed for the design, manufacture and testing of high strength steel alloy, aluminum alloy, and advanced composite cylinders used in the transportation of high pressure gases. Development and evaluation of advanced methods of nondestructive testing of high-pressure gas cylinders will be conducted.

Evaluation of steels used in the construction of tank cars will provide a technical basis for revising the materials standards used to construct tank cars.

Correlation between processing and heat treatment parameters, microstructure and high temperature mechanical properties for the orthorhombic Ti-Al alloys will contribute to the science base of the US Air Force Propulsion Initiative (the Integrated High Performance Turbine Engine Technology (IHPTET) Program.

The findings concerning the metallurgy of the RMS Titanic will greatly increase public awareness of how materials science can be used to understand the behavior and safety of large engineering systems.

External Collaborations:

The work on lead-free plumbing solders is being conducted cooperatively with the CDA and the ASME (Committee B16).

In the work on high pressure gas cylinders, there is extensive collaboration with DOT, the Compressed Gas Association and its member companies, and with the international community through the ISO Technical Committee on Gas Cylinder Design (TC58).

The work on the evaluation of tank car steels has included extensive collaboration with the U. S. Department of Transportation Federal Railroad Administration Office of Research and Safety and with the American Association of Railroads (AAR).

The studies of orthorhombic Ti-Al-Nb alloys are being conducted in collaboration with the U.S. Air Force Wright Laboratory which is also providing material support, and with the aerospace companies and universities participating in the IHPTET Program.

The project on the metallurgy of the RMS Titanic was performed under the auspices of the Discovery Channel and the Society for Naval Architects and Marine Engineers. Collaborators on this project include Prof. Phil Leighly (Univ. of Missouri, Rolla, MO), Dr. Harold Reemsnyder (Homer Labs, Bethlehem Steel, Bethlehem, PA), George Tulloch (RMS Titanic, Inc., New York, NY), Bill Garzke (Gibbs and Cox and SNAME, Arlington, VA), Dr. Jim Matthews (Defense Research Establishment - Atlantic, Halifax, NS), Bob Brigham (CANMET, Ottawa, Quebec), Ed McCutcheon (Cmdr., USCG (Retired), Bethesda, MD), and Prof. Bill Gerberich (Univ. of Minnesota, Minneapolis, MN).

Accomplishments:

In the work on stress rupture of lead-free solders, most testing has been completed on three lead-free solder alloys. These data were presented to ASME Committee B16 and permissible pressure ratings for plumbing joints have been calculated and are being circulated for letter ballot. Studies of the failure mechanisms were conducted and a statistical analysis method was developed to model the life prediction of the solder joints from the test data.

In collaboration with DOT, specifications were developed for the use of ultrasonic methods for retesting high pressure steel cylinders in place of hydrostatic methods. Five ISO draft standards for steel and aluminum cylinders were completed and are expected to be published during FY99.

Final summary reports on the metallurgical properties and the fracture properties of railroad tank car steels have been completed.

The deleterious components of the microstructure of both the hull steel and rivets of the RMS Titanic have been identified. For the hull steel, these include large MnS inclusions, large ferrite and pearlite grain size, coarse pearlite lamellae, low Mn content, and low Mn/C ratio. In the rivets, which were composed of wrought iron, the slag content was found to be 3 to 4 times that normally found in contemporary material (9.2% versus 2.5%). Also, the direction of the stringers within the rivets was found to change from longitudinal within the shaft to transverse at the intersection of the shaft and the head formed during installation. Given that wrought iron has little transverse ductility, this is postulated as a failure mechanism for lost rivets during the collision. Lost rivets and parted seams were found, in other parts of the overall study, to have been a major component of the flooding of the ship, and thus the sinking.

Impacts:

Permissible stress data obtained by NIST on lead-free solder joints is being used by ASME Committee B16 for new lead-free solder codes for potable water systems. Although lead-free solders were mandated by the Safe Drinking Water Act (1982), no adequate design codes were previously available. Significant progress has been made in the process for introducing expanded permissible pressure data for lead-free solders into the ASME Codes. The NIST data will provide the US plumbing industry with more choices of solders for joining copper tube in potable water systems and with more realistic safety factors. The impact will be felt primarily in the construction of high-rise buildings, where costs will be significantly reduced by replacing brazing or mechanical joining by soldering, and, in some cases, by allowing the reduction of wall thickness of the copper tube.

The new ultrasonic methods adopted for retesting steel high pressure gas cylinders significantly reduce the cost of retesting as well as avoiding the generation of hazardous waste material by the previously used hydrostatic testing. The adoption of the ISO standards for high strength steel and aluminum cylinders will permit U.S. manufacturers to produce cylinders that are accepted for worldwide use.

The evaluation of the properties of tank car steels has resulted in revision of the technical standards used to specify the materials of construction in tank cars by the U.S. Department of transportation and the American Association of Railroads.

The work on orthorhombic Ti-Al-Nb alloys will contribute to the IHPTET Program, which, if successful, will double the thrust-to-weight performance of gas turbine engines.

New insights on the sinking of the RMS Titanic have been gained through this investigation, and 85 year-old myths concerning the nature of the damage to the hull have been dispelled. Through media coverage and numerous presentations, the public has seen how materials science can be used to evaluate weaknesses in large structures.

Outputs:

***Publications**:*

Hagwood, C., Clough, R., and Fields, R., "Estimation of Stress Threshold for the Weibull Inverse Power Law," (submitted to IEEE Trans. on Reliability).

Rana, M. D., Smith, J. H., and Tribolet, R. O., “Technical Basis for the Flawed Cylinder Test Specification to Assure Adequate Fracture Resistance of ISO High-Strength Steel Cylinders,” Journal of Pressure Vessel Technology, Vol. 119, page 475, November 1997.

Zahoor, A. and Hicho, G. E. “Materials and Fracture Mechanics Assessment of Railroad Tank Cars,” NISTIR, September 1998.

Hicho, G. E. “A Historical Metallurgical Review of Tank Car Accident Investigations,” NISTIR, September 1998.

Garzke, Jr., W. H., Brown, D. K., Matthias, P. K., Cullimore, R., Wood, D., Livingstone, D., Leighly, Jr., H. P., Foecke, T., and Sandiford, A. "Titanic: Anatomy of a Disaster," accepted Proceedings of The Society of Naval Architects and Marine Engineers Annual Meeting, SNAME, Jersey City, NJ (1997).

Foecke, T. "Metallurgy of the RMS Titanic", NIST-IR 6118 (1998).

Presentations:

Clough, R, "Stress Rupture Data of Lead-Free Solders Used in Copper Pressure Fittings," ASME Copper Pressure Fitting Subcommittee, San Francisco, CA, November 1997.

Clough, R., Hagwood, C., Fields, R., Cohen, A., and Kireta, Jr., A., "Stress Rupture of Lead-Free Soldered Joints Used to Assemble Copper Plumbing Systems," AWS Spring Meeting, Detroit, April 1998

Smith, J. H., "U.S./International Codes and Standards for Steels, Pressure Vessels, and Welding," Fourth NIST-AIST Information Exchange, April 1998, at NIST.

Foecke, T., "Titanic: Anatomy of a Disaster - The Metallurgical Forensic Analysis," Society of Naval Architects and Marine Engineers Annual Meeting, Ottawa, ON, October 1997.

Foecke, T. "What Sank The RMS Titanic?"

Department of Materials Science and Engineering, Carnegie Mellon University, Pittsburgh, PA, February 1998.

University of Minnesota Distinguished Alumni Colloquium, Minneapolis, MN, May 1998.

Foecke, T., "Metallurgy of the RMS Titanic,"

Special Department Colloquium, Department of Materials Science and Engineering, Virginia Polytechnic University, Blacksburg, VA, March 1998.

The Johns Hopkins University, Baltimore, MD, March 1998.

General Electric Corporate Research and Development, Schnectady, NY, April 1998.

ASM DC Chapter Keynote Address, Bethesda, MD, May 1998.

Keynote Presentation, Admiralty Law Bar Association Annual Meeting, Washington, DC, July 1998.

Department Colloquia, Departments of Chemical Engineering and Materials Science and Engineering, Northwestern University, September 1998.

Foecke, T., "What Happened to the Titanic,"

30 students from Sligo Adventist School, January 1998

30 students from Lanham Middle School, February 1998

15 students from the Chen Home School, Bowie, MD, May 1998.

Foecke, T., "Chemical Analysis Using the SEM: Titanic Hull Steel", 25 Montgomery Blair High School students (with Chemistry), March 1998.

Project Title: **PERFORMANCE OF MATERIALS IN CORROSIVE MEDIA**

Investigators: F. S. Biancaniello, J. L. Fink, C. D. Flanigan, E. N. Pugh, R. E. Ricker, S. D. Ridder, R. D. Schmidt (Guest Researcher from the Danish University of Technology), A. J. Shapiro, L. C. Smith, and M. R. Stoudt

Objectives:

The objective of this project is to develop test methods that help U.S. industry evaluate how their products or the materials in their products will resist degradation in corrosive service environments. The challenge is to develop fundamental and scientifically valid relationships between basic materials properties and the performance of these materials in corrosive environments, and then, to develop test methods that measure these properties under well-controlled environmental conditions. In this way, NIST will deliver scientifically sound quantitative measures to industry to help guide them through the critical steps required to develop and market the best possible products.

Technical Description:

Corrosion impacts virtually every industrial product with metallic components and every industrial process that uses corrosive environments. An analysis by Battelle Columbus Laboratories (BCL) in 1995 determined that the annual cost of corrosion to the US economy exceeds $300B. In FY98, our work served several industrial sectors by measurement and analysis of several corrosion-related phenomena.

The first area of study focused on the aircraft industry, for which the 1995 BCL study estimated the annual corrosion costs at $13B. Since the average age of jet aircraft in operation has been increasing steadily since 1965, this industry is concerned with maintaining the reliability and safety of airframes as they become older. The industry prevents corrosion failures by frequent inspections and repairs, but the cost of this approach is increasing dramatically as the average age of aircraft increases. The National Materials Advisory Board's Committee on Aging of U.S. Air Force Aircraft (NMAB-488-2) studied this issue and one of the immediate R&D needs they identified was the establishment of a link between laboratory tests and behavior in service. NIST formed a collaboration with the U.S. Air Force's Wright Laboratory to address this critical need for improved measurement methods and interpretations.

The second area of study focused on the suction roll shells used by the pulp and paper industry. These large structures cost hundreds of thousands of dollars each but have a service life of only five to eight years because of corrosion fatigue failures induced by the combined action of cyclic loading and corrosive attack. Duplex stainless steels are used for these suction roll shells, but the existing measurement methods and models for the two current alloys do not agree with the lives observed in service. To help solve this problem, Sandusky International, the only U.S. manufacturer of these critical components, approached NIST and a CRADA was established. NIST examined the relationships between the electrochemical environment, the microstructure, and pitting and fracture in the two alloys.

In the chemical process industry, austenitic stainless steels are used primarily due to their superior resistance to pitting corrosion. The alloys examined in this study contain high nitrogen contents, known to increase pitting resistance of stainless steels, and are being studied by Crucible Materials Corporation and NIST under a CRADA, using a powder metallurgy approach. The materials produced in this CRADA were so resistant to pitting corrosion that the existing test methods used by industry such as ASTM G61,G48, and critical pitting temperature tests fail to induce this form of attack, and therefore, could not be used to evaluate the alloys. A more agressive test was needed to evaluate these alloys.

The fourth area of study was added to this program when the Department of Transportation requested that NIST conduct a preliminary study into corrosion phenomena in the brake fluids used in anti-lock brake systems.

Planned Outcomes:

The outputs of this project will be test methods, predictive models, data generation and materials characterization as described above.

External Collaborations:

NIST collaborated with the U.S. Air Force on the development of test methods for aging aircraft, with Sandusky International through a CRADA on duplex stainless steels in the pulp and paper processing industry, and with Crucible Materials Corporation through a CRADA on evaluation of the pitting corrosion resistance of nitrogenated stainless steels, the Danish University of Technology in the alloys for biomedical implants, and the Department of Transportation, The Ohio State University’s Vehicle Research and Test Center, and Union Carbide in the brake fluid corrosion study.

Accomplishments:

This project has resulted in the creation of two new measurement methods during this FY: (1) a method for the measurement of crevice corrosion rates in Al alloys during atmospheric exposure that utilizes a unique sample geometry with electrochemical measurement techniques, and (2) a method for evaluation of the influence of alloying elements on the pitting resistance of nitrogenated stainless steels. The first of these could lead to the development of a new standard test method while an existing standard could be modified to incorporate the second (ASTM 061).

A model linking the corrosion damage observed in the laboratory and that which occurs in aircraft during service was developed by assuming that the corrosion rate at any time is determined by the environmental variables in a corrosion rate function, and that the average rate of corrosion damage accumulation for any exposure is the integral of this corrosion rate function over the probability distribution function for each of the significant environmental variables. As a result, the critical laboratory experiments are not accelerated exposure tests under the worst possible environmental conditions, but corrosion rate measurements under carefully controlled environmental conditions that enable determination of the corrosion rate function.

A laboratory test method was then developed to enable determination of the corrosion rate function for atmospheric crevice corrosion, which is a result of environmental species (salts) accumulating in crevices, where they absorb water from the surrounding air and cause corrosion inside the crevice. The corrosion rate function for this form of crevice corrosion was determined by designing a special crevice sample geometry that enabled *in-situ* measurement of the corrosion rate inside the crevice. Measurements verified that the corrosion rate inside the crevice is determined by (1) the salts species present in the crevice, and (2) the activity of water vapor in the air outside the crevice (the relative humidity), and determined that the corrosion rate inside a crevice increases exponentially with increasing relative humidity. The corrosion damage predicted by this model using the data from the measurements correlated well to the output of a corrosion rate sensor being developed by the US Navy.

Examination of a service failure in a suction roll shell found that small pits were present at the origin of the fatigue crack. Electrochemical experiments showed that pitting could be suppressed or stimulated in either of the two alloys which are used, and that pitting stimulated the initiation of fracture in both alloys. It was concluded that the alloy with the shorter service life was failing prematurely due to the initiation of fatigue cracks by small pits in the austenite phase and that relatively simple and quick electrochemical pitting resistance measurements and slow strain rate tensile tests could be used to guide alloy development.

To evaluate the corrosion-resistant high nitrogen stainless steels, NIST modified an existing ASTM test method by changing the environment to one that would be extremely aggressive with respect to pitting corrosion. The usefulness of this new method is now being demonstrated on alloys for the chemical process industry, and alloys for applications in biomedical implants. This same environment was then evaluated as a potential testing environment for slow strain rate tensile tests as a means for guiding the development of alloys resistant to stress corrosion cracking.

The study of brake fluid systems found that metals will corrode in this environment and that electrochemical measurement methods can be used to determine the corrosion rates. It also found that the corrosion rates can vary significantly depending on the inhibitors and contaminants present in the brake fluid. Then, the DoT standard corrosion test for certifying brake fluids for use in the U.S. was examined in light of the findings of this study. This examination concluded that the existing standard test is not representative of all of the possible corrosion scenarios that can occur in ABS systems.

Impacts:

Researchers in the Air Force and in the aircraft industry have begun examining the NIST modeling approach and measurement method as tools to help them develop corrosion prevention technologies, better alloys, or to tailor inspection and repair schedules to usage patterns. Sandusky International reports that they are proposing an alloy development program to take advantage of the knowledge gained from this program. Crucible Materials Corp. is incorporating the test method developed for nitrogenated stainless steels into their alloy development program.

Outputs:

Publications:

Ricker, R. E., Fink, J. L., Shapiro, A. J., Smith, L. C., and Schaefer, R. J., "Preliminary Investigations into Corrosion in Anti-lock Braking Systems," NIST IR 6233, July 1998.

Biancaniello, F. S., Jiggetts, R. D., Ricker, R. E., and Ridder, S. D., "Powder Metallurgy High Nitrogen Stainless Steel," submitted for publication in the proceedings of 5th Intl. Conference on High Nitrogen Steels, Espoo, Finland, Stockholm, Sweden, Swedish Institute for Metals Research, May 1998.

Biancaniello, F. S., Jiggetts, R. D., Ricker, R. E., and Ridder, S. D., "Characterization of Atomized High Nitrogen Stainless Steel as a Possible Implant Material," submitted for publication in the proceedings of Biomedical Materials Conference, April 1998.

Presentations:

"Methods for Evaluation of Fire Suppression Agent Compatibility with Metals," Workshop on Screening Methods for Agent Compatibility with People, Materials, and the Environment, Gaithersburg, MD, November 1997.

"Corrosion Metrology Research for Aging Aircraft," R. E. Ricker and J. L. Fink, Symposium on Corrosion and Structural Integrity Issues in Aging Aircraft, AeroMat '98 The 9th Annual Advanced Aerospace Materials & Processes Conference, ASM Intl., June 18, 1998.

Project Title: **MAGNETO-OPTICAL IMAGING**

Investigators: A. J. Shapiro, R. D. Shull, V. I. Nikitenko*, and V. S. Gornakov*
* Guest Scientist, Institute for Solid State Physics, Russian Academy of Sciences (ISSP RAS).

Objectives:

The NIST-ISSP RAS Magneto-Optical Indicator Film (MOIF) Project is devoted to developing a new advanced imaging technique for direct measurement of the dynamics of magnetization reversal processes. The advanced MOIF technique will be used to characterize the magnetic structure, the magnetization micromechanisms and the influence of crystal lattice defects on the domain wall nucleation and motion in technologically important nanocomposite materials, such as exchange-biased bilayers and magnetic supperlattices. It also can be used as a rapid nondestructive method for assessing film quality during production.

Technical Description:

The MOIF technique utilizes a transparent indicator film, a Bi-substituted yttrium iron garnet with in-plane anisotropy, placed on the top of a sample. Polarized light passes through the indicator film and is reflected back by an Al underlayer. Magnetic stray fields with a component perpendicular to the film plane are observed through the magneto-optic Faraday effect created in the garnet film. As examples, magnetic stray field images of domain walls of different types and detailed information on the spin rotation processes as well as on the domain wall nucleation and motion during the remagnetization of the magnetic materials can be obtained by the MOIF technique. The usefulness of the MOIF technique is being demonstrated in a number of different systems outlined below.

The magnetic properties of exchange-coupled ferro/antiferromagnetic (FM/AFM) bilayers and magnetic superlattices are very important in developing magnetoresistance sensors and read heads in future generations of computers. The unidirectional anisotropy possessed by these materials is used for stabilization of the ferromagnetic layer magnetization. Controlling the relationship between the exchange field and the coercivity of the FM/AFM bilayers is critical for improving the reliability of such magnetoresistive sensors. Many investigators have attempted over the years to determine the origin of the hysteresis loop shift and enhancements in the coercive force in ferromagnetic/antiferromagnetic bilayers. The nature of these effects, however, is not completely understood. It is necessary to have a dynamic method, such as MOIF, for measuring the microscopic remagnetization mechanism in such films in order to improve their properties.

Since the discovery of antiferromagnetic coupling between ferromagnetic layers through intervening nonmagnetic layers in magnetic multilayers, there have been numerous investigations into these systems. As a result, we now know that they exhibit unique magnetic properties not found in bulk materials. Despite the large efforts which have gone toward understanding the mechanisms responsible for these properties, the picture is still not entirely clear, although the properties are known to depend on spin configurations. Co/Cu superlattices are of interest as elements in magnetic sensors because of their very large giant-magnetoresistance effects, up to ~65% at room temperature. The increase in resistance occurs with decreasing external magnetic field as the interlayer bilinear exchange coupling produces antiferromagnetic spin alignment of the neighboring Co layers.

Planned Outcome:

New advanced MOIF methods will provide a standard nondestructive quality control imaging technique for manufacturers of magnetic materials for magnetoresistance sensors, storage devices and read heads of the next generation computers. This work will contribute to the fundamental understanding of the remagnetization process in artificial and conventional magnetic materials.

External Collaborations:

Epitaxial AFM/FM bilayers were fabricated at the Material Science and Technology Division, Lawrence Livermore National Laboratory, Livermore, California. Investigations of the material were conducted in collaboration with Hewlett-Packard Laboratory, Palo Alto, California.

Co/Cu magnetic superlattices were studied jointly with Department of Materials and Nuclear Engineering, University of Maryland, College Park, Maryland.

Accomplishments:

The existing MOIF instrument was modified and redesigned to accommodate much lower MOIF contrast of the bilayer structures.

Magnetization reversal processes in epitaxial NiO/NiFe bilayers were studied using the magneto-optic indicator film and Vibrating Sample Magnatometer (VSM) techniques. For the first time the influence of dislocations on these processes was determined. It was revealed that dislocations not only influence the spatial distribution of spins, resulting in inhomogeneous rotations during remagnetization, but also stipulate the formation of unusual quasi-one-dimensional domains localized on dislocation slip planes. A new phenomenon, an asymmetry in the activity of the domain nucleation centers, was also revealed. Remagnetization parallel to the unidirectional anisotropy axis proceeds by domain nucleation and growth. Magnetization reversal in the hard axis direction occurs by incoherent rotation. The enhanced coercivity and asymmetric nucleation can be explained by taking into account domain wall behavior in the *antiferromagnetic* layer.

The correlation between the magnitude of the giant magnetoresistance effect (GMR) and the micromechanism of the magnetization reversal in electrodeposited Co/Cu superlattices was investigated for a range of Cu spacer thicknesses. The multilayers showing vanishing GMR exhibit a cooperative spin behavior which is similar to that exhibited by thin ferromagnetic films with in-plane fourfold anisotropy. In contrast, sublattices with substantial GMR demonstrate partially coupled noncolinear spin configurations which are responsible for the observed GMR phenomena.

Impact:

The results of our investigations have been transferred to our collaborators at Hewlett-Packard, Seagate and Lawrence Livermore National Laboratory.

Outputs:

Publications:

Nikitenko V. I., Gornakov V. S., Dedukh L. M., Kabanov Yu. P., Khapikov A. F., Shapiro A.J., Shull R. D., Chaiken A., and Michel R. P., "Asymmetry of Domain Nucleation and Enhanced Coercivity in Exchange-biased Epitaxial NiO/NiFe Bilayers." Phys. Rev. B, **57**, R8111 (1998).

Nikitenko, V. I., Gornakov, V. S., Dedukh, L. M., Kabanov, Yu. P., Khapikov, A. F., Shapiro, A. J,. Shull, R. D., Chaiken, A., and Michel, R. P., "Direct Experimental Study of the Magnetization Reversal Process in Epitaxial and Polycrystalline Films with Unidirectional Anisotropy," J. Appl. Phys. **83**, 6828 (1998).

Nikitenko, V. I., Gornakov, V. S., Dedukh, L. M., Shapiro, A. J., Shull, R. D., Chaiken, A., "Influence of Crystal Lattice Defects on Domain Wall Nucleation and Motion in Exchange-biased Films," MRS Symposium Proceedings (1998).

Nikitenko V. I., Gornakov V. S., Dedukh L. M., Kabanov Yu. P., Khapikov A. F. Shapiro A. J., Shull R. D., Chaiken A. and Michel R. P., "Direct Experimental Study of the Magnetization Reversal Process in Epitaxial and Polycrystalline Films with Unidirectional Anisotropy," J. Magn. Magn. Mater. (in press).

Nikitenko, V .I., Gornakov V. S., Dedukh L. M., Kabanov Yu. P., Khapikov A. F., Moffet T. P., Shapiro A. J., Shull R. D., Shima M., and Salamanca-Riba L., "Direct Experimental Study of Microscopic Remagnetization Mechanism in Co/Cu Magnetic Superlattices," J. Magn. Magn. Mater. (in press).

Presentations:

Nikitenko, V. I., Gornakov, V. S., Dedukh, L. M., Kabanov, Yu. P., Khapikov, A. F., Shapiro A. J., Shull, R. D., Chaiken A., and Michel R. P., "Direct Experimental Study of the Magnetization Reversal Process in Epitaxial and Polycrystalline Films with Unidirectional Anisotropy", Joint MMM-Intermag, San Francisco, CA, January 1998.

Nikitenko, V. I., Gornakov, V. S., Dedukh, L. M., Shapiro, A. J., Shull, R. D., and Chaiken, A., "Influence of Crystal Lattice Defects on Domain Wall Nucleation and Motion in Exchange-biased Films", MRS Spring Meeting, San Francisco, CA, March 1998.

Nikitenko, V. I., Gornakov,V. S, Dedukh, L. , Kabanov, Yu. P., Khapikov, A. F., Shapiro, A.,J., Shull, R.,D., and Chaiken, A., "Investigation of Elementary Events of Magnetization Reversal Processes in Exchange-biased Bilayers," APS March Meeting, Los Angeles, CA, March 1998.

Shull , R. D., Shapiro, A. J., Chopra, H. D., Nikitenko, V. I., Gornakov, V. S., Khapikov, A. F. Dedukh, L. M., and Chaiken, A., "Magnetic Domains in Nanocrystaline and Nanocomposite Materials." NANO' 98, Stockholm, Sweden, June 1998.

Nikitenko, V. I., Gornakov, V. S., Dedukh, L. M., Kabanov, Yu. P., Khapikov, A. F. Shapiro, A. J., Shull, R. D., Chaiken, A., and Michel, R. P. "Direct Experimental Study of the Magnetization Reversal Process in Epitaxial and Polycrystalline Films with Unidirectional Anisotropy." 3rd Intern. Symp. on Metallic Mutilayers (MML'98), Vancouver, Canada, June 1998.

Nikitenko, V. I., Gornakov, V. S., Dedukh, L. M., Kabanov, Yu. P., Khapikov, A. F., Moffet, T. P., Shapiro, A. J., Shull, R. D., Shima, M., and Salamanca-Riba, L., "Direct Experimental Study of Microscopic Remagnetization Mechanism in C0/Cu Magnetic Superlattices," 3rd Intern. Symp. on Metallic Mutilayers (MML'98), Vancouver, Canada, June 1998.

Project Title: **DEVELOPMENT OF SCANNING ACOUSTIC MICROSCOPY**

Investigator: Eva Drescher-Krasicka, G. J. McFadden (ITL), and Y. Yacobi (Guest Researcher)

Objectives:

This project develops scanning acoustic microscope techniques for the measurement of stress. This is a novel technique, which enables an assessment of the distribution and level of the sum or the differences of the principal stresses in solid samples based on acoustic microscope images. This technique has been under development for the last three years. We are continuing theoretical modeling of the acoustic behavior as well as improving software and hardware of the acoustic microscope for stress mapping and measurements.

Technical Description:

In certain types of acoustic microscopes one can select the acoustic wave which is used to create an image. The acoustic microscope image contains information from every scanned point of the sample. Until recently all approaches to detect and measure stress by use of acoustic microscopy have employed measurements of the phase *velocities* of the elastic waves. However, these velocities vary only weakly with changes in elastic constants, so that, except for idealized laboratory setups, attempts to use this approach to measure residual stresses have met with only limited success. A program has been underway at NIST to use other characteristics of ultrasonic waves which are more sensitive to changes in elastic constants than phase velocity. In our past work we developed a technique of stress imaging by selecting refracted shear modes for imaging. Another successful approach was applied to stress detection by employing leaky waves. These attempts were particularly successful in electronic packaging. During the last year we concentrated on improving techniques of applying tensile and compressive loads in order to precisely calibrate the accuracy of the measured intensity of the received acoustic modes versus sums or differences of the principal stresses during applied tensile and compressive loads. A significant improvement in quality of the calibration was due to the design and construction of a loading tensile machine for in situ testing on the scanning acoustic microscope. The load is measured by a calibrated load cell. From our previous research we had learned that scanning acoustic microscopy of stress is extremely sensitive to sample bending. This new stage design obviated the sample bending and the associated complex state of stress during tensile loading. In this way we have been able to develop a new theory of the acoustic microscopy of stress and compare theoretical values with the experimental data. The theory of acoustic microscopy of stress is being developed in cooperation with Professor John Willis from Cambridge University (England) and Dr. Geoffrey McFadden from ITL NIST.

Another significant development of this program was an SBIR award won by Sonix Inc.which promotes a separation of the longitudinal mode from the refracted shear wave received by the acoustic microscope transducer. The filtering of this undesirable contribution of the longitudinal wave in a shear wave scanning allows the results of mathematical models to be compared with the acoustic microscope images of stress for a known distribution of stress in tensile or compressive tests.

Planned Outcome:

The ultimate goal of this research is to deliver a new measurement method for applied stresses, and later residual stresses, in industrial products.

External Collaboration:

The 1998 work was done in close collaboration with Professor John Willis from the Department of Applied Mathematics and Theoretical Physics, and with the guest researcher Mr. Yair Yacobi from Israel Atomic Center in Bersheva.

Accomplishments:

In FY98 we proved the sensitivity to stress of longitudinal acoustic modes in loaded and unloaded tensile samples. Significant theoretical progress was achieved in the formulation of a theory of the acoustic microscopy of stress for longitudinal waves. This work will impact the interpretation of the time of flight stress measurements results which still is a commonly used technique in industry.

Outputs:

A two session symposium on the measurement of stresses was organized at ICCE/5 in Las Vegas, July 5-11, 1998.

A one day Workshop was organized at NIST entitled “Residual Stresses: Theory and Experiment,” held the 14th of July 1998, and attracting many of the best people in the field. The main subjects of the workshop were a review of the existing methods of assessing and measuring residual stresses *in situ.* The emphasis of the workshop was a comparison of acoustic methods with other existing techniques.

Publications:

Jiang, L., Kline, R., Yacobi , Y., and Drescher-Krasicka, E., "Acoustoelasticity, Theory and Experiment," Proceedings of the Fifth International Conference on Composites Engineering, editor D. Hui, Las Vegas, NV, July 1998, pp. 425-426.

Yacobi, Y., McFadden, G., and Drescher-Krasicka, E., "Experimental Images of the Distribution of Maximal Shear Stresses in Diametrally Compressed MMc and Aluminum Disks," Proceedings of the 5th International Conference on Composites Engineering, Las Vegas, NV, July 1998, Conference Proceedings, pp. 979-980.

Project Title: **ELECTRON MICROSCOPY**

Investigator: J. E. Bonevich and S. A. Claggett

Objectives:

Transmission electron microscopy (TEM) is used to characterize the structure and chemistry of materials at the atomic scale to better understand and improve their properties. New measurement techniques in electron microscopy are developed and applied to materials science research. The Electron Microscopy Facility primarily serves the Metallurgy and Ceramics Divisions as well as other NIST staff and outside collaborative research efforts.

Technical Description:

Atomic structure and compositional characterization of materials can lend crucial insights to their properties. Direct observation of localized structures by transmission electron microscopy (TEM) provides an important information feedback to the optimization of crystal growth and processing techniques. A wide variety of structures may be observed such as crystal structure and orientation, grain size and morphology, defects, stacking faults, twins and grain boundaries, second phase particles -- their structure, composition and internal defect structure, compositional variations and the atomic structure of surfaces and interfaces. To this end, the Metallurgy and Ceramics Divisions TEM facility consists of three transmission electron microscopes, a specimen preparation laboratory, and an image processing/computational laboratory. The state-of-the-art JEOL3010 TEM has atomic scale resolution as well as detectors for analytical characterization of thin foil specimens; a thin window X-ray detector for compositional analysis and an energy selecting imaging filter (IF) for compositional mapping at atomic resolution. Several studies are underway with scientists of the Metallurgy and Ceramics Divisions.

An active collaboration with the Chemical Science and Technology Laboratory (CSTL) continues for Metallurgy Division scientists to develop electron holography techniques with the 300 keV field-emission TEM. The TEM employs a highly coherent electron source enabling quantitative electron holography in addition to the capability of forming ~1 nm probes with 1 nA currents. The hologram records the phase distribution of electron waves interacting with matter and provides a quantitative measure of electromagnetic phenomena such as the magnetic fields inside materials (magnetic nano-composites) and electric fields emanating from pn junctions. Holography also quantitatively measures specimen thickness, surface topography, mean inner potentials of materials, dislocation strain fields, nano-diffraction and electron microscope lens aberrations.

Planned Outcome:

The feedback of structure and compositional information from electron microscopy will serve not only to help optimize existing materials and the processing techniques used to create them, but also to aid in the discovery of new classes of materials. The investigation of materials by electron holography provides quantitative measurements of electro-magnetic fields as well as fundamental data on mean inner potentials.

External Collaborations:

Dr. D. van Heerden (Johns Hopkins University) is collaborating on analysis of multilayer materials. Prof. R. Hull's research group (University of Virginia) is collaborating on the structure and composition effects of using focused ion beams for sample preparation. Albert Zhang (Rice University) is collaborating on the structure and morphology of nanoscale Fe/Co/C_{60} particles. Prof. Pozzi (Bologna University, Italy) collaborated on interpretating holographic observations of superconducting materials. Prof. P. Searson (Johns Hopkins University) supplied nanoscale ZnO particles for surface morphology and structure measurements.

Accomplishments:

The imaging filters have been improved this year (apertures, workstations, software) to allow rapid acquisition of compositional maps as well as on-line image distortion correction. New capabilities include simultaneous acquisition of energy loss spectra across planar interfaces.

Atomic resolution imaging and compositional mapping were applied to a range of Ti/Al multilayers. Discrete layering has been observed with minimal intermixing of the constituent multilayer elements. Results demonstrate that transformations of hcp-Ti to fcc-Ti can occur when specimens are prepared for electron microscopy. The results have been compared with x-ray diffraction to determine the as-deposited microstructure of the multilayers.

Atomic resolution compositional mapping was applied to a new class of materials with naturally-occurring magnetic multilayers. Phases in the BaFeTiO system were shown to possess an Fe-rich phase separated by a Ba-rich dielectric spacer material. These new materials are expected to find applications in microwave devices.

The amorphous zones revealed by high-resolution imaging of $BaTiO_3$/MgO photonic materials has been analyzed by energy dispersive spectroscopy. These zones near the thin film/substrate interface result from non-stoichiometries in the barium titanate and can be used to tailor the dielectric properties as desired.

The theoretical treatment of vortex image contrast in superconductors has been further refined. The analytical model now can account for distortions of the flux-lines due to pinning defects as well as misalignments of the vortices with respect to the overall magnetic field. The results can explain some of the anomalous vortex contrast observed by Lorentz microscopy and electron holography.

Nanoscale particles of Fe/Co and C_{60} have been observed to determine the microstructural and compositional variations in the materials. Good magnetic particle dispersions were shown with films consisting of high C_{60} content.

Impact:

Support continues for the HolograFREE hologram reconstruction software, developed earlier under this project. The software has been downloaded by research facilities at three corporations (Hitachi, Philips, Exxon) and six universities (Bologna, Stevens Institute, Northwestern, U. C. Berkeley, Wisconsin, Tuebingen). The software provides user-friendly reconstruction of electron holograms.

Outputs:

Publications:

Josell, D., Carter, W. C., and Bonevich, J. E., "Stability of Multilayer Structures: Capillary Effects," Nano98, in press.

Wong, E. M., Bonevich, J. E., and Searson, P. C., "The Growth Kinetics of Nanocrystalline ZnO Colloidal Solutions," J. Phys. Chem. **102**, 7770 (1998).

Josell, D., van Heerden, D., Read, D., Bonevich, J., and Shechtman, D., "Tensile Testing Low Density Multilayers: Aluminum/Titanium," J. Mat. Res. **13**, 1 (1998).

Bendersky, L. and Bonevich, J., "Magnetic Multilayers as a Structural Component in a Series of $BaO:TiO_2:Fe_2O_3$ Compounds," Phil. Mag. Lett. **77**, 279 (1998).

Josell, D., Cezairliyan, A., and Bonevich, J., "Thermal Diffusion Through Multilayer Coatings: Theory and Experiment," Proc. of the 13th Symp. on Thermophys. Prop., International Journal of Thermophysics **19**, 525 (1998).

Bonevich, J., Capacci, D., Harada, K., Kasai, H., Matsuda, T., Patti, R., Pozzi, G., and Tonomura, A., "Measurement of the London Penetration Depth from Holographic Images of Superconducting Vortices: The Influence of Specimen Thickness," Phys. Rev. B **57**, 1200 (1998).

Bonevich, J. E., Pozzi, G., and Tonomura, A., Electron Holography of Electromagnetic Fields, in: Electron Holography, eds. L. Allard et al., (Plenum, New York, 1998) pp. 129-156.

Presentations:

Bonevich, J., "Electron Holography of Materials," Invited oral presentation at Lawrence Berkeley National Laboratory, Berkeley, CA, April 1998.

Bonevich, J., "Practical Electron Holography," Invited oral presentation at Dept. of Materials Science, Rensselaer Polytechnic Institute, Troy, NY, February 1998.

Bonevich, J., "Electron Holography," Seminar presentation for the Magnetic Materials Group, NIST, Gaithersburg, MD, November 1997.

METALS PROCESSING

The properties of metals and their alloys depend strongly on their processing history. For example, the distributions of phases, grain structure, alloy compositional segregation, and defects in final commercial products depend not only on their compositions but also on the conditions under which their materials are fabricated. These distributions are crucial in determining the alloy strength, ductility, homogeneity, and other properties important for industrial applications. The Metals Processing Program focuses on measurements and predictive models needed by industry to design improved processing methods, provide better process control, develop improved alloy and coating properties, and reduce costs.

Major successes in applying measurements and modeling to processing applications have been achieved through NIST's interactions with the aerospace, powder metallurgy, electroplating and electronics industries. Predictive models developed at NIST for solidification and microstructural evolution during processing have been incorporated by industry into design systems for casting of aerospace alloys and production of defect-free electronic materials, helping to reduce rejection rates arising from defective parts. Cooperative research and development projects with industry have resulted in significant improvements in process control for welding and for atomization of steel and superalloy powders. Standard Reference Materials, certified for coating thickness, microhardness or chemical composition, are being fabricated by electrodeposition techniques and powder metallurgy. Data and understanding concerning mechanistic, chemical and process variables controlling the structure/properties of coatings and thin films produced by electrodeposition are being developed to take further advantage of this electrochemical process, which does not require high purity starting materials and is readily adaptable to large scale production.

Measurements and predictive models for processing are being developed to aid industry in tailoring materials properties for particular applications. Intelligent processing of materials through *in situ* property measurements combined with control systems based on process models is being pursued. Specifically:

- Measurements and models are developed to help design materials production processes. This work includes measurements and thermochemical evaluations to provide alloy phase diagrams, which are the roadmaps alloy designers use to predict the alloy phases that can be produced under specific processing conditions. These evaluations are playing key roles in NIST collaborations with industrial companies on electronic solders and casting of superalloys for aerospace applications.

- Measurements are made under dynamic conditions to monitor, in real time, properties of materials while they are actually being produced and to determine difficult-to-measure process parameters while the process is occurring. Special fast response sensors, simulations and imaging techniques have been developed for application to powder atomization and thermal spray processes, and workshops have been held to transfer these techniques to industry. Here, dynamic models of the process are important both for design of manufacturing procedures and for applications of real time feedback and control.

- To evaluate the adequacy of process models, it is important to measure the properties of the final materials and relate them to the process conditions. Work in this respect includes evaluation of methods used to optimize properties of electrodeposited coatings, corrosion resistance of rapidly solidified nitrogenated steels, and liquid phase bonding of alloys.

In all of this work, the goal is to help U.S. industry apply measurements and predictive modeling to produce improved materials at reduced cost.

Project Title: **PROCESSING OF ADVANCED MATERIALS**

Investigators: F. S. Biancaniello, P. A. Boyer, J. L. Fink, R. D. Jiggetts, U. R. Kattner, R. L. Parke, R. E. Ricker, S. D. Ridder, R. J. Schaefer, M. R. Stoudt, and M. E. Williams

Objectives:

Objectives of this project are to provide industry with measurements, sensors, predictive models, methodologies and standards needed to apply intelligent processing techniques to the production of advanced alloys. To aid industry, techniques are developed to prepare improved standard reference materials and reference samples, relate processing conditions to final properties of materials, and provide measurements that can be used for feedback and control. These efforts will result in improved materials processing efficiency and reliability.

Technical Description:

State of the art techniques are employed in the processing and synthesis of high performance materials. Predictive models and thermodynamic assessments are developed to aid in microstructure, composition, porosity and property control. This research is part of a long-term research effort on advanced processing, emphasizing rapid solidification and powder metallurgy. One outgrowth of the program was a highly successful NIST/Industry Consortium project on applying intelligent processing concepts to rapidly-solidified nickel-based superalloy powders produced by atomization techniques.

Current research is focused on three main areas. The first area is collaboration with powder metallurgy companies to apply NIST-developed models and intelligent processing techniques to increase atomization efficiencies, thus reducing powder handling and waste. These techniques are also being extended to thermal spray processes used in producing coatings for automotive, aerospace and other industrial applications. The second is the novel application of rapid solidification processing and powder metallurgy methods to produce state-of-the-art standard reference materials with enhanced chemical homogeneity. The third area is research on atomized high nitrogen stainless steel, including support for an industrial ATP project involving studies of thermodynamic and kinetic effects on nitrogen solubility, and methods of measuring corrosion properties of these highly corrosion-resistant alloys.

In addition, the Metallurgy Division's alloy preparation facility is critical to maintaining a world-class materials science and engineering program at NIST. Advanced processing equipment and methods are used to produce specimens for measurements within NIST and also for collaboration with industry and academia.

Planned Outcome:

This activity is designed to produce measurements, diagnostics, and sensors for feedback and control of advanced processing techniques. The plan is to develop predictive models for metals processing and to acquire data and measurements for expert systems development. This work is planned to help industry produce more reliable, higher quality material at lower cost.

The activity endeavors to produce fully-dense standard reference materials with enhanced chemical homogeneity for a wide variety of users, including but not limited to automotive, aerospace, powder producer and the metals casting industries.

An understanding of the effects of processing conditions and final microstructure on the properties of metal alloys is essential to achieving reproducible properties and accurate models of metals. Having an in-house NIST fabrication facility allows us to explore processing-structure and property relationships in a meaningful way.

External Collaborations:

Collaborations with Crucible Materials Corporation through a CRADA produced (1) thermodynamic predictions, (2) corrosion measurements, (3) kinetic models of nitrogen dissociation and reassociation, and (4) predictive models on the enhanced corrosion properties of high nitrogen stainless steels produced by atomization and HIP consolidation. These results aided Crucible in its ATP project aimed at producing new corrosion resistant alloys. A CRADA project with Carpenter Technology Corporation is continuing on nozzle design optimization via gas flow diagnostics and modeling, using techniques developed at NIST. The goal in this project is enhanced production of fine powder for the metal injection molding industry. Cooperative activities with Los Alamos National Labs include the NIST design of “zero-exposure” gas atomization equipment intended for beryllium alloys. NIST will begin testing of this equipment using surrogate alloys in FY99. Collaborative studies have been initiated with D. Shechtman at the Technion University in Haifa and C. Lang at the University of Capetown, South Africa on use of rapidly solidified powders for production of stable quasi-crystal coatings.

Accomplishments:

A system has been installed to perform diagnostics on gas flows in industrial-sized powder atomization systems. Flow plumbing in this system can supply gas mass flow rates up to 1 kg/s.

Optical sensors for measurement and diagnostics of advanced powder production systems have been developed through SBIR company and NIST interactions.

Three new prototype standard reference materials, C1150b (white cast iron), 1267a (446 ferritic stainless steel), and 1245a (Inconel 625) have been produced by rapid solidification of gas atomized powders and HIP consolidation. These more homogeneous SRM’s, requested by ASTM Committee E1 and currently undergoing round-robin testing, will allow improved measurement of industrial materials.

Impact:

Control techniques and melt practice developed at NIST for production of superalloys and corrosion-resistant nitrogenated stainless steel have been adapted by industry to improve commercial products and reduce production costs.

New high nitrogen austenitic stainless steel powder when applied as thermal spray coatings have potential to replace hexavalent Cr and electrolytic Ni.

More homogeneous standard reference materials have been produced, allowing improved measurements of industrial materials.

Outputs:

Publications:

Biancaniello, F. S., Ridder, S. D., Williams, M. E., and Jiggetts, R. D., “Characterization of Nanostructured Tungsten Heavy Alloy Produced by Double Ball Milling,” Proceedings of 4th International Conference on Tungsten and Refractory Metal Alloys: Processing, Properties and Applications, Metal Powder Industries Federation, Lake Buena Vista, FL, November 1997, in press.

Biancaniello, F. S., Jiggetts, R. D., Ricker, R. E., and Ridder, S. D., “Powder Metallurgy High Nitrogen Stainless Steel,” Proceedings of 5th International Conference on High Nitrogen Steels, Helsinki and Stockholm, May 1998, in press.

Biancaniello, F. S., Jiggetts, R. D., Ricker, R. E., and Ridder, S. D., “Characterization of Atomized High Nitrogen Stainless Steel as a Possible Implant Material,” Proceedings of 9th International CIMTEC Conference, Forum on New Materials, Topical Symposium XI: Materials in Clinical Applications, Florence, Italy, June 1998, in press.

Presentations:

Biancaniello, F. S., “Characterization of Nanostructured Tungsten Heavy Alloy Produced by Double Ball Milling,” 4th International Conference on Tungsten and Refractory Metal Alloys: Processing, Properties and Applications, Lake Buena Vista, FL, November 1997.

Biancaniello, F. S., “Powder Metallurgy High Nitrogen Stainless Steel,” 5th International Conference on High Nitrogen Steels, Stockholm, May 1998.

Biancaniello, F. S., “Characterization of Atomized High Nitrogen Stainless Steel as a Possible Implant Material,” 9th International CIMTEC Conference, Forum on New Materials, Topical Symposium XI: Materials in Clinical Applications, Florence, Italy, June 1998.

SRMs in Production:

SRM #C1150b	White Cast Iron
SRM #C1267a	Ferritic Stainless Steel (446 SS)
SRM #1245a	Inconel 625

SRM’s Under Development:

SRM #861	Aerospace Nickel Alloy

Project Title: **SOLIDIFICATION MODELING**

Investigators: S. R. Coriell, J. A. Warren, and W. J. Boettinger

Objectives:

Analytical and numerical models of alloy solidification and crystal growth processes are being developed with special emphasis on the prediction of microstructure and solute segregation as a function of processing conditions, for example, solidification velocity, thermal gradient, and alloy composition.

Technical Description:

The properties of solidified materials, e.g., castings and electronic materials, depend on the distribution of solutes or dopants, on the phases present, and on the defect structures within these materials. Modeling of the solidification process involves solution of the heat flow, diffusion, and fluid flow equations with boundary conditions on external surfaces and at the solid-liquid interface, which is a free boundary. The role of fluid flow on interface stability and microsegregation is investigated with application to possible microgravity experiments which would elucidate the role of fluid flow in terrestrial processes. Dendritic growth is always present in castings and determines the scale of microsegregation; phase field models are being implemented which allow the calculation of solute distribution for complex dendritic morphologies. These calculations allow studies of tip kinetics, solute redistribution, and coarsening.

Planned Outcome:

Models of various alloy solidification and crystal growth processes will be formulated. These models will provide information on the parameters controlling these processes and aid industry in designing production systems that increase product yield and performance.

External Collaborations:

Modeling and interpretation of experiments on the directional solidification of lead bromide doped with silver bromide in collaboration with scientists at Northrop Grumman Science and Technology Center has continued.

A model of the growth of in-situ composites in the monotectic aluminum-indium system was developed in collaboration with Prof. J. B. Andrews of the University of Alabama at Birmingham.

Phase field calculations of solute trapping have been conducted with Prof. A. Wheeler, Southampton University, and of grain boundary formation with Prof. R. Kobayashi, Sapporo University.

NIST participated with scientists from the University of Florida, NASA-Lewis Research Center, Centre National d'Etudes Spatiales, Departement d'Etudes des Materiaux at CEA, Societe Europeene de Propulsion, and the University of New South Wales on the in situ monitoring of growth of Bi-Sn using MEPHISTO during STS-87 space flight. Collaboration with Marshall

Space Flight Center, University of Alabama at Huntsville, and Binghamton University on the effect of fluid flow on interface instabilities during melt and solution growth has also continued.

Accomplishments:

Interface morphology and solute segregation patterns during directional solidification have been examined near the high velocity (absolute stability) condition for planar growth using the alloy phase-field method. The dynamics of the breakdown of initially planar interfaces into cellular structures were shown. The cell spacings, depths, tip temperatures, tip radii, and concentration patterns were determined as a function of solidification velocity. The presence of solute trapping is manifest in the variation of the degree of solute partitioning across the interfacial region with interface speed.

The alloy phase field equations were also explored in detail regarding their predictions about solute trapping and solute drag during rapid solidification. An important result was the prediction that the critical speed for the onset of solute trapping scales with the equilibrium partition coefficient, a fact consistent with experiments.

A new phase field model was formulated that includes grain orientation as a variable. This model simulates grain boundary formation via impingement of dendritically solidifying crystals of different orientation and has produced highly realistic simulations of grain microstructure in as-cast materials. In addition, in collaboration with the Information Technology Laboratory, research into massively parallel computations of 3D dendritic microstructures using the phase field method have been realized, and should allow us to repeat much of the two dimensional work in the physically correct number of dimensions.

Numerical calculations using Floquet theory have been performed to determine whether an oscillating flow of a given frequency can be used to avoid step bunching during crystal growth in ADP and KDP; large crystals of KDP are required for laser fusion applications.

Under certain conditions, nonunique (multiple) similarity solutions (propagation proportional to the square root of time) are possible for free boundary problems that require simultaneous diffusion of heat and solute such as occurs during soldering. This loss of uniqueness is quite disturbing, as it complicates our ability to predict microstructure evolution. The conditions under which these multiple solutions occur has been delineated for binary alloys, and the stability of these solutions is being investigated. These methods are also applicable to isothermal diffusion in ternary alloys.

The morphological stability of a binary alloy during directional *melting* at constant velocity has been investigated and numerical calculations of the critical concentration above which the interface is unstable as a function of melting velocity for a model system have been calculated. Various approximate stability criteria were proposed.

Modeling of the crystal growth of lead bromide has continued in collaboration with scientists at Northrup-Grumman Corporation; lead bromide is a transparent material with non-linear optical applications. The quality of the material has been related to crystal-liquid interface curvature during directional solidification.

Impact:

Phase field models of solidification can now be used to predict the grain structure of cast materials. Predicting these structures is important for the design of high performance castings.

Artificially induced oscillating fluid flow patterns have been theoretically shown to be capable of preventing step bunching during the crystal growth of KDP crystals and hence improve their quality. These KDP results are significant for laser fusion applications

Outputs:

Publications:

Coriell, S. R., Chernov, A. A., Murray, B. T., and McFadden, G. B., “Step Bunching: Generalized Kinetics,” J. Crystal Growth **183**, 669-682 (1998).

Coriell, S. R., McFadden,G. B., Boettinger, W. J., and Sekerka, R. F., “Multiple Similarity Solutions for Solidification and Melting,” J. Crystal Growth **191**, 573-585 (1998).

Ahmad, A., Wheeler, A. A., Boettinger, W. J., and McFaddden, G. B., “Solute Trapping and Solute Drag in a Phase Field Model of Rapid Solidification,” Phys. Rev. E, **58**, 3436 (1998).

Warren, J. A., Carter,W. C., and Kobayashi, R., “A Phase Field Model of the Impingement of Solidifying Particles,” Physica A, in press.

Kobayashi, R., Warren, J. A., and Carter, W. C., “Vector-Valued Phase Field Model for Crystallization and Grain Boundary Formation,” Physica D, **119**, 415-423 (1998).

Presentations:

Coriell, S. R., “Convection Effects,” Second Zermatt Workshop on Solidification Microstructures, Zermatt, Switzerland, July 1998.

Coriell, S. R., “Interface Morphology during Crystal Growth: Effects of Anisotropy and Fluid Flow,” Fourth Microgravity Fluid Physics and Transport Phenomena Conference, Cleveland, OH, August 1998.

Boettinger, W. J., “Numerical Simulation of Dendritic Alloy Solidification Using a Phase Field Method,” Materials Science & Engineering Dept. Seminar, Carnegie-Mellon University, October 1997.

Boettinger, W. J., “Fundamentals of Rapid Solidification,” Materials Week, San Antonio, TX, February 1998.

Boettinger, W. J., “Numerical Simulation of Dendritic Alloy Solidification Using a Phase Field Method,” Materials Science & Engineering Dept. Seminar, University of Connecticut, April 1998.

Boettinger, W. J., “Numerical Simulation of Dendritic Alloy Solidification Using a Phase Field Method,” Marshall Space Flight Center (NASA), Huntsville, AL, April 1998.

Warren, J. A., “Phase Field Modeling of Grain Boundary Collision,” Collective Phenomena in Physics '98, U. West Indies, Barbados, January 1998.

Warren, J. A., “Phase Field Modeling of Grain Boundary Collision,” APS March Meeting, Los Angeles, CA, March 1998.

Warren, J. A., “Phase Field Modeling of Alloy Solidification,” Gordon Research Conference: Physical Metallurgy, Plymouth NH, June 1998.

Project Title: **SENSORS AND DIAGNOSTICS FOR THERMAL SPRAY PROCESSES**

Investigators: S. D. Ridder, F. S. Biancaniello, R. D. Jiggetts, P. A. Boyer, and R. L. Parke

Objectives:

The primary focus of this project is to develop tools for the measurement and control of process conditions for plasma spray systems. This includes off-line analysis tools (e.g., high-speed cinematography, imaging thermography and holography) and real-time sensors suitable for process control. In addition, mathematical modeling techniques will be used to provide predictive calculations of process variables and product characteristics. Appropriate process sensors and controls will then be incorporated into an expert-system-driven process controller with generic applicability to a wide range of metal processing equipment and computer platforms.

Technical Description:

The focus of the thermal spray project is the development of measurement tools to provide diagnostic and control capabilities for the production of reproducible industrially important spray coatings such as ceramic-based Thermal Barrier Coatings (TBC's) and metallic based diffusion barriers, corrosion protection coatings and wear reducing layers with predictable properties.

The intended expert-system-driven or intelligent process controller requires the acquisition of an extensive data base that maps the effects of all the process variables or parameters on the resulting coating characteristics. Process parameters must be measured, identified as either dependent or independent variables and reduced using dimensional analysis. A process model must be determined that provides a mapping of the process parameter space to the resulting coating properties and process efficiency. Finally, a control system is developed incorporating the process model, sensors and actuators that provides the necessary heuristics and response time for achieving the product goal. This will ultimately allow US industry to produce the advanced materials that this process can provide with reliable performance and acceptable cost.

In the NIST thermal spray system, independent programmable manipulators are used to move the plasma gun, the substrate and the process sensor. These "robots" provide adequate flexibility for the production and diagnostic monitoring of reproducible coatings on two-dimensional test coupons measuring up to 1 m^2. High-speed cinematography, multi-exposure laser holography and high-speed video cameras will be developed to provide diagnostic tools for thermal spray systems. A new Infra-Red (IR) thermal imaging sensor, currently capable of measuring the temperature of rough, variable emissivity surfaces, is now being modified to provide, in addition, on-line measurement of particle temperature and velocity.

Planned Outcome:

Robust process sensors will be developed and provided to industry for monitoring and control of atomizers and plasma spray systems. New mathematical modeling tools will be developed to aid in equipment design and improve process efficiencies. Expert-system-driven process controllers will be developed by NIST and its industrial and academic partners with hardware and software supplied and supported by third party companies which have established national distribution networks.

External Collaborations:

Collaborative work on thermal spray processing includes NIST SBIR funded research with Stratonics, Inc., The Cooke Corporation and North Dancer Labs, Inc. all aimed at developing new sensor and diagnostics technology. In addition, an NIST SBIR funded project with Intelligent Computing Technologies, Inc. was begun that will provide a means to more efficiently program complex process control software. A cooperative exchange of expertise has been initiated with scientists at Los Alamos National Laboratory. NIST has provided assistance in the design and operation of an inert gas atomization system for beryllium alloys and Los Alamos has provided technical assistance in the operation of the NIST D.C. plasma thermal spray equipment. A collaborative effort with Ford Motor Company on the use of thermal spray technology for automotive body panel seam-filling has been established. Praxair Surface Technologies has joined in this effort and has provided to NIST a twin wire arc spray system suitable for use in spraying low-temperature metal seam-filling Cu and Sn alloys. Collaborative studies have been initiated with C. Levi of the University of California at Santa Barbara on the reliability of TBC's and with D. Shechtman at the Technion University in Haifa and C. Lang at the University of Capetown, South Africa on the powder production, thermal spraying, characterization and wear properties of stable quasi-crystal coatings.

Accomplishments:

The NIST thermal spray system was upgraded with motion control hardware consisting of a high-speed, 3-axis manipulator for the plasma gun, a 2-axis substrate manipulator and a 4-axis sensor manipulator. These manipulators will be used to establish coating "repeatability" and to provide better spatial resolution of the data generated by the process sensors.

A collaborative effort with Ford Motor Company and Praxair Surface Technologies on automotive body panel seam-filling has been established.

A collaborative effort between The Cooke Corporation and Stratonics, Inc. has resulted in a prototype instrument for measuring temperature, velocity and size of thermal spray particles in-flight. A thermal imaging sensor by Stratonics, Inc. combined with an intensified video camera from The Cooke Corporation provides the necessary sensitivity for this application. This work is supported through NIST SBIR funding.

The Phase I SBIR with North Dancer Labs, Inc. on developing a holographic diffuse light source for spray diagnostics was completed. This technology provides illumination suitable for specularly reflective materials such as metal powder, droplets and coatings. This measurement tool will be valuable for many materials processing systems. In particular, it will improve the resolution of spray coating surface texture and allow droplet impact studies that can not be realized with currently available light sources.

Impact:

NIST SBIR funded research has resulted in dramatic improvements to a new imaging pyrometer with wide applicability in the materials processing area. This “Thermal Spray Imaging” sensor, available from Stratonics, Inc. of Laguna Hills, CA uses special IR optics to produce a high resolution two-color image of the material under test. This approach provides both temperature and emissivity data with spatial resolution as high as 15 µm. A new intensifying camera has been tested that provides temperature, velocity and size of particles as they are sprayed.

Project Title: **ELECTRODEPOSITION OF ALUMINUM ALLOYS**

Investigator: G. R. Stafford

Objectives:

This project seeks to develop an understanding of electrolyte behavior, morphological development and crystal structure operative during the electrodeposition of aluminum alloys from both organic halide and alkali halide based chloroaluminate electrolytes.

Technical Description:

Aluminum and many of its alloys can impart excellent corrosion protection when applied as a thin coating to other materials. Typical coating technologies include hot-dipping, flame spray and physical vapor deposition (PVD). Electrodeposition may offer an inexpensive method for producing homogeneous and fine-grained aluminum-based thin films. Unfortunately, aluminum can only be electrodeposited from aprotic, nonaqueous solvents or molten salts. Several molten salt systems have been investigated for the electrodeposition of aluminum and its alloys. Binary mixtures of $AlCl_3$ and alkali metal chlorides are molten at temperatures as low as 108 °C. Systems which are molten at room temperature can be obtained when the alkali chloride is replaced with certain unsymmetrical quaternary ammonium chloride salts such as 1-methyl-3-ethylimidazolium chloride (MeEtimCl).

Aluminum alloys can be electrodeposited from either of these electrolytes with the addition of the appropriate chloride salt of the solute metal. Alloys such as Al-Cr, Al-Mn, Al-Ti, and to a limited extent, Al-Nb have been electrodeposited at potentials negative of the aluminum reversible potential while aluminum-transition metal alloys such as Al-Ni and Al-Co can be formed at potentials positive of the aluminum reversible potential. The mechanism leading to the formation of this latter group of alloys involves the underpotential deposition (UPD) of aluminum during the mass-transport-limited electrodeposition of the transition metal. This may be quite interesting from a technological view point since the composition of alloys formed by UPD phenomena should depend exclusively on the electrode potential.

The electrodeposition of Al-Ni and Al-Co alloys at underpotentials is consistent with reports that UPD related phenomena are likely to be observed when the work function of the less noble alloy component is smaller than that of the more noble component. One would therefore expect the underpotential alloying of aluminum with silver, cobalt, copper, iron, nickel and palladium whereas it would be less expected with lead, antimony and zinc. It has recently been reported that the underpotential codeposition of aluminum does not occur during the electrodeposition of zinc. Our activities over the past year have focused on the Al-Cu and Al-Sb systems.

Planned Outcome:

This project will result in the evaluation of Al-Cu and Al-Sb alloys electrodeposited from a room temperature $AlCl_3$-MeEtimCl molten salt electrolyte. It is likely that the underpotential alloying of aluminum will occur during the electrodeposition of copper; it is less likely to be observed during the electrodeposition of antimony. The melt chemistry, alloy composition and crystal structure will be evaluated for each of these systems.

External Collaborations:

We are working with Professor Charles Hussey of the University of Mississippi, an expert in room temperature chloroaluminate electrolyte, and one of the first to develop the $AlCl_3$ - MeEtimCl system.

Accomplishments:

Sampled current and rotating ring-disk electrode voltammetry experiments indicated that is was possible to produce Cu-Al alloy deposits at potentials positive of that corresponding to the electrodeposition of bulk aluminum. The onset of aluminum codeposition was found to occur at +0.3 V with respect to aluminum. The Cu-Al alloy composition was found to be independent of the Cu(I) concentration in the electrolyte and reached a maximum value of 43 % atomic fraction aluminum at 0 V. Cu-Al deposits containing less than about 7.2 % atomic fraction Al were single phase, face-centered cubic (fcc) copper solid solutions. When the composition reached 12.8 % atomic fraction Al, a second phase identified as ß' - Cu_3Al was co-deposited with the copper solid solution. This phase appears to form before the fcc copper becomes saturated with aluminum.

A similar electrochemical examination of the antimony-aluminum system indicates that underpotential alloying of aluminum does not occur during the electrodeposition of antimony. This is supported by EDS and x-ray diffraction examination which show that deposits formed at potentials positive of the aluminum reversible potential are pure antimony. When the deposition potential is negative of the aluminum reversible potential, two distinct morphologies are observed in the electrodeposit. The first is a dendritic structure that we have determined to be pure antimony while the second is a flat, plate-like structure consisting of pure aluminum. There was no evidence for alloying of any kind in this system.

Outputs:

Publications:

Tierney, B. J., Pitner, W. R., Mitchell, J. A., Hussey C. L., and Stafford, G. R., "Electrodeposition of Copper and Copper-Aluminum Alloys from a Room-Temperature Chloroaluminate Molten Salt," J. Electrochem. Soc. **145**, 3110 (1998).

Stafford, G. R. and Haarberg, G. M., "The Electrodeposition of Al-Nb Alloys from Chloroaluminate Electrolytes," Proc. NATO Advanced Research Workshop on Refractory Metals in Molten Salts, Apatity, Russia, August 1997.

De Long, H. C., Mitchell, J. A., Hagans, P. L., Carlin, R. T., Stafford, G. R., and Trulove, P. C., "Electrodeposition of Aluminum-Manganese Alloys from Room Temperature Chloroaluminate

Molten Salts," Eleventh International Symposium on Molten Salts, Vol. 98-11, 193 Meet. Electrochem. Soc., San Diego, CA, May 1998.

Project Title: **ELECTRODEPOSITED COATING THICKNESS STANDARDS**

Investigators: C. R. Beauchamp, H. B. Gates, and D. R. Kelley

Objectives:

The objective of the work is to re-supply SRM Coating Thickness Standards number 1358, 1359, 1362a, 1363a, and 1364a used by the organic and inorganic coating industries.

Technical Description:

These standards consist of pre-configured sets of coupons of fine grained copper with thickness ranging from 2.5 µm to 2 mm, which has been electrodeposited onto low carbon steel substrates. The uniform coatings are then overplated with a thin protective layer of chromium and the coupon's total coating thickness is then certified. They are primarily intended for use in calibrating coating thickness measurement instruments based on the magnetic induction principle and are used by the organic and inorganic coating industry for the non-destructive measurement of non-magnetic coatings over magnetic substrates.

Planned Outcome:

The process employed for the production and certification of Coating Thickness Standards 1357 through 1364a will be completed. All 1273 units required to satisfy all outstanding OSRM work orders dating back from 1995 to the present will be delivered.

Accomplishments:

The complete process for the manufacture and certification of Coating Thickness Standards has been overhauled. With the new primary standards produced earlier and the mathematical algorithm developed for the calibration of the instrumentation that employs these standards, the process has been statistically analyzed for uncertainties with the help of the Statistical Engineering Division under the guidance of Stephan Leigh.

The necessary secondary standards, sold to the customers, that were required to satisfy all outstanding work orders since 1995 have been produced (1273 units). Overall, uncertainties for these certifications have been lowered from 5% down to a maximum of 2%.

Impact:

There has been siginificant industrial demand for these SRMs. In FY 1998, units to comply with outstanding work orders dating back to 1995 have been manufactured and are in the process of being packaged for delivery. Tthe overall uncertainties of SRMs 1357 through 1364a have been lowered from 5% down to a maximum of 2% throughout the complete family of standards.

Outputs:

SRM's in Production:

SRM # 1358	Cu & Cr Coating on Steel
SRM # 1359	Cu & Cr Coating on Steel
SRM # 1362a	Cu & Cr Coating on Steel
SRM # 1363a	Cu & Cr Coating on Steel
SRM # 1364a	Cu & Cr Coating on Steel

To date, all of the 1273 SRM's owed from work orders from FY'95 to present have been manufactured. Units are undergoing packaging for their delivery to OSRM.

Project Title: **GOLD MICROHARDNESS STANDARDS**

Investigators: D. R. Kelley and C. E. Johnson

Objectives:

The objective of the work is to develop a gold (Au) microhardness standard which will be used to verify the calibration of microhardness instruments when used for measurements of soft materials at low loads.

Technical Description:

The request for this standard has come mainly from the electronics industry where gold is electrodeposited on printed circuit board contacts. Also, the general plating industry for precious metals has requested the standard for process control of addition agents to Au electrolytes. The demand has been for a standard in the range of 60-100 Knoop or Vickers microhardness when measured at a load of 0.245 Newton.

Successful production of a prototype for this electrodeposited low load, microhardness standard requires a scale-up of the Au electrodeposition process that produces a uniform grain size and hardness over the electropated panel, a means to cut the material uniformly and accurately, a system to mount the samples in the mounting media and a jig to diamond turn up to eight samples at a time. In FY 1998 we expected to reduce the hardness variation across the sample surface by scaling up the electrodeposition process and electroplating a large square panel, perhaps 400 $cm.^2$. This is analogous to a method successfully implemented to reduce the thickness variation in our electrochemically produced coating thickness standards. In order to cut the larger panels into 1.5 cm^2 samples, we proposed in FY 1998 to use a diamond saw blade on a table saw with a traversing table. Traditional methods of cutting using a silicon carbide abrasive wheel are unacceptable since abrasive media is often incorporated into the gold electrodeposit.

Planned Outcome:

The technology to reliably produce microhardness standards in the range of 60-100 Knoop or Vickers, at a reasonable cost, will be established.

Accomplishments:

Having produced a successful prototype, by a process in which a mirror finish with a surface roughness of 63.5 nanometers peak to valley was produced by diamond turning, we have since mounted and diamond turned nine standards. These standards are in the process of being indented and certified. A new, automated microhardness testing machine and image analyzer have been installed and their operation verified. Use of the image analyzer provides an objective means of measuring indentation size.

Impact:

This microhardness standard is expected to fill a void in the low hardness, low load standards presently offered. It will allow the electronics and precious metals plating industry to verify the proper operation of the microhardness measuring devices presently used for quality assurance.

Outputs:

The Electrochemical Processing Group has produced a 24K gold, low load microhardness standard prototype with an average hardness of 75.5 Knoop +/- 10%.

SRM's Under Development:

SRM#1870 Gold Microhardness Standard

Project Title: **LIGHTWEIGHT MATERIALS FOR AUTOMOTIVE APPLICATIONS**

Investigators: R. B. Clough, R. deWit, R. J. Fields, T. J. Foecke, G. E. Hicho, L. E. Levine, and J. L. Fink

Objectives:

The primary objective of this project is to facilitate the introduction of lightweight materials into automobiles in support of the U.S. auto industry's goal to develop automobiles with substantially higher energy efficiency and lower emissions. This will be accomplished by providing models for lightweight metal consolidation and forming, measurements and data for model validation, software that readily transfers the models, and standard test methods for obtaining the data required for implementing the models to the auto companies and their suppliers.

Technical Description:

Major research efforts within the U.S. auto industry are driven by the need to reduce the weight of future vehicles to meet USCAR and PNGV goals. This can most readily be accomplished by the substitution of lightweight materials for the heavy materials currently used. This project consists of two parts: (1) development of a low cost powder processing technology for aluminum alloy and particle reinforced aluminum (PRA) parts, and (2) advancement of formability technology for lightweight sheet metals. In the first part, aluminum alloy and aluminum composite powder metallurgy (PM) materials would be substituted for iron-based PM products. In the second part, more formed aluminum or high strength steel sheet would be used in the body of cars, replacing conventional grades of steel sheet. Both of these approaches have been recognized by the auto industry, and the technical barriers to success have been identified.

In the case of PM aluminum and PRA, the cost of existing processing routes is too high, and efforts to produce acceptable parts using press-and-sinter and direct powder forging are underway. The NIST part of this effort is focused on modeling each step in these consolidation processes from powder to fully dense part. Modeling provides the basis for knowing what properties and parameters of a powder or a process need to be measured in order to more rapidly design successful processes and to monitor consistency. Physical modeling of the process can be used with a cost model to make decisions that optimize cost and properties. The modeling is complex and is carried out with significant academic and industrial collaboration. NIST's primary role has been to coordinate the modeling efforts between academia and industry, validate the models, and provide industry with working models and a preliminary data base. In collaboration with MatSys Inc., the modeling is being made available to industry in a user-friendly, commercially supported software package.

A technical barrier to expanding the use of lightweight sheet metals is the limited industrial experience and expertise in forming operations for these materials. The forming of aluminum and high strength steel sheet is significantly different from the forming of convention-al sheet steel. The expertise developed over many years by tool and die makers for steel does not always apply. To date, only relatively simple shapes, like hoods, have been successfully formed on a commercial basis. The availability of high speed computing and advanced finite element methods (FEM) brings the prediction of forming within reach and provides a way to avoid the trial-and-error approach to metal forming that, while fairly effective with conventional alloys, cannot be efficiently applied to new materials. The automobile industry is currently developing advanced computer programs based on FEM that will predict the forming behavior of materials. NIST is helping industry implement this approach in three ways: improved, physically based models for material behavior during forming, a model for the surface roughening (or smoothing) and consequent changes in die wall/sheet metal friction during forming, and standard test methods for developing data bases of materials deformation behavior under forming conditions. The models provide the equations used in the FEM code, while the test methods provide the precise data for each material that is inserted into and used by these codes.

Planned Outcome:

The NIST powder consolidation modeling effort will result in a validated set of equations that describe the densification of reinforced (or unreinforced) metal powder in terms of the processing conditions. This will result in a commercial software package that accurately models potential processes and that saves U.S. industry time and money which would otherwise have to be spent on trial-and-error investigations.

The NIST forming research will provide new methods for determining the internal defect structure of deformed metals. The information obtained with these methods will be used to establish physically based equations describing the deformation behavior of metals for computer calculations. In addition, a model for the roughening of metals during forming will be developed so that industry can predict the local die surface/sheet metal friction coefficient (a quantity needed for the computer calculations). Lastly, standard test methods will be developed to provide industry with consistent methods for obtaining the needed data base of metal deformation behavior under complex loadings.

External Collaborations:

In the case of the powder consolidation research, a consortium formed by USAMP meets quarterly and the efforts are coordinated at these meetings. The industrial consortium consists of the Big Three, Valimet, Stackpole, and Mascotech. In addition, staff from Ames Lab, ORNL, and University of Michigan are involved. This collaboration consists mainly in the exchange of material and data. NIST also collaborates with MatSys, Inc. and University of Cambridge's Micromechanics Centre (Profs. Fleck and Ashby) to carry out the modeling and the commercial-ization of the modeling. In addition, a totally new method of compaction, dynamic magnetic compaction, is under investigation as an ATP project. NIST collaborates with IAP, Inc., GM, and Zenith in this effort by providing modeling and measurements of densification by extremely high pressures on powders supplied by the industrial participants.

Formability research has largely been carried out in conjunction with the ATP and NAMT project participants: Chrysler, Ford, General Motors, Budd, Alcoa, U.S. Steel, Livermore Software Technology Corporation and the Autobody Consortium, consisting of 20

OEM's and suppliers to the industry, as well as the University of Ohio, the University of Michigan, and Northwestern University. Collaboration has mainly involved Alcoa, General Motors, Prof. Ghosh at the University of Michigan, and Prof. Wilson at Northwestern. Material and advice on commercial forming processes were supplied by the industrial collaborators.

Accomplishments:

A database for the room temperature compaction of aluminum-based powders mixed with varying amounts of reinforcement has been developed. It was found that certain alloy powders could not be consolidated commercially due to their high hardness. The modeling approach developed here was used to predict how much and what size soft aluminum powder needs be added to consolidate the harder alloys. These predictions have now been shown to be correct and the USAMP consortium is pursuing the use of this approach to make PM parts. In addition, this modeling approach was used to quickly find the best size ratio of aluminum to SiC powders to achieve good strength in the final part. Studies of the green strength of aluminum powders showed that bonding was by an interlocking mechanism, rather than oxide rupture followed by metal bonding. As a consequence, it was found that small additions of SiC resulted in increased green strength due to a particle shape that was conducive to interlocking. However, at higher SiC concentrations the strengthening was compromised by increased SiC to SiC contacts which have virtually no strength.

The theory of small-angle scattering by dislocation structures was completed and the results indicated that ultra-small-angle X-ray scattering (USAXS) could prove to be an extremely powerful and versatile tool for studying the evolution of dislocation structures. The theory also showed that the relevant experiments would require extremely precise alignment of the sample and the x-ry beam and several months were spent redesigning the experiment. Extensive computer codes were then written to control the experiments. The USAXS experiments were conducted using NIST's materials science beam line at Brookhaven's National Synchrotron Light Source. The data confirmed every major prediction of the scattering theory and demonstrated that the technique was even more powerful than anticipated. The experiments probed positional correlations between dislocations, measured the changing "diffuse width" of the dislocation walls, detected the presence of dislocation dipoles, examined the inhomogeneity of the microstructure, and allowed measurement of dislocation structure relaxation during creep.

A new theoretical connection has been made between the microstructure of a plastically deformed metal and its mechanical characteristics. It has long been recognized that such a connection must be made in order to develop new microstructure-based constitutive laws. The new theoretical "framework" describes plastic deformation as a self-organizing critical process where strain percolates through the structure. This process is stochastic in nature and is determined by the interactions of mobile dislocations with dislocation walls. Two parameters come out of the analysis that can be considered as internal state variables. The stress-strain law is then given by integrals of some partial derivatives of these variables.

A database of surface roughness measurements was made on sheet metal deformed under complex stress states. Data were obtained as both Ra and Rz in principal strain directionsfor uncoated as well as galvanized sheet metal. While these data were provided to ATP project participants, its main purpose was to calibrate the computer simulation being developed.

Impact:

The USAXS experiments were the first successful attempts at using SAS to study dislocation structures in nearly 50 years of attempts by the scientific community. Following a NIST press release and a press conference at the American Crystallographic Association Annual Meeting, several popular press articles were written about our experiments including write-ups by New Scientist, ScienceNOW, the American Institute of Physics Bulletin of Physics News, the Federal Technology Report, Journal of Metals, the Huntsville Times, American Machinist, and NIST Connections. This new measurement method has been developed to quantify the dislocation content of deformed metals. When used to develop an improved prediction of metal deformation, coupled with our work on surface roughening and data from standard test methods, this research could save industry at least 50 to 100 million dollars per year.

Models of reinforced powder consolidation are now available and have been incorporated in commercially available process modeling software. This software can help industry reduce the amount of trial and error testing required to develop a new process. As part of the modeling of die filling and powder flow, a Phase II SBIR project developed a method of more uniformly filling dies. This has resulted in commercially available feedshoe technology that can improve the mass uniformity of pressed powder parts by a factor of four with a corresponding reduction in part distortion.

Outputs:

Publications

Livne, Z., Munitz, A., Rawers, J. C., and Fields, R. J., "Consolidation of Nanoscale Iron Powders," NanoStructured Materials, **10**(4), pp. 503-522 (1998).

Levine, L. E., Thomson, R., Long, G. G., Black, D. R., and Fields, R. J., "Internal NIST Research Complementing the Springback Predictability and Agile Precision Sheet Metal Stamping Projects," in Advanced Technology Program/Motor Vehicle Manufacturing Technology/Public Workshop, edited by J.C. Boudreaux and T.R. Lettieri, NISTIR 6079, October 1997.

Levine, L. E., Thomson, R., Long, G. G., and Black, D. R., "New Synchrotron X-ray Techniques for In Situ Deformation Studies," in Proceedings of the Fifth International Conference on Composites Engineering (ICCE/5), edited by D. Hui, University of New Orleans (1998).

Thomson, R., Levine, L. E., and Long, G. G., "Small Angle Scattering by Dislocations," Accepted by Acta Cryst. A.

Thomson, R. and Levine, L. E., "Theory of strain percolation in metals," Phys. Rev. Lett., in press.

Campbell, G., Raman, R., and Fields, R. J., "Manufacture of Al/SiC Metal Matrix Composites by the Press and Sinter Route", NISTIR 6235, September 24, 1998.

Fields, R. J., Foecke, T. J., deWit, R., Hicho, G. E., and Levine, L. E. "Standard Test Methods and Data for Modeling Crashworthiness," NISTIR 6236, September 24, 1998.

Presentations:
Invited Talks
Foecke, T. J., "NIST's Program on Metal Forming," Inst. of Mechanics of Materials Workshop in Ann Arbor, MI, October 1997.

Fields, R. J., "Progress in Modeling the Consolidation of Reinforced Metal Powders," quarterly meeting of the U. S. Automobile Manufacturing Partnership Consortium on Low Cost PM Technology for Particle Reinforced Aluminum Parts, at Valimet, Inc., Stockton CA, November 1997.

Fields, R. J., "NIST's Program on Metal Forming," ASME Symp. on Sheet Metal Forming in Dallas, TX, November 1997.

Clough, R. B., "Progress on Fundamental Parameter Measurements on Powder Compacts," GM Powertrain, Romulus, MI, November 1997.

Fields, R. J., "Progress in Modeling the Consolidation of Reinforced Metal Powders," quarterly meeting of the U.S. Automobile Manufacturing Partnership Consortium on Low Cost PM Technology for Particle Reinforced Aluminum Parts, at National Center for Manufacturing Science, Ann Arbor, MI, February 1998.

Levine, L. E. and Thomson, R., "Some Recent Developments in Metal Deformation," Lawrence Livermore National Laboratory, March 1998.

Fields, R. J., "Progress in Modeling the Consolidation of Reinforced Metal Powders," quarterly meeting of the U.S. Automobile Manufacturing Partnership Consortium on Low Cost PM Technology for Particle Reinforced Aluminum Parts, at Oak Ridge National Lab., Oak Ridge TN, May 1998.

Levine, L. E., "Deformation of Metals: The Inside Story," Ohio State University, June 1998.

Levine, L. E., Thomson, R., Long, G. G., and Black, D. R., "New Synchrotron X-ray Techniques for In Situ Deformation Studies," Distinguished Lecture at the Fifth International Conference on Composites Engineering (ICCE/5), Las Vegas, NV, July 1998.

Fields, R. J., "Progress in Modeling the Consolidation of Reinforced Metal Powders," quarterly meeting of the U.S. Automobile Manufacturing Partnership Consortium on Low Cost PM Technology for Particle Reinforced Aluminum Parts, at Ames National Lab., Ames, IA, August 1998.

Contributed Talks

Levine, L. E., Long, G. G., and Thomson, R., "In Situ Measurements of Dislocation Structure Evolution," TMS Annual Meeting, San Antonio, TX, February 1998.

Thomson, R. and Levine, L. E., "Percolation of Strain Through Dislocation Structures," TMS Annual Meeting, San Antonio, TX, February 1998.

Levine, L. E., Thomson, R., and Long, G. G., "AnalyticalTheory for Small-angle Scattering from Dislocation Walls in Deformed Metals," American Physical Society, Los Angeles, CA, March 1998.

Long, G. G., Levine, L. E., and Thomson, R., "In Situ ultra-small-angle X-ray Scattering by Dislocation Structures in Single-crystal Al Under Uniaxial Deformation," Los Angeles, CA, March 1998.

Thomson, R. and Levine, L. E., "A Percolation Model of Deformation," Los Angeles, CA, March 1998.

Levine, L. E. and Thomson, R., "In Situ Ultra-Small-Angle X-ray Scattering Measurements of Dislocation Structure Evolution," 1998 NIST/LLNL Workshop on Work Hardening & Dislocation Patterning in Metals, Pleasanton, CA, June 1998.

Thomson, R. and Levine, L. E., "Theory of Strain Percolation in Metals," 1998 NIST/LLNL Workshop on Work Hardening & Dislocation Patterning in Metals, Pleasanton, CA, June 1998.

Thomson, R. and Levine, L. E., "Stress-Strain Response During Plastic Deformation: A New Theoretical Approach," Workshop on Residual Stresses: Theory and Experiment, NIST, Gaithersburg, MD, July 1998.

Long, G. G. and Levine, L. E., "Observation of Small-Angle X-Ray Scattering from Dislocations," 1998 Annual Meeting of the American Crystallographic Association, Arlington, VA, July 1998.

News Releases and Popular Press Reports:

"Advance Could Lead Eventually to Big Savings in Metal-Forming Industry," NIST News Release, July 21, 1998.

Project Title: **ELECTROGALVANIZED COATINGS ON STEEL**

Investigators: G. R. Stafford, C. R. Beauchamp, and D. R. Kelley

Objectives:

The long term objective of our electrogalvanizing research is to develop the electrochemical expertise that will enable our group to produce coating thickness and composition standards which will be used by the steel industry to establish wet chemistry procedures and calibrate on-line x-ray fluorescence instruments for process control of continuous strip plating of electrogalvanized coatings such as Zn-Ni and Zn-Fe.

The objective of this work is to continue the development of a zinc electrodeposition process which will be used for the eventual production of two zinc coating thickness SRMs. The first is a 2 to 5 μm deposit or pure zinc onto a 3 cm x 3 cm steel coupon in which the coating thickness uniformity is within 5% of the certified value. The second is a 2 - 5 μm deposit of pure zinc onto a 10 cm x 15 cm steel coupon in which the coating thickness uniformity is within 10% of the certified value.

Technical Description:

The domestic electrogalvanizing market is approximately 2.5 billion dollars per year. In recent years, electrogalvanized steel has developed well beyond simple elemental coatings towards rather sophisticated alloys such as Zn-Ni, Zn-Fe, and Al-Zn. Today pure zinc still maintains about 82% of the domestic market, followed by Zn-Ni and Zn-Fe at about 9% each. Coating thickness and composition standards have failed to keep pace with the development of the alloys and the tighter constraints imposed by the competitive markets; consequently, there is little accountability among most sheet steel manufactures both here and abroad.

There is a critical need for standards in this area, particularly in light of anticipated ISO 9000 regulations. A variety of standards are required. Coating thickness standards of pure zinc are required for the calibration of on-line x-ray fluorescence instruments for process control of continuous strip plating. Smaller yet equally uniform coupons for destructive analysis are required for laboratories using gravimetric techniques ("weigh-strip-weigh") for determining coating thickness. As the Zn-alloy market continues to grow, standards which are certified for both composition and thickness will be required.

Planned Outcome:

This project will result in the development of a process for producing Zn coatings on steel with crystal orientations similar to those sought by the electrogalvanizing industry. The process will produce coatings with uniform mass per unit area so they will be usable for the production of calibration standards for x-ray fluorescence techniques as well as for gravimetric testing methods.

Accomplishments:

Previous results demonstrated the feasibility of electrodepositing zinc coatings with a mass per unit area variation of less than 5% uncertainty. Based on these results, we have initiated the production of 100 prototype SRM coupons measuring 3 cm x 3 cm, which will be used by customers verifying their destructive gravimetric testing protocols. In addition, the evaluation of further modifications to our electrodeposition cell geometry is underway with the objective of obtaining a more uniform deposit over a larger area which is required for the wide beam x-ray fluorescence instrumentation. The expected increased deposit uniformity, coupled with a more rigorous measurement protocol, will allow us to produce the larger 10 cm x 15 cm coupon with an overall uncertainty of less than 10%. Finally, the instability of the additive-free electrolyte is being addressed by adjusting the metal content and varying operating conditions during electrodeposition.

Impact:

The standards under development will fill a void in the present line-up of available standards, since the current marginally acceptable standards are intended for measurement techniques that are not suitable for on-line quality assurance purposes. In addition, the proposed process for the manufacture of these standards is suitable for further modification which will allow them to comply with the additional needs presented by industry as new alloys emerge in the electrogalvanizing field.

Outputs:

SRM's Under Development:
Electrogalvanized Coatings on Steel

Project Title: **ELECTRODEPOSITED CHROMIUM AND CHROMIUM ALLOYS FROM TRIVALENT ELECTROLYTES**

Investigators: J. L. Mullen and C. E. Johnson

Objectives:

The program has two focus areas. One involves determining the effects of electrolyte composition and operating parameters on the composition, structure and properties of chromium electrodeposits in which a trivalent electroactive chromium species is used. The structure and properties of the chromium coatings from trivalent electrolytes will be compared to coatings from hexavalent electrolytes. The second focus area is investigating the use of amorphous alloy coatings of Co-Cr, deposited from a modified trivalent chromium electrolyte, as potential bearing surfaces for orthopaedic implants.

Technical Description:

Chromium is widely used as an electrochemically applied coating on metal for wear resistance, to reduce friction, or for a desired appearance. In present commercial electroplating processes, chromium is deposited from electrolytes in which it is in the toxic hexavalent (Cr^{+6}) state. Present commercial deposition of chromium from non-toxic trivalent electrolytes (Cr^{+3}) is limited solely to decorative application where the coating thickness is on the order of 0.5 μm to 5.0 μm. The thicker deposits required for functional applications cannot be obtained from the commercial bath chemistry. A Cr^{+3} - based electrolyte, recently developed at NIST (U.S. Patent 5,415,763), allows one to electrodeposit chromium coatings which are thick enough (50 μm to 250 μm) to be suitable for engineering applications; however, the wear resistance is somewhat lower than coatings made from hexavalent electrolytes. This area of the program focuses on the structural characterization of chromium coatings electrodeposited from the NIST trivalent electrolyte, paying particular attention to structural features which may lead to the observed lower wear resistance.

Because wear debris from orthopaedic implants has been implicated as a major cause for the end-of-effective-service of orthopaedic implants, there is a strong interest in exploring new bearing designs, including new material couples, that may reduce wear debris effects and, hence, help to prolong effective implant service. Glassy (amorphous) metals have some unique properties that may render them attractive candidates for the surfacing of metal-implant bearing surfaces. Metastable glasses of metal alloys, with uniform compositions and homogeneous structures that are not attainable under usual quasi-equilibrium processing conditions, can often result in alloys with exceptional corrosion resistance and high hardness. Amorphous coatings that contain surface scratches have been reported to project only 1/7 as much wear of Ultra-High Molecular Weight Polyethylene (UHMWPE) as scratched stainless steel against UHMWPE. One explanation given is the absence of material build-up around a scratch in the less ductile, amorphous material. The absence of secondary phases may reduce the abrasive and asperity-initiated wear observed in UHMWPE. One method of producing glassy alloys is electrodeposition. This area of the program focuses on the characterization of amorphous cobalt-chromium-carbon alloy coating electrodeposited from an electrolyte developed at NIST (U.S. Patent 5,672,262).

Planned Outcome:

The processing conditions which cause the properties, hardness and wear resistance, of as-deposited and heat-treated chromium deposits from trivalent electrolytes to be equal or superior to deposits from hexavalent electrolytes will be identified. The commercial success of the use of trivalent electrolytes as an alternative to hexavalent electrolytes for depositing chromium coatings for engineering applications will be further enhanced by the understanding of the effects of processing conditions.

The correlations between processing conditions and structure, which affects performance factors such as adherence, corrosion and wear resistance, will be investigated for the glassy Co-Cr-

C system. If the material shows promise as an orthopaedic implant bearing surface, toxicity will need to be considered.

Accomplishments:

The influence of electrolyte chemistry and mass transport on the composition, structure and properties of trivalent chromium deposits is continuing. The as-deposited hardness and wear resistance of trivalent chromium coatings are inferior to deposits from hexavalent electrolytes. With heat treatment, however, the trivalent chromium deposits have superior properties due to precipitation of the chromium carbide phase.

The potential applicability of metallic glasses for improving the wear resistance of orthopaedic joint bearing couples is being investigated with the electrodeposition of an amorphous Co-Cr-C multi layer coating obtained from a modified trivalent chromium electrolyte. The as-deposited hardness of the Co-Cr coatings is 690 HK_{25}. Heat treatment of the coatings at 600 ^{o}C resulted in hardness of 1350 HK_{25} due to the precipitation of carbides. Wear and adherence tests for both the as-deposited and heat treated coatings are in progress.

Outputs:

Presentations:

Tesk, J. A. and Johnson, C. E., "Glassy Alloys as Potential Bearing Surfaces for Orthopaedic Implants," ASTM Symposium on Alternative Bearing Surfaces in Total Joint Replacement, San Diego, CA, November 1997.

Patents Filed:

Glassy Alloys as Potential Bearing Surfaces for Orthopaedic Implants
J. A. Tesk and C. E. Johnson
Patent Appl. No. 60/064,873 - October 20, 1997

Project Title: **ELECTROCHEMICAL PROCESSING OF NANOSCALE MATERIALS**

Investigator: T. P. Moffat

Objectives:

This project seeks to develop an understanding of the physical chemistry and processing parameters required for producing novel materials via electrochemical processing.

Technical Description:

The electrochemical synthesis of a variety of low dimensional structures, such as Cu/Co strained-layer superlattices and spin valves, are being explored. These materials are produced by electrodeposition from a single electrolytic solution using a variety of substrates ranging from copper single crystals, to highly oriented evaporated copper seed-layers, to semiconductors such as silicon and GaAs. Work is underway to establish the relationships between the magnetic behavior, film structure and the processing parameters. Understanding the linkage between the processing parameters and the dynamics of nucleation and growth is central to developing well-defined materials. A deeper understanding of some of these issues is being pursued by using in-situ scanning probe microscopy (SPM) to characterize the structure and dynamics of solid/electrolyte interface. Specifically, the role of inorganic and organic absorbates on the evolution of thin film microstructure and morphology during homo- and heteroepitaxial growth is been actively explored.

Planned Outcome:

Electrodeposition is a convenient, low temperature, inexpensive process for producing thin films for a variety of important technological applications ranging from metallization of semiconductor devices to the synthesis of magnetic materials. Our activities range from fundamental investigations of electrochemical deposition to the fabrication of devices. Studies of the deposition of ultrathin cobalt and copper films should help contribute towards the development of magnetic devices based on these materials. More generally, our studies using scanning tunnelling microscopy (STM) to characterize metal deposition processes promise to contribute valuable information on the relevant physical mechanism, kinetics and morphological evolution associated with film growth by electrodeposition. In a generic sense, the success of the electroplating industry stems largely from the remarkable influence of electrolyte additives on the physical properties of the deposited film. Chloride ion is a ubiquitous species in most commercial copper electroplating processes thus, our STM studies contribute fundamental insight into the way these adsorbates influence microstructural evolution. This is likely to be of importance as submicron copper metallization is introduced into the fabrication of semiconductor devices via electrochemical or CVD processes.

External Collaborations:

We are working with Prof. L. Salamanca-Riba to explore the magnetic properties of electrodeposited strained-layer superlattices. Mr. Mutsuhiro Shima, a Ph.D. student at the University of Maryland is involved in the synthesis and characterization of Cu/Co multilayers. A collaboration has been initiated with Prof. Larry Bennett to explore the use of the magneto-optic Kerr effect (MOKE) and the second harmonic Kerr effect (SHG-MOKE) to perform insitu characterization of the magnetic properties of electrodeposited thin films.

Accomplishments:

A scheme for depositing highly oriented copper seed layers as a substrate on Si(100) and Si(111) has been adopted as the basis for electrochemically growing oriented Cu/Co strained-layer superlattices. In collaboration with the NIST Magnetic Materials Group, and M. Shima and L. Salamanca-Riba of the University of Maryland, $[Cu/Co]_N$ Si(100) films were shown to exhibit magnetoresistive behavior. The magnetoresistance was shown to be dependent on in-plane orientation due to the magnetocrystalline anisotropy of the expitaxial structure. However, magnetoresisitve behavior was only observed for long wavelength multilayers. TEM studies of the films revealed significant grooving of the small angle grain boundaries. The resulting orange-peel structure may explain the absence of antiferromagnetic coupling observed at small wavelengths. However, the possibility of ferromagnetic coupling due to cobalt segregation in the boundaries remains to be excluded from consideration.

The dissolution of artificially structured alloys may be used to develop a clearer understanding of anodic stripping voltammetry and alloy dissolution in general. This study takes advantage of our ability to construct Cu/Co multilayers under conditions where the quasi-reversible electrokinetics of the constituent elements are well defined. Specifically, the anodic dissolution of an ultrathin cobalt film buried beneath a copper overlayer was studied using voltammetry and chronoamperometry. The blocking efficiency of the copper overlayer is a strong function of its thickness and the stripping potential. Furthermore, the inhibition provided by the copper overlayer was found to be quite sensitive to the thickness of the buried cobalt layer. For copper overlayers between 13-29 monolayer equivalents of charge (MEQ) a sharp transition in the dissolution behavior of the buried cobalt layer was observed. Namely, negligible dissolution was observed if the cobalt layer was less than 30 MEQ while almost complete dissolution occurred when the cobalt layer was thicker than 45 MEQ. For the thicker films, cobalt dissolution may well be described by a quasi-two dimensional instantaneous nucleation and dissolution model. These experiments may provide a sensitive measure of the defects which exist in such films as well as guidance in the selection of appropriate processing parameters for the deposition of Cu-Co multilayers. Finally, artificially structured materials represent a novel model system for decoupling physical and chemical effects during the study of alloy dissolution.

An effort has been initiated to directly deposit metals onto semiconductor substrates. Long wavelength Cu/Co multilayers have been deposited directly on Si. The films exhibit a GMR of ~7% although XTEM reveals the film to be polycrystalline due to the presence of a thin SiO_2 layer. More recent studies using GaAs substrates have allowed us to grow highly oriented metal films. Specifically, a set of symmetric Cu/Co spin valves was grown on GaAs from a single electrolyte. The materials exhibit intriguing magnetoresistive sensitivity, 0.22 % ($\Delta \rho/\rho$) per Oe, at low fields, ~30 Oe.

In situ STM has been used to study the structure and dynamics of the deposition/dissolution of Cu, and the influence of anion adsorption and metal underpotential deposition on step dynamics. Studies to date have focused on chloride adsorption and lead underpotential deposition onCu(100), Cu(111) and more recently Cu(110). Potential dependent order-disorder transitions have been observed along with step faceting due to the formation of the ordered halide adlayer. In the case of lead underpotential deposition, 2-D alloying/dealloying has been observed as a function of lead coverage. Interestingly, lead has received significant attention from vacuum scientists studying the effect of surfactants on metal on metal epitaxy such as Cu/Cu and Co/Cu. The use of underpotential deposition and anions as surfactants in the electrochemical deposition of copper is likely to prove even more interesting than vacuum deposition since the surfactant coverage and its effect on mesocopic structure can be continuously and easily manipulated by potential control.

Outputs:

Publications:

Moffat, T. P., "Oxidative Chloride Adsorption and Lead UPD on Cu(100): Investigations into Surfactant-Assisted Epitaxial Growth," J. Phys. Chem., in press, (1998).

Shima, M., Salamanca-Riba, L., Moffat, T. P., and McMichael, R. D., "Structural and Magnetic Properties of Electrodeposited Co/Cu Multilayers," J. Mag. Magn. Matls., in press, (1998).

Nikitenko, V .I., Gornakov, V. S., Dedukh, L. M., Khapikov, A.F., Moffat, T. P., Shapiro, A. J., Shull, R. D., Shima M., and Salamanca-Riba, L., J. Mag. Magn. Matls., in press, (1998).

Shima, M., Salamanca-Riba, L., Moffat, T. P., and McMichael, R. D., "Structural and Magnetic Anisotropy of Electrodeposited Co/Cu Multilayers," MRS Symp. on Materials for High Density Magnetic Recording, in press, (1998).

Moffat, T. P., "STM Studies of Metal Electrodes," Chapter to be published in Electroanalytical Chemistry Monograph Series, ed. A. J. Bard, Marcel Dekker, in press, (1998).

Shima, M., Salamanca-Riba, L., Moffat, T. P., McMichael, R. D., and Swartzenruber, L. J., "Structural and Magnetic Fourfold Symmetry of Co/Cu Multilayers Electrodeposited on Si(001) Substrates," J. Appl. Phys., 84, 1504, (1998).

Moffat, T. P., "STM Study of Cu(100) in 10 mM HCl," Electrochemical Nanotechnology, In-situ Local Probe Techniques at Electrochemical Interfaces, eds. W. J. Lorenz and W. Plieth, Wiley-VCH, New York, (1998).

Presentations:

Moffat, T. P., "Investigations into Surfactant-Assisted Epitaxial Growth by Electrodeposition," Contributed short talk at Gordon Conference on Electrodeposition, Colby Sawyer College, New London, NH, August 1998.

Shima, M., Salamanca-Riba, L., and Moffat, T. P., "Dissolution Dynamics of Artificially Structured Alloys," Colby Sawyer College, New London, NH, 1998. Poster presented at Gordon Conference on Electrodeposition, Colby Sawyer College, New London, NH, August 1998.

Shima, M., Salamanca-Riba, L., Moffat, T. P., and McMichael, R. D., "Structural and Magnetic Anisotropy of Electrodeposited Co/Cu Multilayers," Poster presented at Gordon Conference on Electrodeposition, Colby Sawyer College, New London, NH, August 1998.

Moffat, T. P., "Electrodeposition of Strained-Layer Superlattices," Symp. on Processing-Structure Property Relationships in Electrochemically Prepared Materials, 193rd Meeting of the Electrochemical Society, Inc., San Diego, CA, May 1998.

Shima, M., Salamanca-Riba, L., Moffat, T. P., and McMichael, R. D., "Structural and Magnetic Properties of Electrodeposited Co/Cu Multilayers," Poster presentation at 3rd Int'l Symp. on Metallic Multilayers (MML'98) and EMRS Symp. of Magnetic Ultrathin Films and Nanostructures, Toronto, Canada, June 1998.

Shima, M., Salamanca-Riba, L., Moffat, T. P., and McMichael, R. D., "Structural and Magnetic Anisotropy of Electrodeposited Co/Cu Multilayers," MRS Symp. on Materials for High Density Magnetic Recording, San Francisco, CA. Poster Presentation by M. Shima was awarded one of eight prizes for the best poster presented at the Spring '98 MRS meeting, May 1998.

Moffat, T. P., "Electrodeposition of Strained-Layer Superlattices," The 7th Joint MMM-Intermag Conference, San Francisco, CA, January 1998.

Project Title: **GENERATION OF GRAIN DEFECTS NEAR CORNERS AND EDGES IN CASTINGS**

Investigators: R. J. Schaefer, R. E. Napolitano, W. J. Boettinger, D. R. Black (852), and M. D. Vaudin (852)

Objectives:

This project seeks to provide the aerospace casting industry with understanding and quantitative models which can be used to minimize the occurrence of grain defects in single crystal superalloy castings. By analysis of the thermal conditions experienced by the solidification front as it propagates through a casting, the project will make it possible to identify likely sites of defect formation in computer simulations of the casting, and modify the design without requiring a long series of test castings.

Technical Description:

Single crystal superalloy castings enable aircraft turbine engines and, more recently, industrial gas turbines (IGTs), to operate at higher temperatures and thus at higher efficiency. Defects such as stray grains or regions of crystallographic misalignment reduce the high-temperature performance of such castings, and their presence causes a significant number of the castings to be rejected during inspection. Models which are capable of predicting when and where these defects form will enable the industry to improve the casting process and thus decrease the lead time on newly designed parts, reduce the costs associated with high reject rates, and produce a viable yield of much larger single crystal components for IGT applications. This project analyzes the defect structure in single crystal superalloys and develops models to describe their formation.

Several different mechanisms, such as nucleation of new crystals, fragmentation of dendrites, and convective flow effects, can lead to the formation of grain defects. An important part of this project is analysis of the detailed geometry and crystallography of the defects, using techniques such as synchrotron X-ray topography and analysis of electron back-scattering patterns (EBSP). This information helps to identify the geometry of the defect structures, which provides an indication of the actual mechanism of formation.

Single crystal growth of superalloys occurs by propagation and branching of dendritic crystals along specific crystallographic axes, and the rate of propagation is a function of the temperature at the dendrite tips. In order to determine the thermal conditions which prevail at the time a crystal reaches a specific point in the casting, it is not sufficient to simply follow the spreading of the liquidus isotherm, one must determine the actual path by which the branching dendrite reached that point. When combined with a model for the growth kinetics of the dendrite tips and an analysis of the thermal field in the casting, the growth path information can be used to predict the undercooling ahead of the dendrite tips. The undercooling can then be used to estimate the probability of stray grain nucleation.

Planned Outcome:

This project will result in guidelines and models which can be used by the casting industry to predict when certain types of grain defects will form. The work will provide a method for predicting the thermal conditions at the solidification front which result from transient growth behavior as the dendrites propagate around corners and edges of the casting. The ability to predict defect formation by processes such as nucleation depends in part on the outcome of other studies which are quantifying the nucleation behavior of superalloys.

External Collaborations:

This project was carried out as part of the NIST Consortium on Casting of Aerospace Alloys and involved collaboration with most of the members of this group. NIST provided guidance to Howmet Corp. and PCC Airfoils on the design of test castings to evaluate defect formation processes, and they made the castings and supplied them to NIST and other consortium members for evaluation. PCC Airfoils and Pratt & Whitney have provided guidance on the conditions which lead to defect formation. NIST has collaborated with UES, Inc. on strategies for linking growth path models to their commercial ProCAST™ software for modeling metal casting. Howmet and the University of Wisconsin provided nucleation data for use with the model.

Accomplishments:

Superalloy single-crystal test castings were analyzed, primarily by optical metallography and x-ray topography, to determine the location and geometry of low-angle boundaries. Particular attention was devoted to a platform region of the casting, into which the dendritic structure spread by sometimes complex three-dimensional paths. The castings had been produced by Howmet to study the effects of mold geometry on the development of grain defects, such as spurious grains, low angle boundaries, and freckle grains. Spurious grains were identified in some areas of the platform region, where the undercooling may have become relatively high before the arrival of the solidification front.

Two methods were developed for analysis of the spreading of dendritic structures into regions such as the platform of a superalloy single crystal. Both of them are based upon the well-known behavior of nickel dendrites to grow and branch along the directions of the crystallographic cube axes. The first method used a lattice model which continuously tracked the growth of the entire body of dendrites and branches as they propagated through a casting. This method provides a full three-dimensional mapping of values of several important parameters of the dendrite growth, including the local primary direction and the undercooling at the time of solidification. It also maps out those surfaces within the volume of the casting along which dendrite structures grow together after reaching the surface by different paths. These surfaces, referred to as convergence faults, are probable locations for low-angle boundaries. There is, however, no model presently available to predict the expected misorientation at these boundaries.

The lattice model was applied to an idealized test casting having a simple geometry and thermal field, but having features such as a platform region which are commonly found in real single-crystal castings. The geometry of dendrite growth modeled in this test casting was shown to have several features observed in the real test castings provided by Howmet, with the dendrites following complex three-dimensional paths on the platforms and forming patterns of convergence faults similar to the low-angle boundaries found in the test casting.

The second method of analysis is referred to as the growth-path method. This method enables one to select a point or array of points in an area of the casting where the possibility of stray grain formation is believed to be high, and to determine the path by which the dendrites reach that point and the entire thermal history at all points along that path. When this information is combined with a model for nucleation, it leads to a quantitative prediction of the probability of stray grain formation in this region.

The growth-path method was initially applied to an idealized casting and thermal field, similar to that used for the lattice model. It has now been adapted for application to the geometry and thermal field of a real casting, as modeled by commercial finite element casting simulation software. In addition, real experimental data for a superalloy were used in the nucleation model. Incorporation of these data required development of a formulation for converting the limited set of experimental data, obtained in a series of painstaking experiments by Prof. J. Perepezko of the University of Wisconsin at Madison, to a continuous function describing the probability of nucleation as a function of temperature and time.

Impact:

The current project has demonstrated that the conditions leading to defect formation cannot be predicted solely on the basis of analysis of local conditions within the casting, but must take into account the path by which the growing dendritic crystals reach each point. The Growth-Path method has provided a way to predict this path and to incorporate nucleation data into a defect-formation model. The lattice model has shown how dendrite growth paths through regions of complex geometry can be analyzed and used to predict boundaries where crystallo-graphic misalignment is likely to occur.

Outputs:

Publications:

Napolitano, R. E., Roosen, A. R., and Schaefer, R. J., “The Growth-Path Method for Prediction of Spurious Grain Nucleation in Single-Crystal Castings,” accepted for publication in Proceedings of 3rd Pacific Rim International Conference on Advanced Materials and Processing, Honolulu, HI, July 1998.

Presentations:

Napolitano, R.E. and Schaefer, R. J., “Defect Formation in Single-crystal Castings,” ICCA/NIST Semi-annual Program Review, NIST, October 1997.

Napolitano, R. E., “Cellular Automaton Finite Difference Modeling of Morphological Evolution During Alloy Solidification,” International Symposium on Processing of Metals and Advanced Materials: Modeling, Design, and Properties, TMS Annual Meeting, San Antonio, TX, February 1998.

Napolitano, R. E., “The Growth-Path Method for Prediction of Spurious Grain Nucleation in Single-Crystal Castings,” Ibid.

Project Title: **REACTIONS OF ZINC VAPOR WITH ZIRCALOY**

Investigators: J. R. Manning, M. E. Williams, and W. J. Boettinger

Objectives:

The objective of this project is to measure the rates of reaction between zinc vapor and Zircaloy to allow an estimate of the importance of these reactions for the safe storage of spent nuclear fuel rods. These fuel rods are enclosed in Zircaloy cladding which in some configurations may be exposed to zinc vapor during storage.

Technical Description:

A major concern of the electric utility companies that operate nuclear power plants and the U.S. Nuclear Regulatory Commission (NRC) is the safe storage of radioactive fuel rods after their removal from nuclear power reactors. In some storage configurations currently projected to last for 100 years or more, it is believed that zinc vapor may come into contact with the Zircaloy cladding which encloses the fuel rods. The NRC asked NIST to conduct short-time tests to identify metallurgical reactions and diffusion processes that might arise between this zinc vapor and Zircaloy-4, which is a zirconium-base alloy with a small fraction of alloying elements. The NRC then could use these results to evaluate possible reaction effects during storage. Since diffusion and reaction rates increase strongly with temperature, the technical approach was first to do tests at higher temperatures, where measurable reaction layers were expected to form in a few days or weeks of exposure of Zircaloy to zinc vapor. The temperature and time dependences measured in these tests will aid the NRC in estimating effects to be expected from these high temperature reactions during 100-year exposures at storage temperatures, typically 350^{o}C and below. In addition, a longer time (6 months) exposure test was performed at 350^{o}C to provide a test under conditions closer to real storage temperatures.

Planned Outcome:

Measurements of the rates of growth of reaction layers on Zircaloy after exposure to zinc vapor will be used to identify diffusive reactions that occur. NRC will use these results, along with other information obtained elsewhere, to estimate whether these reactions might cause cracking of the Zircaloy cladding during long-time dry storage. Such cracking would be very undesireable since it could allow radioactive material to escape from the fuel rods.

External Collaborations:

This project was planned under an interagency agreement with the U.S. Nuclear Regulatory Commission and funded by them. Progress and results were discussed periodically with the NRC and their consultants on this topic.

Accomplishments:

The temperature dependence of reaction layer growth on Zircaloy-4 exposed to zinc vapor was measured in the temperature range 650^{o}C to 725^{o}C. This dependence corresponded to an activation energy of about 140 kJ/mole.

Project Title: **REACTIVE BONDING IN METALS**

Investigators: C. E. Campbell, W. J. Boettinger, U. R. Kattner, M. E. Williams, F. S. Biancaniello, and L. C. Smith

Objectives :

Thermodynamic and kinetic models will be developed to predict time-dependent diffusion paths associated with finite-sized diffusion couples for application to reactive bonding in metals. Emphasis is placed on modeling the diffusion mechanisms associated with the transient liquid phase bonding of Ni-based superalloys proposed for use in aerospace applications. The kinetic analyses include consideration of the formation of transient phases during processing.

Technical Description:

Transient liquid phase (TLP) bonding is one of many industrial applications that rely on finite-sized diffusion couples to join materials efficiently. To join high temperature structural materials with a homogeneous composition profile across the joint, TLP bonding uses a thin filler material, which has a significantly lower melting temperature than the bulk material, to wet the base metal. The filler material then solidifies isothermally through rapid interdiffusion of one of its constituent elements, such as boron. However, difficulties arise when applying TLP bonding to multicomponent commercial Ni-based superalloys: brittle precipitates may form during the bonding process, degrading the mechanical properties of the joint. To avoid these unwanted precipitates requires the correct thermal processing schedule for a given substrate alloy and filler composition, or the correct filler material for a given thermal processing schedule and substrate alloy. To predict the time-dependent diffusion paths, and thus thermal processing, requires both thermodynamic and kinetic descriptions of the systems. To make this possible, the Ni-based superalloy database developed by the Metallurgy Division will be expanded to include boron. From the existing diffusion data for the binary and ternary systems comprising the Ni-base superalloy systems, a kinetic database will be constructed to be compatible with a diffusion code. The numerical simulations of the diffusion paths will be verified with the experimental results of selected alloys.

Planned Outcome:

A systematic method of choosing time-temperature schedules and of optimizing filler compositions will be developed for Ni-based superalloys with Ni-B based filler compositions. This methodology will include the development of thermodynamic and kinetic databases.

External Collaborations:

NIST has consulted with scientists at Westinghouse, Howmet, and PCC to establish the direction of this research. Extensive discussions with Prof. John Morral, at the University of Connecticut, have been conducted on multiphase diffusion couples.

Accomplishments:

The Al-B system has been reassessed to use a simpler liquid phase description. The AlB_{12} and boron ß-rhombohedral phase descriptions were revised to more accurately represent recent experimental data.

The Ni-Al-B system was assessed, using the binary Ni-Al descriptions by Dupin and Huang and the revised binary Al-B assessment.

A mobility database was constructed for Ni-Al-B using the Ni-Al assessment of Engström and the limited available literature data for Ni-B and Al-B.

A comparison of DICTRA simulations and theoretical predictions of Tuah-Poku et al for the transient liquid bonding of Ni-Ni_3B was completed.

TLP bonding experiments for the Ni-5 wt.% Al substrate with a Ni-1.9 wt.% B filler composition were completed for the following temperatures and times: 1200 °C for 1 hour; 1150 °C for 1 hour; 1315 °C for 0.25 0.5 1, 2, and 3 hours; and 1350 °C for 0.167 hours. For each joint created, the Al profiles were collected, using EDS, and compared to the numerical simulations.

Impact:

Phase diagram assessments and diffusion models should reduce the experimental time and cost industry devotes to determining the correct time-temperature processing schedules for the TLP bonding of Ni-base superalloys.

Outputs:

Presentations

Campbell, C. E., "Transient Liquid Phase Bonding of Ni-Based Superalloys," Seminar at Howmet Corp., Whitehall, MI, May 1998.

Campbell, C. E., and Boettinger, W. J., "Analysis of Diffusion Paths During TLP Bonding of Ni-Al Alloys with Ni-B," International Conference on Joining of Advanced Materials, Rosemont, IL, October 1998.

PHASE EQUILIBRIA

Thermodynamic phase equilibrium data, which indicate the identities and quantities of the final, stable products of any given process, are essential tools for developers and manufacturers of engineering materials. The Phase Equilibria Program encompasses not only data compilations and experimental measurements of phase equilibria, but also development of thermodynamic and first-principles models which form the underlying basis of the equilibria. In addition, several projects go beyond the direct graphical representation of equilibria to include characterization of the physical and crystallographic properties of the constituent phases, or to incorporate the equilibrium information into kinetic models of non-equilibrium processes. MSEL phase equilibrium work includes the following main projects:

High Temperature Superconductors
The objective of this activity is to conduct experimental studies of copper-based materials with emphasis on regions and conditions pertinent to the improved manufacture of bulk superconducting wires and tapes. Efforts have been largely directed to the Bi-Sr-Cu-Ca-O systems which are currently of greatest commercial interest. The successful processing of wires with high current-carrying capacities and excellent superconducting properties is known to require the *in situ* coexistence of high quality superconducting solid plus a liquid phase to induce texturing and grain alignment. The phase diagram work is therefore directed toward determining the location in composition-P-T space of the primary crystallization fields of the BiSCCO superconductors; that is, the regions where only 2 phases are present - the superconducting solid plus a liquid. Considerable efforts are also directed to developing graphical and other practical methods for end users of the complex data. This research is carried out in close collaboration with the U.S. Department of Energy (DOE) Superconductivity Program for Electric Systems and its participating national laboratories.

Dielectrics for Wireless Communications
Dielectric ceramics are used to fabricate a variety of components in cellular communications circuits that store, filter, and/or transfer electromagnetic energy with minimal loss (e.g., resonators, bandpass filters, circulators). The required properties for the ceramic materials include high dielectric constant, minimal dielectric loss, and essentially zero temperature dependence of dielectric properties. Knowledge of phase equilibria relations is important because all ceramic components are processed as controlled mixtures to achieve temperature stabilization; furthermore, the existence of previously unknown compounds with potentially useful properties may be revealed. This research activity emphasizes experimental determination of ternary (or higher) phase diagrams that contain one or more components or compounds that exhibit useful properties, and the correlation of chemical composition, atomic arrangement, and dielectric performance within each system. The experimental work includes synthesis, structural analysis, determination of phase relations, and microwave characterization (via collaborators at NIST/Boulder) of dielectric properties.

Computational Studies of Ferroelectrics and Dielectrics
Ferroelectric ceramics exhibit unique dielectric properties that are widely exploited to produce multilayer capacitors and transducers. Related ceramic systems are useful as high performance dielectric resonators for wireless communications. The electronic properties of these materials are strongly dependent on the exact ordering patterns adopted by the atoms within the ceramic material; only certain, precise arrangements result in electronically useful properties. Understanding of why and how these particular arrangements occur is needed by industry to improve processing control, reduce the associated costs, and enable the rational design of improved materials. The objective of this research activity is to develop and apply computational tools to model the structural behavior of these important materials as a function of chemical composition and temperature. The work is

carried out using first principles phase diagram calculations, including the Ising model and Monte Carlo methods.

NIST-ACerS Phase Equilibria Diagrams Database
The objective of this project is to prepare and publish evaluated phase equilibria data for the industrial and academic communities. Technical evaluation of original literature containing phase diagram information is carried out under NIST supervision. The preparation of the evaluated diagrams for dissemination as the reference series, Phase Equilibria Diagrams (formerly Phase Diagrams for Ceramists), is conducted at NIST in collaboration with on-site personnel of the American Ceramic Society (ACerS). The ACerS personnel are primarily supported by funds raised by the Society from industry, academia, and individuals. The collaboration represents an over-60-year agreement with ACerS to provide technically evaluated phase diagrams for the ceramics industry.

Solidification Path for Multicomponent Superalloys
This project develops a thermodynamic data base for Ni-base superalloys, which is then used to calculate phase equilibrium information and subsequently the alloy solidification behavior. This information is incorporated into commercial software used by the aerospace industry to analyze the casting of numerous multicomponent alloy compositions. The thermodynamic and solidification models predict the identity and volume fraction of all phases present in the casting microstructure, as well as other important information such as enthalpy and liquid density as functions of temperature. This approach greatly reduces the need for experimental measurements of alloy solidification behavior.

Project Title: **SOLIDIFICATION PATH MODELING FOR CASTING OF MULTICOMPONENT AEROSPACE ALLOYS**

Investigators: W. J. Boettinger, U. R. Kattner, S. R. Coriell, and A. Davydov

Objective:

The objective of this project is to provide simulations and predictive models that aerospace companies can apply to optimize the quality of superalloy investment castings and reduce reject rates.

Technical Description:

This project provides a method to predict the fraction solid (and heat content) vs. temperature relationship for multicomponent superalloys. This information is necessary for accurate macroscopic heat flow modeling used to determine soundness of design of casting processes. The information also predicts the identity and volume fraction of all phases present in the microstructure. A combination of multicomponent phase diagram calculations with a kinetic analysis of solidification microsegregation is used to determine the path in composition space followed by the superalloys as they solidify. Models are implemented into a commercial software code for castings as part of the industry/NIST Consortium on Casting of Aerospace Alloys.

Planned Outcome:

A thermodynamic data base for Ni-base superalloys for the calculation of the tie-line information required by the solidification models will be developed. Solidification kinetic models for multicomponent superalloys will be developed, to treat the dendritic aspects of solidification.

The thermodynamic data base and solidification kinetic models will be integrated into commercial casting software.

External Collaborations:

This work was performed as part of the industry/NIST Consortium Project on Casting of Aerospace Alloys. Consortium members (Howmet Corp., PCC Airfoils, GE Aircraft Engines, Pratt & Whitney and UES) shared fully in the selection of the focus of this research and provided consultation and advice concerning this work. The phase diagram data assessments combine NIST, University of Florida, and University of Wisconsin-Madison research.

Accomplishments:

A detailed assessment of the thermodynamic parameters for all of the phases in the Co-Mo and Ni-Ti-W phase diagrams have been completed.

A thermodynamic data base for the Liquid and FCC phases has been constructed for the Ni-Al-Cr-Ti-Co-Re-W-Mo-Ta system. This database has been delivered to the members of the Consortium on Casting of Aerospace Alloys and is essential for the modeling of single crystal investment castings.

Metallurgy Division scientists not only developed the databases, they assisted in the final implementation of NIST-developed phase diagram subroutines and kinetic models into the commercial casting simulation software platform of our consortium partner, UES.

Impact:

The models developed in this project enable industry to predict the detailed solidification behavior of complex alloy systems without the need for experimental testing programs. The improved quality of simulation of investment castings is providing more reliable prediction of casting defects and is allowing industry to eliminate the need for a series of test castings to reach an acceptable design.

Outputs:

Publications:

Zhang, F., Chen, S. L., Chang, Y. A., and Kattner, U. R., “A Thermodynamic Description of the Ti-Al System,” Intermetallics **5**, 471-482, (1997).

Ansara I., Chart, T. G., Fernandez-Guillermet, A., Hayes, F. H., Kattner, U. R., Pettifor, D.G., Saunders, N., and Zeng,K., “Thermodynamic Modelling of Selected Topologically Closed-Packed Intermetallic Compounds," CALPHAD **21**, 171-218, (1997).

Kattner, U. R., “Thermodynamic Modeling of Multicomponent Phase Equilibria,” J. Metals **49,** 14-19, (1997).

Davydov, A. and Kattner, U. R. “Thermodynamic Assessment of the Co-Mo System,” J. Phase Equilibria, in press.

Boettinger, W .J., Kattner, U. R., and Banerjee, D. K. , “Analysis of Solidification Path and Microsegregation in Multicomponent Alloys,” in Modeling of Casting, Welding and Advanced Solidification Processes, VIII, ed. by B. Thomas and C. Beckermann, TMS, Warrendale, PA, p. 159, (1998).

Presentations:

Kattner, U. R., “Multicomponent Alloy Thermodynamic Data Bases,” Semi-Annual Meeting, Consortium on Casting of Aerospace Alloys, NIST, October 1997.

Boettinger, W. J., “Phase Diagrams,” TMS Short Course on Solidification, Savannah, GA, May 1998.

Boettinger, W. J., “Solidification Path in Multicomponent Alloys,” TMS Short Course on Solidification, Savannah, GA, May 1998.

Boettinger, W. J., “Solidification Path for Multicomponent Areospace Alloys,” Final Annual Meeting, Consortium on Casting of Aerospace Alloys, NIST, May 1998.

Boettinger, W. J., “Analysis of Solidification Path and Microsegregation in Multicomponent Alloys,” Conference on Modeling of Casting, Welding and Advanced Solidification Processes, VIII, San Diego, CA, June 1998.

Boettinger, W. J., “Solidification Path and Microsegregation in Multicomponent Alloys,” Second Zermatt Workshop on Solidification Microstructures, Zermatt, Switzerland, July 1998.

Project Title: **MICROSTRUCTURAL STUDIES OF COMPLEX PHASES**

Investigator: L. A. Bendersky

Objectives:

Wireless communication technology requires better ceramic materials with higher dielectric constants, lower losses and zero thermal coefficient for use in a wide range of frequencies. Some new candidates for these applications are complex layered oxides. The main objective of this project is to determine atomistic details of structures and phase transformations in the newly discovered compounds in the $BaO-Fe_2O_3-TiO_2$ and $SrO-Nb_2O_5-TiO_2$ systems. Knowledge of the atomistic details will provide the necessary bridge between chemistry and dielectric properties of the oxides.

Technical Description:

Work on a series of layered compounds from the $SrTiO_3-Sr_2Nb_2O_7$ section has been conducted in close collaboration with I. Levin and T. A. Vanderah of the MSEL Ceramics Division. The first part of the work is theoretical, in which the work of Glazer on the effect of octahedra tilting on the symmetry of the perovskite structure was extended to the much more complex crystallography of $A_nB_nO_{3n+2}$ layered structures. Two complementary approaches, one with the tabulation of layered G_2^3 groups and another with group-subgroup analysis, are used. Symmetry tree analysis predicting the possible phase transitions has also been used.

The second part of the work is a TEM study of incommensurate and commensurate modulations found in the $SrTiO_3-Sr_2Nb_2O_7$ compounds. Such modulations apparently can be detected and studied only by electron diffraction.

Planned Outcome:

Tabulation of space groups according to the effects of stacking of layers and type of octahedra tilts in the $A_nB_nO_{3n+2}$ layered structures will provide the reference data for crystallographic studies of such compounds. The important result of the work is that the symmetries of previously determined $A_nB_nO_{3n+2}$ layered structures can be explained in the approximation of rigid tilting of octahedra. These studies will result in an understanding of structural principles and magnetic properties of complex multilayered compounds.

External Collaborations:

Collaboration with Prof. J. Cohn from Physics Department, University of Miami on PLD deposition and characterization of novel Ba-Fe-Ti-O magnetic phases.

Collaboration with Profs. A. Roytburd and R.Ramesh from Department of Materials and Nuclear Engineering, University of Maryland on PLD deposition and characterization of ferroelectric PZT thin films for memory applications.

Accomplishments:

Tabulation of space groups according to the effects of stacking of layers and type of octahedra tilts in the $A_nB_nO_{3n+2}$ layered structures was completed and will provide the reference data for future crystallographic studies of such compounds.

Phase equilibria in $SrTiO_3$-$Sr_2Nb_2O_7$ section of the phase diagram have been established.

Structural characterization of six novel magnetic BaO-Fe_2O_3-TiO_2 compounds with unusual multilayered structure was completed.

Formation of a large field of existence of the metastable cubic perovskite Ba(Ti,Fe)O_3 in PLD-deposited films was demonstrated.

Impact:

This structural study of BaO-Fe_2O_3-TiO_2 and SrO-Nb_2O_5-TiO_2 compounds using HRTEM is essential for the NIST phase diagram effort to characterize oxides of interest to U.S. industries involved in wireless communications systems. This work has also contributed to the understanding of the physics of formation of ordered intergrowth compounds.

Outputs:

Publications:

Levin, I., Bendersky, L. A., Vanderah, T. A. , Roth, R. S., and Stafsudd, O. M. “Series of Incommensurately Modulated $A_nB_nO_{3n+2}$ Phases Formed in the $SrTiO_3$-$Sr_2Nb_2O_7$ Quasibinary System,” Materials Research Bulletin, **33** , 501(1998).

Bendersky, L. A. and Bonevich, J. E., “Magnetic Multilayers as a Structural Component in a Series of Bao:Fe_2O_3:TiO_2 Compounds,” Phil. Magazine Letters, **77**, 279 (1998).

Bendersky, L. A., Vanderah, T. A., and R. S. Roth, “Structural Study of a Group of Magnetic Multilayered Oxides in the Bao:Fe_2O_3:TiO_2 System. Part I: High Resolution Electron Microscopy,” to appear in Phil. Magazine A (1998).

Levin, I., Bendersky, L. A.,Vanderah, T. A., and Roth, R. S., “TEM Study of the Incommensurately Modulated Structures in the $SrTiO_3$-$Sr_2Nb_2O_7$ System,” Proceedings of 14th International Congress on Electron Microscopy, Cancun Mexico (1998).

Bendersky, L. A. and Bonevich, J. E., “Magnetic Multilayers in a Series of Bao:Fe_2O_3:TiO_2 Compounds,” Proceedings of 14th International Congress on Electron Microscopy, Cancun Mexico (1998).

Presentations:

Bendersky, L. A., "Self-assembled Magnetic Multilayers In A Series of BaO : TiO_2 : Fe_2O_3 Compounds,” invited seminar at Rutgers University, March 1998.

Bendersky, L. A., "Self-assembled Magnetic Multilayers In A Series of BaO : TiO_2 : Fe_2O_3 Compounds,” invited seminar at Penn State University, March 1998.

Bendersky, L. A., "Self-assembled Magnetic Multilayers In A Series of BaO : TiO_2 : Fe_2O_3 Compounds," MSEL Bag Lunch Seminar, March 1998.

Bendersky, L. A., Shull, R. D. , Bonevich, J. E., Vanderah, T. A., and Roth, R. S. "Magnetic Multilayers in a Series of BaO : TiO_2 : Fe_2O_3 Compounds," invited talk at American Crystallographic Association Annual Meeting, Washington, DC, July 1998.

Bendersky, L. A., Bonevich, J. E., Shull, R. D., Vanderah, T. A., and Roth, R. S., "Natural Magnetic Multilayers in a Series of BaO : TiO_2 : Fe_2O_3 Compounds," talk at the MRS 1997, Symposium: *Metallic Magnetic Oxides.*

Bendersky, L. A., Bonevich, J. E., Shull, R. D., Vanderah, T. A., and Roth, R. S., "Natural Magnetic Multilayers in a Series of BaO : TiO_2 : Fe_2O_3 Compounds," talk at the American Ceramic Society Annual Meeting, April 1998.

DENTAL AND MEDICAL MATERIALS

The Dental and Medical Materials Program provides basic materials science, engineering, test methods, and standards to sectors of the health care industry for the development of new or improved materials and delivery systems. This program focuses on (1) development of improved dental restorative materials with greater durability, wear resistance and clinical acceptability; (2) development of improved bone fixation materials and (3) evaluation of biomaterials.

Dental restorative composites are heterogeneous materials having three essential phases: (1) a polymeric matrix which comprises the continuous phase, (2) fillers of various types, sizes, shapes and morphologies which constitute the disperse phase and (3) an interfacial phase that, in varying degree, bonds the continuous and disperse phases into a unitary material rather than a simple admixture. While all three phases are important in determining the properties of the composites, this program is focused primarily on the interfacial and polymer matrix phases. Since the polymerization shrinkage that occurs in the matrix phase is one of the most commonly cited deficiencies of dental restorative composites, resources are allocated to develop high conversion, durable, low shrinkage polymeric materials for use in dental resin and composite applications. The polymeric matrix of a dental composite typically is formed by free radical polymerization of a resin which is one or more vinyl monomers, usually of the methacrylate class. Polymerization is started either by the formation of initiating radicals from chemical reduction-oxidation (redox) reactions or by photochemical redox reactions.

Although only a minor component of these composites, the interfacial phase that develops from the interaction of the silane coupling agent with the polymer matrix and the siliceous filler exerts a profound effect on the properties of the composites. Because these composites are used in an aggressive, aqueous environment that constantly challenges the vulnerable silane mediated polymer-filler bond, understanding of this critical interfacial phase is being acquired so that strategies can be developed for its improvement.

The occupational and environmental hazards associated with the use of mercury-containing dental alloys are a recurring source of public concern. Since dental amalgams have performed exceedingly well over more than one hundred years, the development of a direct filling material still based on the common constituents of dental amalgams, other than mercury, is desirable. This project is focused on acid-assisted consolidation of chemically precipitated silver powders and property measurements of hand consolidated test compacts prepared with the tools and procedures normally employed by dentists. The observed values of flexural strength for the silver compacts were equal or superior to mercury amalgams. Corrosion resistance, microleakage and marginal toughness values of the compacts were found to be superior to those of amalgams. Wear and biocompatibility studies on the hand consolidated compacts are in progress.

Besides the dental materials projects, efforts are directed toward the development of improved bone fixation materials and the evaluation of biomaterials. A project, carried out in collaboration with the American Dental Association and the National Institute of Dental Research, is directed at enhancing the biocompatibility and mechanical properties of composite bone cements. The biomaterials evaluation effort centers on the NIST Orthopedic Wear Consortium which consists of four companies to develop accelerated wear test procedures for rapid screening of materials used in hip and knee replacements. This will accelerate the introduction of new biomaterials into practice.

Dental and medical research directions in support of the goals are established in collaboration with the American Dental Association (ADA), the National Institute of Dental Research, the National Heart, Lung and Blood Institute, the US Food and Drug Administration, and guest scientists from the U.S. Navy and the U.S. Public Health Service. NIST has hosted research associates from ADA since 1928. Currently, the ADA Health Foundation sponsors 30 research associates at NIST. The collaborative relationship between that professional association and the federal government is unique, and continues to develop and transfer important new technologies to dentistry and medicine.

Project Title: **ADVANCED RESTORATIVE DENTAL MATERIALS**

Investigators: G. R. Stafford, C. E. Johnson, and D. R. Kelley

Objectives:

The project seeks to provide to the dental industry a mercury-free, metallic restorative that can be hand consolidated while maintaining critical mechanical properties. The project is also striving to reduce the time required to place the alternative restoration to match that of amalgam, without sacrificing mechanical properties.

Technical Description:

The development of a direct filling material still based on some of the common constituents of dental amalgams, other than mercury, is the focus of this program. A search for a metallic substitute to the amalgams has to begin with the problem of the consolidation of an easily deformable very plastic material into a strong solid, under the strict temperature, pressure and time limitations by common dental practice.

The approach taken by NIST under sponsorship of the National Institute of Dental Research (NIDR) has been to provide an appropriate surface treatment to individual silver powders which are then cold-welded under low pressures to a cohesive solid. The silver powders are derived from a chemical precipitation process. The surface treatment involves the use of a dilute acid to remove the naturally occurring oxide layer on the powders. Subsequently, a slurry, consisting of the wet mixture of the surface-treated powder particles, is placed and consolidated in a prepared dental cavity. The liquid film surrounding each particle serves both to maintain a clean surface, and to constrain the micron-size particles, so that they present no inhalation danger to the patient. The powders are consolidated into a solid mass using instruments normally employed in dental practice. The term “acid-assisted consolidation” was coined for the consolidation technique.

Planned Outcome:

The ability to densify surface-treated silver powder into a cohesive solid displaying reasonable mechanical strength, as well as the established and approved use of silver as a dental restorative material, will lead to a mercury-free metallic dental restorative in the event that mercury-containing restoratives are curtailed.

External Collaborations:

The American Dental Association is providing support for this project by conducting biocompatibility studies on the silver-based alternative dental restorative.

Collaboration with the American Dental Association Health Foundation is focused on other factors associated with the use of the silver-based alternative restorative, such as the nature and shape of the condensing tools and the placement procedures to be followed.

Accomplishments:

Significant progress has been achieved towards developing a technology for a silver-based, mercury-free, direct restorative material. By using appropriate precipitation and thermal anneal procedures, acid-assisted hand consolidation is capable of producing silver compacts which are nearly 80% dense. The current state of the art, hand consolidated silver equals or exceeds the transverse rupture strength, shear strength, creep, toughness, corrosion resistance, microleakage, and wear properties of conventional silver amalgam. At present, the compressive strength, elastic modulus, hardness and replacement time are inferior to those of conventional amalgam.

The most favorable source of silver that best suits hand consolidation is the precipitation of a ductile and soft silver from an aqueous solution. The chemistry most extensively explored in this study consists of a mixture of silver nitrate and tin fluoborate in a 1.0 mol/L fluoboric acid solution. The addition of an anionic surfactant, alumina dispersing agent, and colloid results in a powder agglomerate which is 80 % by weight less that 25 µm in diameter. This powder can be annealed to 750 °C for two hours in air with minimal sintering. This effectively reduces the initial yield strength of the powder and dramatically improves the density and rupture strength of the hand consolidated powder. In addition, these silver particles can be used with a minimal amount of sieving so that little work hardening is imparted to the particles.

Although acid-assisted consolidation is relatively well established empirically, we still lack an in-depth understanding of the underlying mechanism. It had generally been assumed that the function of the HBF_4 is to remove the silver surface oxide and thereby promote cold welding. Ag_2O is soluble in acid media with the formation of Ag^+ in solution. We have determined by potentiometric measurements of the resultant Ag^+ concentration, that 1 g of annealed silver powder requires 8.1×10^{-6} moles of H^+ to remove the surface oxide so that cold welding can occur. This is within a factor of two of that expected for a monolayer of oxide. Further, the amount of oxide removed from the powder is essentially independent of pH for HBF_4 concentrations of 3×10^{-4} mol/L and higher. This implies that powder activation can be accomplished in 25 mL at a pH of 3.5 or less. The amount of oxide removed is significantly less when the pH of the HBF_4 is greater than 3.5.

Biocompatibility studies over this reporting period were performed in the laboratory of Dr. Chakwan Siew of the American Dental Association and focused on the components and corrosion products of the proposed restorative. Hemolysis, cytotoxicity and Ames examination of the constituents (precipitated silver powder and 2% HBF_4) and corrosion products resulting from immersion of hand-consolidated material into artificial saliva solution were performed under the direction of Dr. Chakwan Siew of the American Dental Association. In none of these tests did the 7-day and 21-day corrosion products reach the threshold level to be considered non-biocompatible. Under the conditions employed by the Ames test, silver powder and fluoroborate showed no mutagenic potential. The hemolysis examination indicated that silver powder and fluoroborate (0.02 % and greater) were severely hemolytic. An equal mass of consolidated silver powder was marginally hemolytic indicating that the extent of hemolysis is clearly a function of the surface area of silver exposed to solution. In a clinical situation most of the consolidated Ag would be surrounded by hard tissue. The cytotoxicity examination indicates that fluoroborate is not cytotoxic while silver powder is severely cytotoxic. This should not preclude the use of the silver alternative restorative since precedence has been set with other approved-for-use dental materials that are cytotoxic. The results of biocompatibility testing thus far encourage further study and development of the mercury-free silver restorative.

Impacts:

The program has demonstrated that a metallic mercury-free dental restorative material, based essentially on metallic silver, can be obtained using chemically precipitated silver powder and acid-assisted consolidation. Technologies developed during the program have been transferred to industry by way of exclusive licensing of patents. Patents involving electrochemical coating of powders and acid-assisted consolidation of metallic powders have been licensed to Materials Innovation, Inc., for use in other than dental applications. These technologies are presently in use in the manufacture of thermal management devices. The American Dental Association Health Foundation has been given exclusive license to use the acid-assisted consolidation patent for dental applications.

Outputs:

Patents Granted:

Acid Assisted Cold Welding and Intermetallic Formation

Christian E. Johnson and David R. Kelley
U.S. Patent 5,711,866 issued 01/27/98

Patents Pending:

Chemical Precipitation of Metallic Silver Powder Via a Two Solution Technique and Applications Thereof
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Disclosure filed

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