Metallurgy Division of the
Materials Science and Engineering Laboratory
National Institute of Standards and Technology
Report of Technical Activities 1999

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INTRODUCTION

Carol A. Handwerker, Chief

This report describes areas of scientific expertise, major technical activities and accomplishments of the Metallurgy Division of the NIST Materials Science and Engineering Laboratory (MSEL) in 1999.

The mission of the NIST Metallurgy Division is to provide leadership in developing measurement methods, standards, and fundamental understanding of materials behavior needed by the U.S. materials metrology infrastructure for the more effective production and use of both traditional and emerging materials. As a fundamental part of this mission we are responsible not only for developing new measurement methods 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.

With that mission in mind we have established our research priorities thorough extensive consultation and collaboration with our customers in U.S. industry and with our counterparts in the international metrology community. Research 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, clear industrial need and mission relevance are not enough. In order for us to undertake a new program or project within an existing program, the NIST expertise and resources must be sufficient to accomplish the goals. In addition, there must be a clear path for implementation of NIST results, whether the results are in the form of fundamental understanding of materials behavior, measurement techniques, standards, evaluated data, software, or sensors for on-line process control.

In 1999 we have carried out major programs that focused on meeting specific, high priority metrology needs of importance to 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 and metrology 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 impact of our programs presented 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 materials metrology 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 and encourage increasing collaboration with them to this end.

In 1999 Metallurgy Division staff members were recognized for their outstanding contributions to materials science and technology in the areas of giant magnetoresistance (GMR) spin valve processing, modeling of solder interconnects and alloy solidification, environmentally induced fracture, corrosion, and fatigue, and nanoscale materials. William F. Egelhoff, Jr. was awarded the NIST Samuel Wesley Stratton Award for his internationally acclaimed research on metrology needed for the control of thin film processing for GMR spin valves; this is NIST's highest award for scientific excellence. The NIST Solder Interconnect Design Team, in close collaboration with industrial and university team members, developed software modeling tools for evaluating the manufacturability of solder joint designs and distributed the public domain software through the WWW and through NIST workshops. The NIST program team included James Warren, Carol Handwerker, Daniel Josell, Frank Gayle, and Adam Powell from the Metallurgy Division, Craig Carter from the Ceramics Division (now at MIT), and Kenneth Brakke from Susquehanna University. For its achievements the Federal Laboratory Consortium recognized the Solder Interconnect Design Team through its 1999 award for excellence in technology transfer. Richard Ricker was awarded the George Kimball Burgess Memorial Award from the Washington DC's Chapter of ASM International in recognition of his outstanding achievements and innovative research in environmentally induced fracture, corrosion, and fatigue. Daniel Josell was presented with the 1999 Young Scientist Award for Excellence in Scientific Research from the NIST Chapter of Sigma Xi for his contributions in theoretical and experimental studies of the structure and behavior of nanoscale multilayers. For his pioneering research in crystal growth, Samuel Coriell was awarded the 1999 Bruce Chalmers Award from The Minerals, Metals & Materials Society (TMS). James Warren and William Boettinger were awarded the Champion H. Mathewson Award for the paper that represents the most notable contribution to metallurgical science in 1998. This paper, "The Phase-Field Method: Simulation of Alloy Dendritic Solidification During Recalescence," demonstrated the applicability of the powerful yet conceptually simple phase-field method to the detailed understanding of a complex metallurgical phenomenon. Carol Handwerker was named a Fellow of ASM International for her contributions to interface science.

SIGNIFICANT ACCOMPLISHMENTS AND IMPACTS

Electronic Packaging, Interconnection and Assembly

- ***Solderability Measurements for Microelectronics*** - . New electrochemical measurements are being developed at NIST for assessing the solderability of metal surfaces based on the type, quantity, and distribution of surface oxide. These quantitative techniques hold the promise of replacing more qualitative tests of solderability that indicate soldering performance but do not reveal the underlying reasons for loss of solderability. In FY1999 an electrochemical quartz crystal microbalance (EQCM) technique has been demonstrated to have sub-monolayer resolution of mass and charge transfer for copper oxidation and reduction.

- ***Solder Interconnect Design* —** The software developed in this project for modeling the interaction between optical fibers and the solder which aligns and holds it in position in optoelectronic circuits was successfully transferred to Boeing. This software models displacement of the optical fiber due to forces from both the solder wetting and solidification. The Solder Interconnect Design Team's efforts have resulted in wide dissemination of solder joint modeling software in the electronics industry through its workshops and its web page, with over 1500 software downloads to date.

- ***Lead-free and High-temperature Solders* —** In response to impending legislation in the European Union and marketing trends in Japan, the US electronics industry is preparing for the possible replacement of Pb-Sn eutectic solder with Pb-free solders. NIST scientists have been assisting in this effort by providing needed phase diagram data on possible candidate alloys, data on the effects of Pb contamination on melting behavior and joint performance, analyses of manufacturing and reliability data used to determine the NEMI Pb-Free Solder Task Group work plan, and briefings of the materials science issues in conversion to Pb-free solders to various industrial groups including IBM at IBM Academy's Lead Solder Elimination Workshop, Alpha Metals/Cookson, and the NEMI Pb-Free Solder Task Force. NIST has helped organize the IPC international meeting on lead-free solders, including establishment of a Pb-free solder roadmap for the assembly and PWB industry, and an international meeting in Japan on environmentally conscious design and manufacturing.

- ***Metallurgy of Electrical Contacts to Gallium Nitride Semiconductors* —** Phase diagram data and models of reactions in GaN and related systems have been developed and their value in understanding the design and processing of Group III nitride semiconductors have been established. Experimental study and modeling of the stability of GaN thin films in atmospheres of N_2, H_2, HCl, and NH_3 have provided guidelines for suitable processing conditions. Important parts of the phase diagrams involving GaN and Ti or Ni have been established, and X-ray data on several of the intermetallic phases of these systems have been obtained as an aid to interpretation of phase formation in the Ti/GaN thin films. The thermochemical and phase diagram information is yielding understanding of the reaction products forming at the interface between GaN and Ni or Ti electrical contacts.

- ***Copper Metallization* —** A study has been initiated to determine the mechanisms by which addition agents inhibit and catalyze the electrolytic deposition of copper, which is currently being developed for on-chip metallization, and to determine the role of these additives in the recrystallization of the deposited copper. Halide adlayers have been shown to form on the copper surface during deposition, and the effect of the organic additives is believed to be related to their interaction with the halide. Recrystallization of electrodeposited 1.0 µm copper films has been studied by a 4-point resistivity probe and x-ray diffraction, and has been shown to depend on the specific combination of additives present in the electrolyte.

Magnetic Materials

- ***GMR Materials* —** The Magnetic Engineering Research Facility (MERF) has expanded its studies to an examination of magnetic tunnel junctions (MTJs), which are a variant of GMR materials in which Al_2O_3 is used in place of Cu as the spacer between the magnetic layers. MTJs are well suited to being the memory element in nonvolatile computer memory chips (MRAM). Using the well-controlled environment of the MERF, it was found that oxidation of the magnetic layer, prior to depositing the aluminum, could prevent an undesirable diffusion of Al into the magnetic metal.

- ***Processing and Micromagnetics of Thin Magnetic Films* —** NIST leadership in micromagnetic modeling as applied to standard problems has continued to gain international attention and has resulted in significant improvement of the reliability of the modeling. After different modeling groups had produced wildly different results for standard problem #1, a second standard problem was developed and an analytical solution for it in the small-particle limit was obtained in collaboration with the NIST Information Technology Laboratory. Modelers thus have a known solution with which to compare their results, and several have now obtained close matches to this solution.

- ***Magnetic Properties of Nanomaterials*** and ***Magneto-Optical Imaging* —** The MOIF technique was used to examine the remagnetization behavior of an epitaxial antiferro-magnet/ferromagnet bilayer. Remagnetization in the two different directions was shown to be accomplished by two different processes, with the asymmetry being due to defects such as dislocations in the antiferromagnet.

Metals Data and Characterization

- ***Rockwell Hardness Standards* —** Additional C-scale test blocks have been characterized to replenish stock which was sold through the Standard Reference Materials Program, and traceability in U.S. hardness measurements was promoted by holding two workshops and by completing the technical requirements for use in the NVLAP accreditation program. Standardization of the Rockwell B scale was complete and a contract was awarded for a hardness block producer to provide NIST with uncalibrated test blocks for the HRB scale.

- ***High-resolution Thermophysical Measurements During Pulse Heating —*** Measurement of the rapid melting behavior of a Nb-Ti alloy lead to the development of a model for the melting process, based on initiation of melting at grain boundaries. The measured melting behavior was also correlated to a thermodynamic model of the alloy, and demonstrated the need to account for the non-equilibrium initial state of the alloy. Understanding of the melting behavior was obtained through analysis of samples with different grain sizes and heating rates. The experiments indicated how useful physical property data can be extracted from the melting curves of alloy systems, the interpretation of which had previously been uncertain.

Metals Processing

- ***Sensors and Diagnostics for Thermal Spray —*** The Particle Imaging Pyrometer (PIP) for measuring temperature, velocity, and size of thermal spray particles in flight, developed with SBIR support, has been tested by simultaneous measurements with a broad bandwidth spectrometer system. It has been applied to measurements in the NIST thermal spray system, and the results correlated to a thermodynamic model of the gun. The results indicate the possibility of independent control of particle temperature and velocity, important for possible feed-back control to obtain more reproducible coatings.

- ***Lightweight Materials for Automotive Applications —*** Models and data have been developed for the prediction of the consolidation of powder-based aluminum matrix particulate reinforced composites. The effort has been carried out in collaboration with USAMP and the models have been transferred to Matsys, Inc., for incorporation into their software. With NIST SBIR support, Matsys also developed a fluidized feed-shoe technology which results in extremely uniform distribution of the aluminum and reinforcement powder particles, yielding a factor of four improvement in the mass uniformity of pressed powder parts, with a corresponding reduction in part distortion.

- ***Electrodeposited Coating Thickness Standards —*** SRM coating thickness standards are widely used by the organic and inorganic coating industries for the non-destructive measurement of non-magnetic coatings over magnetic substrates. In FY1999 the redesign of the production, certification, and delivery processes for these standards was completed and these SRMs are again available for purchase.

- ***Electrodeposited Chromium and Chromium Alloys from Trivalent Electrolytes —*** A non-toxic trivalent chromium electrolyte developed at NIST as a replacement for the present commercial process of depositing chromium from a toxic hexavalent electrolyte is serving as the basis of a study on the use of Cr-based amorphous alloys as wear-resistant coatings for surgical tools and orthopedic implants and as a tissue-engineered coating alternative to calcium phosphate. The trivalent chromium electrolyte modified with cobalt and phosphorus additions was found to produce Co-Cr-C-P coatings with improved corrosion resistance over chromium-free coatings. In FY2000 the formation of calcium phosphate on these coatings will be investigated.

- ***Reactive Bonding in Metals —*** A model has been developed describing the transient liquid phase (TLP) bonding process, which can be an important step in fabricating advanced superalloy components. The model is based on thermodynamic and kinetic models of the alloy systems of the base alloys and the filler material, and it analyzes the time-dependent diffusion paths which occur in the system, predicting if unwanted brittle precipitate phases may form. The model has been applied, and compared to experiment, for a basic model system (Ni-Al-Cr-B) which is a simplified description of a superalloy. The model showed qualitative agreement with the experiments: a more quantitative agreement for a real commercial superalloy composition would require significant additional thermodynamic and mobility data.

Phase Equilibria for Ceramics and Metals

- ***Thermodynamic Databases as the Basis of Prediction of Industrial Processes* —** Thermodynamic models and the databases which support them contribute to, and in many cases form the foundation of, an ever-widening group of the Division's projects. They have been used to predict the melting ranges for lead-free and high-temperature solders, they are the basis for predicting reactions between GaN semiconductors and metallic electrical contacts, and they are the basis for models of casting and transient liquid phase bonding processes in superalloy systems which are being used by ATP awardees.

Dental and Medical Materials

- ***Advanced Restorative Dental Materials* —** The four-year program to develop a mercury-free substitute for dental amalgams, supported by the National Institute of Dental Research, has concluded. A system based on chemically precipitated silver powder and a process of acid-assisted consolidation was developed. The mechanical properties of the consolidated material were measured and found to compare favorably with those of currently used amalgams. Biocompatibility tests were also completed on this material. The placement time of the alternative materials is greater than that of conventional amalgams, and reduction of this time warrants further study. The material would be a prime candidate for use if restrictions should be placed on the use of mercury-containing restoratives.

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 early 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; and electromigration and stress voiding. These projects are 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*, IPC, Lincolnwood, IL, 1995, 1997; *National Electronics Manufacturing Technology Roadmap*, National Electronics Manufacturing Initiative, Inc., Herndon, VA, 1996, 1998.

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

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

Project Title: SOLDERS AND SOLDERABILITY MEASUREMENTS FOR MICROELECTRONICS

Investigators: W. J. Boettinger, F. W. Gayle, C. A. Handwerker, U. R. Kattner, K. Moon, L. C. Smith 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. New electrochemical measurements are being developed for assessing the solderability of metal surfaces based on the type, quantity, and distribution of surface oxide. These quantitative techniques hold the promise of replacing more qualitative tests of solderability that indicate soldering performance but do not reveal the underlying reasons for loss of 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 high temperature, fatigue resistant solders for underhood automotive and die attach applications. In this consortium, organized by the National Center for Manufacturing Sciences (NCMS), NIST is applying its expertise in phase diagram and metallurgical science to provide processing and performance data on solder alloys which are candidates for these applications.

Building on its participation in an earlier NCMS consortium on lead-free alloys, NIST is an active member of the NEMI Task Force on Lead-Free Solders whose charter is to prepare the US microelectronics infrastructure for the possible conversion from Pb-Sn eutectic soldering to lead-free solder assembly processing. In this Task Force, NIST has provided needed impartial evaluation of phase diagrams, solderability data, and reliability data.

Planned Outcome:

Improved solderability test methods will lead to increased manufacturability and reliability in microelectronic devices. 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 area array interconnects, where small size scales and limits on visual inspection make rework of improperly soldered connections difficult or impossible. Guidelines for identifying and testing lead-free and high temperature fatigue-resistant solders will be established. Such guidelines for lead-free solders are urgently needed by the microelectronics industry to comply with a proposed European Union ban on lead-tin solders and to compete effectively in markets where lead-free manufacturing is a product discriminator. A wider range of high temperature solder alloys for underhood and die attach applications will provide greater flexibility in microelectronic design and assembly.

External Collaborations:

On an industry-wide basis, collaborations are on-going with IPC, its standards-writing committees, and NCMS on high temperature, fatigue resistant solders, and NEMI on its Pb-free activities. NIST works closely with the NCMS Consortium Project on High Temperature Fatigue Resistant Solders and with consortium members Delphi Delco, Ford, AlliedSignal, Rockwell International, Indium Corporation of America, Heraeus Cermalloy, Johnson Manufacturing, and Ames Laboratory, and provides leadership for the consortium's Materials Task Group. NIST is collaborating with the NEMI Task Force that includes 3Com, AIM, Alpha Metals, Amkor, Celestica, Compaq, Delphi, Heraeus, HP, Intel, Intersil, Lucent, Motorola, Multicore, Nortel Networks, Solectron, Indium Corp., Johnson Mfg, Newbridge Networks, PraxAir, Raytheon, Shipley-Ronal, Storage Tek, and Visteon. NIST scientists also serve as mentors for projects in universities funded by the industry-supported Semiconductor Research Corporation.

Accomplishments:

During soldering, intermetallic compounds are formed at the interface between the liquid solder and the base metal by a combination of isothermal solidification and solid state reaction. This process is a necessary part of solder wetting and spreading. However, excessive growth of intermetallics can compromise the integrity of the joint. Previous experimental data from various authors show much scatter on intermetallic growth rate. This scatter is due to the effect of solder thickness on the growth rate of intermetallics, a parameter not usually controlled. Isothermal studies of Pb-Sn liquid on Cu were carried out, and the interface positions were measured with respect to the initial Cu/liquid interface. Care was taken to provide rapid heatup and cooldown from the test temperature. From this data we were able to infer the following motions of the interfaces: 1) Dissolution of Cu accompanied by motion of Cu/Cu_3Sn, Cu_3Sn/Cu_6Sn_5 and Cu_6Sn_5/L interfaces towards the Cu as Cu diffuses into the liquid. Only thin intermetallic layers form during this regime. 2) Reversal of the direction of motion of the Cu_6Sn_5/L interface (solidification) as the liquid solder becomes saturated with Cu. During this regime, the thickness of the Cu_6Sn_5 layer rapidly increases. Saturation occurs more quickly for a small solder thickness. Thus for the same amount of time, the Cu_6Sn_5 thickness is largest for the smallest solder thickness. Additional features regarding the Cu_6Sn_5/L interface shape and grain size are interpreted as ripening and grain boundary grooving processes.

The effect of Pb contamination on the solidification path of various Pb-free Sn-Bi solders has been examined. This situation arises from the possibility that Pb-free solders may be used with leads and/or pads that have been pretinned with Pb-Sn eutectic solder. Estimates of Pb content in the final joint as high as 8 wt % are obtained using typical solder volumes and pretinning thicknesses. Using a thermodynamic assessment and computation of solder phase diagrams, Scheil calculations reveal the possible Pb levels that can lead to the formation of low temperature ternary eutectics. For example, in the widely considered Sn-Bi solders, a ternary eutectic at 100 °C occurs in the Sn-Bi-Pb system. Several other Pb-free solders will be examined.

Tests have been conducted to experimentally verify the liquidus surface of the Sn-rich corner of the Sn-Ag-Cu phase diagram. A ternary eutectic has been reported in the literature, but its precise location is uncertain. Knowledge of this composition is important to prevent the formation of excess amounts of intermetallic Ag_3Sn and/or Cu_6Sn_5 from the melt or from Ag or Cu metallizations. Precise cooling curves have been obtained which verify the 217 °C eutectic temperature. Due to the shallow liquidus of the Sn phase and the steepness of the intermetallic liquidus surfaces, measurement of the melting points is difficult. Results are being compared to thermodynamic models of the ternary system. The results of this work are being reported on a weekly basis to the NEMI (National Electronics Manufacturing Initiative) Pb-free Solder Task Group.

In collaboration with the IPC Wetting Balance Task Group, wetting balance test conditions for accurately assessing the solderability of different surface finishes were established in collaboration with Rockwell International and Raytheon (formerly TI). Current methods designed for assessing the solderability of Pb/Sn surface finishes were found to be inadequate for Pb-free non-fusible surface finishes. New test conditions were found that provided an acceptable signal-to-noise ratio for both Pb-containing and Pb-free surface finishes. It is expected that these results will serve as a basis for changes to ANSI/J-STD-003. An electrochemical quartz crystal microbalance (EQCM) technique has been demonstrated to have sub-monolayer resolution of mass and charge transfer for copper oxidation and reduction.

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. Emphasis this year has focussed on lead-free solders; a thermo-mechanical fatigue test was completed on the candidate lead-free solders, and a long term reliability surface mount test vehicle was assembled by consortium members. Metallographic examinations performed by NIST provided data for the evaluation of candidate alloys.

NIST scientists have participated in national and international activities regarding the implementation of lead-free solders in electronics manufacturing. NIST has provided briefings of the materials science issues in conversion to Pb-free solders to various industrial groups including IBM at IBM Academy's Lead Solder Elimination Workshop, Alpha Metals/Cookson, and the NEMI Pb-Free Solder Task Force. NIST has helped organize an IPC international meeting on lead-free solders, including establishment of a Pb-free roadmap, and an international meeting in Japan on environmentally conscious design and manufacturing.

Impact:

NIST work on lead-free solders has been made publicly available through NCMS and NEMI providing technical information needed by industry and government bodies considering replacement of lead-containing solders. Results from NIST solderability measurements were incorporated into new IPC solderability test standard documents.

Outputs:

Publications:

Bailey, C. and Boettinger, W. J., "Modeling the Fillet Lifting Defect," ASME EEP Vol. 20, Advances in Electronic Packaging.

Handwerker, C.A., "Lead-free Solders: A Change in the Electronics Infrastructure," CircuiTree, September 1999, 94-98.

C.A. Handwerker and the NCMS project team, "Research Trends in Lead-Free Soldering in the U.S.: NCMS Lead-Free Solder Project," Proceedings of the First International Symposium on Environmentally Conscious Design and Inverse Manufacturing (EcoDesign '99), Tokyo, 1999, 602-605.

Presentations:

Gayle, F.W., "The NCMS High Temperature Fatigue Resistant Solder Consortium - A Status Report," NEMI Lead-free Solder Roadmapping Meeting, Anaheim, CA, February 1999.

Gayle, F.W., "Microstructural Evaluation of Lead-free Solders in Surface Mount Printed Circuit Board Application," NCMS High Temperature Fatigue Resistant Solder Consortium Spring Meeting, Heraeus Cermalloy, West Conshohocken, PA, March 1999.

Handwerker, C.A., "Research Trends in Lead-Free Soldering in the U.S.: NCMS Lead-Free Solder Project", EcoDesign '99, Tokyo, Japan, February 1999.

Handwerker, C.A., "Materials Issues in Lead-Free Soldering," IBM Academy Workshop on Lead Elimination, East Fishkill, NJ, March 1999.

Handwerker, C.A., "Materials Issues in Lead-Free Soldering," NEMI Task Group meeting, Chicago, IL, May 1999.

Handwerker, C.A., "Materials Issues in Lead-Free Soldering", Alpha-Cookson Workshop on Strategies for Implementing Pb-Free Solders, June 1999.

Project Title: SOLDER INTERCONNECT DESIGN

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

Objectives:

The main objective of this program is to develop modeling tools for predicting the geometry 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 to 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/World-Wide Web.

In addition, the SIDT also seeks to hold 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 NIST's Center for Theoretical and Computational Materials Science (CTCMS), has been formed to address several pressing issues in the design and fabrication of circuit boards. This multibillion dollar industry is highly dependant on solder interconnects as the dominant method for attaching components to circuit boards. Over the past five years, in partnership with both academic and industrial researchers, the team has established an agenda for solving modeling problems concerning equilibrium solder joint shapes, and the consequential thermal and mechanical properties of the formed joint.

Our ultimate goals are 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 extremely effective for computing equilibrium solder meniscus shapes.

Problems 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), optoelectronic interconnects, and the simultaneous formation of solder joints and wafer level underfill.

Planned Outcome:

The project will result in development of improved software tools for the modeling of solder interconnects.

External Collaborations:

The SIDT is an industry-academia-government laboratory collaboration. Participants over the past few years have included individuals representing a large number of organizations. Organizations represented at different workshops include 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 National Laboratory in addition to NIST.

The CTCMS successfully concluded its support of research at the University of Greenwich (Chris Bailey, PI). This work examined the buildup of stress during the solidification of optical interconnects, as well as the behavior of the solder-flux paste under reflow.

An ATP/CRADA with Boeing and the ATP program in optoelectronics concluded this year. It is expected that the research fostered by the SIDT will play an important role in modeling solder interconnects in optoelectronic devices, where solder is used solely as an adhesive.

Accomplishments:

The Metallurgy Division's modeling effort into optoelectronic interconnects concluded this year with a successful transfer of modeling software to Boeing. This effort included development of both solder wetting models and the capability to model solidification of solder joints using the software package PHYSICA. Much of the developed technology is available on the World Wide Web (see below).

A workshop was held on August 23 and 24, 1999. The industrial concerns of Motorola and Lucent as well as exciting new scientific work from our academic and government partners were highlighted in the presentations. The meeting also included reassessment of the SIDT mission, as dissemination of solder shape modeling tools, the major focus of the SIDT to date, has been largely accomplished.

In recognition of the highly effective way in which they disseminated the technology developed in this project, the Solder Interconnect Design Team was awarded the Federal Laboratories Consortium's Award for Excellence in Technology Transfer

Impact:

As a direct result of SIDT activities, most academic engineers who work in the area of solder interconnect issues in electronic packaging have now heard of the Surface Evolver. Indeed, we field inquiries from researchers on a frequent basis and refer them to our WWW page (approximately 1500 software downloads to date). The infiltration of this solder modeling tool into the relevant communities is nearly complete. The SIDT is therefore moving on to more fundamental research into the more complex, multi-physics, dynamic processes that occur during solder reflow. More material can be found at http://www.ctcms.nist.gov/programs/solder.

Outputs:

The CTCMS WWW page now includes the fiber shift model and ball grid array underfill model on its archive of solder models at www.ctcms.nist.gov/programs/solder.

The modeling effort was presented to the Precision Optoelectronics Assembly Consortium meeting, April 1999.

The modeling effort was presented to the NIST Solder Interconnect Design Team meeting, August 1999.

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

Investigators: A. V. Davydov, W. J. Boettinger, F. S. Biancaniello, D. Josell, U. R. Kattner, and A. J. Shapiro

Objectives:

This project examines the interaction of metals with Group III nitride semiconductors with the aim of developing guidelines for the design of thermally stable metal-to-semiconductor interfaces for optoelectronic and electronic device application.

Technical Description:

Gallium nitride, a wide band gap compound semiconductor, is an attractive material for microelectronics, including optoelectronic, high-frequency microwave, high-power and high-temperature devices. The rapid development of GaN-based technology over the past five years has lead to the commercialization of blue and green light emitting diodes in 1999, along with demonstrations of a variety of electronic devices. However, materials-related complexity of the compound semiconductors, compared to the elemental Si and Ge, still hampers the development of the optoelectronic and electronic devices based on Group III nitrides. In particular, performance and reliability of the GaN-based devices is impeded by obstacles in manufacturing defect-free epitaxial semiconducting layers, controlling high-level concentration of n- and p-type dopants in GaN and by electrical contact issues. The latter problem of poor metal-to-semiconductor contacts is associated with thermal instability and large electrical losses at the metal-to-GaN interface, impacting the device performance. In order to achieve optimum behavior of the devices, it is crucial to develop thermally stable, low-resistance Ohmic metal contacts to GaN-based semiconductors, as well as to design Schottky-type contacts to GaN with defined energy barriers.

The characteristics of metal contacts to gallium nitride are affected by the chemical reactions occurring at a metal and compound semiconductor interface. Selection of a contact metal element that provides low contact resistance is extremely difficult due to lack of fundamental studies for the multicomponent reactions. Therefore, information on phase equilibria and diffusion paths in potential metal-Ga-N systems is highly desirable to control the mechanism of contact formation.

This project addresses the contact metallurgy and its effect on thermal stability and the electrical characteristics for the Ni- and Ti-GaN systems with nickel and titanium being the most promising elements for the industrial ohmic contacts to n- and p-type GaN, respectively.

Planned Outcome:

The above knowledge will contribute to a better understanding of the effect of the phase reactions at the metal-semiconductor interface on thermal and electrical performance of metal contacts to the Group III nitride materials. Coupling information on interfacial reactions with fundamental phase diagram and thermodynamic data can lead to the development of thermally stable metal contacts with improved characteristics for electronic industry needs.

External Collaborations:

Throughout this project the Metallurgy Division collaborated closely with the University of Florida: Prof. T. J Anderson from the Department of Chemical Engineering provided thin films of GaN for the follow up metal contact deposition at NIST, and Prof. P. H. Holloway from the Department of Materials Science and Engineering provided experimental results for the Ni/GaN thin film reactions. These data are correlated with the bulk Ni-Ga-N phase diagram study performed at NIST.

We also interacted with Dr. L. Rowland from Sterling Semiconductor, Inc., Dr. V. Dmitriev from the Technologies and Devices International, Inc., and Dr. E. C. Bretschneider from Uniroyal Optoelectronics, LLC., requesting gallium nitride thin films deposited on silicon carbide and sapphire substrates for future metal-to-semiconductor studies.

Accomplishments:

Experimental study and modeling of chemical and thermal stability of gallium nitride thin films in N_2, H_2, HCl, and NH_3 atmosphere have been completed, thus providing limiting conditions for GaN processing.

Key features of the Ni-Ga-N phase diagram have been established; a) equilibrium tie-lines were experimentally determined at temperatures and ambient pressures typical for the Ni/GaN thin film processing conditions; b) no ternary phases were found in the system as opposed to some literature data; and c) the experimental phase diagram was correlated with the thin film Ni/GaN interfacial reactions.

The Ti-Ga phase diagram, an important binary constituent of the Ti-Ga-N system, was experimentally determined at 800 °C.

Ti/Ga diffusion couple studies correlated well with the $Ti_{1-x}Ga_x$ (x=0 to 1) alloy experiments. X-ray powder diffractograms for eight intermetallics phases were collected and prepared for submission to the JCPDS databank to fill in the missing data. These data can be utilized to interpret phase formation in the Ti/GaN thin films.

Impact:

This project is yielding improved understanding of the Ni- and Ti-to-GaN contact formation mechanisms. Combining thermochemical and phase diagram information with knowledge of interfacial products in the metal-to-GaN contacts can be used to develop thermally stable electrical contacts to semiconductors with most advantageous characteristics for electronic industry needs.

Outputs:

Publications:

Ahonen, M., Liu, B., Davydov, A., Ristolainen, E., and Holloway, P., "Interfacial Reactions Between Metals and Gallium Nitride," in: "31st State-of-the-Art Program on Compound

Semiconductors," Ed. D. N. Buckley, S. N. G. Chu, and F. Ren, (ECS, Boston), PV99-17, page 114, 1999.

Davydov, A. and Anderson, T., "Thermodynamic Analysis of the Ga-N System" in: "III-V Nitride Materials and Processes III," Ed. T. D. Moustakas, S. E. Mohney and S. J. Pearton, (ECS, Boston), PV98-18, page 38, 1998

Presentations:

Davydov, A., "Application of Phase Diagrams for Selected Compound Semiconductors to the Electronic Materials Processing," Invited Presentation at the National Renewable Energy Laboratory, Golden, CO, June 1999.

Davydov, A., Kattner, U., Boettinger, W., Ider, M., Zhuang, W., and Anderson, T. J., "Thermodynamic Analysis of Selected Group III — Nitrogen Systems," XXVIII International Conference on Calculation of Phase Diagrams, Grenoble, France, Abstracts, page 26, May 1999.

Davydov, A., "Thermal Decomposition of Gallium and Indium Nitrides," Seminar at the Technologies and Devices International, Inc., Gaithersburg, MD, April 1999.

Davydov, A., "Thermodynamic Analysis of Thermal Stability of GaN," Invited Presentation at the North Carolina State University, Raleigh, NC, January 1999.

Davydov, A., "Phase Diagrams of the Group III - Nitride Semiconductor Systems," Invited Presentation at the Naval Research Laboratory, Washington, DC, December 1998.

Project Title: COPPER METALLIZATION

Investigators: G. R. Stafford, T. P. Moffat, D. R. Kelley, U. Bertocci, M. D. Vaudin, and N. G. Armstrong

Objectives:

This project seeks to develop a fundamental understanding of the mechanisms by which various addition agents inhibit/catalyze the electrolytic deposition of copper, which is currently being developed for on-chip metallization.

Technical Description:

Electrodeposited copper is being introduced quickly into chip interconnection technology as a replacement for aluminum. Implementation of the copper damascene process requires the use of inhibitors to ensure complete filling of vias and trenches. The addition agents include an inhibitor (polyalkylene glycol), an accelerator (molecules with thiol and sulfonic acid functionality), in some cases a leveler which suppresses deposition, and chloride. The use of these addition agents is responsible for the observed room temperature recrystallization which results in a 20 % to 25 % decrease in resistivity and an order of magnitude increase in grain size. The rate at which recrystallization occurs depends on feature size, but the relationships between recrystallization rate and feature geometry, residual stresses, texture, and the distribution of impurities are not well understood. It is believed that the small grains observed in as-deposited copper are initially pinned by particles, solute, or other pinning sites (defects) introduced during the electroplating process. Since the additive chemistry is the primary source of particles and is generally responsible for the introduction of defects, dislocations and stresses into the electrodeposited film, an understanding of additive chemistry may lead to a better understanding of the copper recrystallization behavior.

The mechanism by which copper electrodeposition promotes the bottom-up filling of the trench is still under debate. There are two schools of thought on this subject. The first is based on a diffusion gradient of inhibitor into the trench. The lack of inhibitor at the bottom of the trench results in high deposition rates compared to that of the surface. The second involves the accumulation of accelerator in the trench which catalyzes the copper deposition reaction in this region. It is currently recognized, but not well understood, that chloride must be present for the polyalkylene glycol to inhibit copper deposition. Competitive adsorption of halide has not been seriously considered in these models.

Planned Outcome:

We have identified three additives commonly used in $CuSO_4$ — H_2SO_4 plating baths. We expect to identify the additive or combination of additives which promote copper recrystallization at room temperature and gain an understanding of the reaction mechanism and kinetics.

Accomplishments:

Our work has shown that at potentials typically associated with copper deposition, ordered halide adlayers form spontaneously and segregate or float on the surface during film growth. More negative potentials lead to order-disorder transitions and eventual desorption of the halide. The kinetics associated with these adsorption/desorption surface reactions depends strongly on the copper crystallographic orientation. For example, pseudo-reversible responses are observed on Cu(100) and Cu(110) while the redox behavior on Cu(111) is highly irreversible. When polyether-thiol-chloride based additives are used, the copper deposition rate is significantly inhibited relative to deposition from a simple acid copper sulfate electrolyte. The inhibition is clearly due to some interaction between the halide overlayer and the organic molecules. We suspect that the ordered halide adlayers facilitate the formation of a well-ordered organic layer which inhibits copper deposition. The blocking layer of this organic overlayer may be subsequently disrupted at more negative potentials where the halide layer becomes mobile due to an order-disorder or some other phase transition.

The recrystallization behavior of 1.0 µm copper films, electrodeposited from a copper sulfate - sulfuric acid plating bath, into which various combinations of NaCl, 3-Mercapto-1propanesulfonic acid (MPSA) and polyethylene glycol (PEG) had been added were examined by 4-point resistivity probe and x-ray diffraction. Copper films electrodeposited from electrolytes containing (a) no additives, (b) NaCl + MPSA, and (c) NaCl + PEG show identical resistance-time behavior. These films have the lowest initial resistance which decreases by less than 3 % over 72 h at room temperature. This behavior suggests that adsorbed chloride limits the interaction of MPSA and PEG with the surface when they are present separately in the electrolyte. Films electrodeposited from chloride-free electrolytes containing (d) MPSA and (e) PEG show a 6 % higher initial resistance (with respect to films deposited from additive-free electrolytes) which is at least partially due to grain refinement. The resistance of these films also decreases by less than 3 % over 72 h. Significant room temperature recrystallization is observed only when MPSA and PEG are present in the electrolyte together, particularly in the presence of chloride. Films electrodeposited from electrolytes containing (f) MPSA + PEG show a 9% higher initial resistance which decreases by 19 % in 72 h, while films electrodeposited from electrolytes containing (g) MPSA + PEG + NaCl show a 12 % higher initial resistance which decreases by 23% in 24 h. The Cu(111) integral widths obtained from x-ray diffraction patterns of the as-deposited films indicate that a higher film resistance can be correlated to a finer grain size. This relationship may provide some insight into the effectiveness of the various addition agents on grain refinement.

Impact:

We present data which suggests that chloride adsorption/desorption contributes to the inhibition of copper deposition in polyether-thiol-chloride based plating baths. The dependence of desorption kinetics on copper crystallographic orientations further suggests that inhibition may be locally dependent on seed layer texture. We have also determined that the kinetics for copper recrystallization following deposition is dependent on the initial grain size of the electrodeposit. Additive induced grain refinement enhances the recrystallization kinetics.

Outputs:

Publications:

Stafford, G. R., Vaudin, M. D., Moffat, T. P., Armstrong, N. G., and Kelley, D. R., "The

Influence of Additives on the Room-Temperature Recrystallization of Electrodeposited Copper," Proc. of the Advance Metallization Conference, Orlando, FL, September 28-30, 1999, Materials Research Society, Warrendale, PA.

Presentations:

Stafford, G. R., "The Influence of Additives on the Room-Temperature Recrystallization of Electrodeposited Copper," Advance Metallization Conference, Orlando, FL, September 28-30, 1999.

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 the NIST Center for Neutron Research, 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:

- preparation and measurement of spintronic systems wherein spin dependent magnetic devices are integrated directly onto semiconductor chips
- 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

preparation of magnetic measurement standards

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), G. Serpa (Guest Researcher), D. Barak (Guest Researcher), and W. W. Miller (Guest Researcher)

Objectives:

The objective of this program is to provide assistance to U.S. companies manufacturing products based on 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 adequately 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
Read-Rite	Sanyo	
Nonvolatile Electronics	Alps	
Quantum	Toyota	
Applied Magnetics	Fujitsu	
Ford	Nisshin Steel	
CDC Vacuum	TDK	

Seagate	Matsushita
Veeco	Mitsubishi
	Shimadzu

Computer memory and hard-disk-drive products are a major force in today's economy, representing over $50 billion in annual sales, worldwide. The U.S. has a strong, but precarious, position in hard-disk-drives and is trying to make a comeback 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. 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 breaking 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 fabricate 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 such as IBM and Sony.

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.

The Department of Defense is also very interested in GMR materials (again for a wide range of applications) and our work has been supported for the past three years by a grant from the Defense Advanced Projects Research Agency (DARPA).

External Collaborations:

We have collaborated with a number of industries in the area of GMR materials, including Motorola, IBM, Nonvolatile Electronics, Honeywell, Commonwealth Scientific, and Veeco. We have also collaborated with a number of university groups, including those of Prof. Charlie Falco, U. of Arizona, Prof. Mel Gomez, U. of Maryland, Prof. Ami Berkowitz, U. of California, San Diego, Prof. Karen Kavanvagh, U. of California, San Diego, Prof. Dave Smith, Arizona State, and Prof. Jack Judy, U. of Minnesota, and with scientists from two national labs, George Sandos of NRL and Bill Butler of 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, the most elaborately instrumented thin-film deposition facility in the world, was maintained at an operational status of approximately 95 % of available time, meaning the facility was down only 5% of the time.

This year we continued to investigate a promising 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 (MJTs) and are particularly well suited to being the memory element in nonvolatile computer memory chips. In studying MJTs we observed Al diffusing into the underlying magnetic metal and found that oxidation of the magnetic layer, prior to Al-deposition, can suppress this undesirable effect. We are currently working with U.S. industry to find ways to make use of this discovery in a production environment.

One of the important accomplishments of FY1999 was our work with Commonwealth Scientific. A GMR thin-film deposition system that Commonwealth had built for Honeywell did not meet acceptance criteria. After we identified the problem, Commonwealth was able to correct it. Due to our work, the system is now up and running at Honeywell and will help keep the U.S. in the lead in the international race to commercialize GMR-based random access memory chips.

Impacts:

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 and by frequent telephone and e-mail contacts. Our key collaborators are Motorola, IBM, Seagate, Nonvolatile Electronics, and Read-Rite. These collaborators are attempting to implement our findings in their production equipment. This advanced knowledge together with our supporting consultations is giving U.S. companies a head start in developing the next generation of production facilities.

Output:

Publications:

Egelhoff, Jr., W. F., 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, IEEE Publications, Piscataway, NJ, page 34, 1998.

Fry, R. A., Bennett, L. H., Della Torre, E., Shull, R. D., Egelhoff, Jr., W. F., Farrow, R. F. C., and Lee, C. H., "Magneto-Optical Measurements of Ultrathin Co-Pt(111) Multilayers," J. Mag. Mag. Mat. **193**, 162, 1999.

Egelhoff, Jr., W. F., Chen, P. J., Powell, C. J., Parks, D., McMichael, R. D., Judy, J. H., Martien, D., Berkowitz, A. E., and Daughton, J. M., "Surface Effects in the Growth of GMR Spin Valves," MRS Symp. Proc. **517**, 289, 1999.

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

Egelhoff, Jr., W. F., Chen, P. J., Powell, C. J., Parks, D., Serpa, G., McMichael, R. D., Martien, D., and Berkowitz, A. E., "Specular Electron Scattering in Metallic Thin Films," Proc. 26th Conf. on the Physics and Chemistry of Semiconductor Interfaces, J. Vac. Sci. Technol. B **17**, 1702, 1999.

Chopra, H. D., Yang, D. X., Chen, P. J., Brown, H. J., Swartzendruber, L. J., and Egelhoff, Jr., W. F., "Nature of Magnetization Reversal in Exchange Coupled NiO-Co bilayers," accepted by Physical Review B.

Yang, D. X., Chopra, H. D., Chen, P. J., Brown, H. J., Swartzendruber, L. J., and Egelhoff, Jr., W. F., "Modification of Magnetic Properties in Giant Magnetoresistive Spin Valves Using Pb as a Surface Modifying Species," accepted by J. Appl. Phys.

Chopra, H. D., Yang, D. X., Chen, P. J., Brown, H. J., Swartzendruber, L. J., and Egelhoff, Jr., W. F., "Magnetization Reversal in Polycrystalline Exchange Coupled NiO-Co bilayers," accepted by J. Appl. Phys.

Bae, S., Judy, J. H., Egelhoff, Jr., W. F., and Chen, P. J., "The Dependence of Exchange Coupling on the Surface Roughness and Structure in -Fe_2O_3 and NiFe/ - Fe_2O_3 Bi-layers," accepted by J. Appl. Phys.

Bae, S., Judy, J. H., Egelhoff, Jr., W. F., and Chen, P. J., "Bottom GMR Spin Valves Using a RF Reactive Bias Sputtered - Fe_2O_3 Antiferromagnetic Layer," accepted by J. Appl. Phys.

Lu, R. P., Morgan, B. A., Kavanagh, K. L., Powell, C. J., Chen, P. J., Serpa, G., and Egelhoff, Jr., W. F., "Hot Electron Attenuation Lengths in Ultrathin Magnetic Films," accepted by J. Vac. Sci. Technol.

Presentations:

W. F. Egelhoff, Jr., "Surface Effects in the Growth of GMR Spin Valves," Physics Dept., Invited Talk, Montana State Univ., October 1998.

W. F. Egelhoff, Jr., "Recent Studies of the GMR Effect at NIST," Motorola/DARPA Workshop, Invited Talk, Miami, FL, November 1998.

W. F. Egelhoff, Jr., "Surface and Interface Effects in the Growth of GMR Spin Valves," MSEL Invited Lunch Talk, Gaithersburg, MD, December 1998.

W. F. Egelhoff, Jr., "Specular Electron Scattering in Metallic Thin Films," (poster) 26th Conf. on the Physics and Chemistry of Semiconductor Interfaces, Invited Talk, San Diego, CA, January 1999.

W. F. Egelhoff, Jr., "Surface and Interface Effects in the Growth of GMR Spin Valves," 26th Conf. on the Physics and Chemistry of Semiconductor Interfaces, Invited Talk, San Diego, CA, January 1999.

W. F. Egelhoff, Jr., "Surface and Interface Effects in the Growth of GMR Spin Valves," Invited Talk, Physics Dept., U.C. San Diego, CA, February 1999.

W. F. Egelhoff, Jr., "Optimizing GMR Spin Valves: The Outlook for Improved Properties," Read Rite Corp., Invited Talk, Fremont, CA, April 1999.

W. F. Egelhoff, Jr., "Interdiffusion in the Growth of Al on Magnetic Metals," Nonvolatile Electronics, Invited Talk, Eden Prairie, MN, May 1999.

W. F. Egelhoff, Jr., "Interdiffusion in the Growth of Al on Magnetic Metals," Seagate Research Labs, Invited Talk, Minneapolis, MN, May 1999.

W. F. Egelhoff, Jr., "Interdiffusion in the Growth of Al on Magnetic Metals," (invited poster), DARPA Spintronics Workshop, Invited Talk, White Plains, NY, July 1999.

W. F. Egelhoff, Jr., "New Materials for Ultrahigh density Digital Data Storage," ATP Intramural Project Review, NIST, Invited Talk, August 26, 1999.

Project Title: PROCESSING AND MICROMAGNETICS OF THIN MAGNETIC FILMS

Investigators: R. D. McMichael, A. J. Shapiro, H. J. Brown, D. E. Mathews, Gino Serpa, Chan-Gyu Lee, and Jason Eicke

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/antiferro-magnet interface in exchange biased layers, and dynamic measurements of thin magnetic films. In FY1999, the emphasis has been on exchange biasing and micromagnetics.

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, measurement methods, models and data will be available for industry to evaluate different schemes for magnetization control in magnetic thin films used in devices. 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:

On exchange biased materials, Mark Stiles, PL, NIST, collaborated on theoretical modeling of exchange F/AF interfaces and exchange bias effects. Seagate provided specially deposited samples for exchange bias and rotatable anisotropy measurements.

On micromagnetics, the Center for Theoretical and Computational Materials Science (MSEL) supported a micromagnetics workshop and graduate student help. Mike Donahue and Don Porter, NIST, ITL, are the main authors of the OOMMF public micromagnetics software, and have contributed solutions to micromagnetic standard problem #2. The Institute for Magnetics Research, George Washington University, collaborated on micromagnetic modeling of domain wall trap structures and contributed to OOMMF public code. IFW of Dresden, Germany, INESC, of Lisbon, Portugal, and Max-Planck-Institut fur Metallforschung of Stuttgart, Germany contributed solutions to micromagnetic standard problems #2 and #3.

Accomplishments:

A method for determining the hysteretic, "unused" fraction of the ferromagnet/antiferro-magnet interaction in exchange biasing applications was refined and tested on a wider range of materials. In exchange biasing applications, stable antiferromagnetic spin configurations give rise to an effective field, the exchange bias field. Unstable antiferromagnetic spin configurations give rise to less-desirable hysteretic effects. Following up on the initial technique development and measurements on NiO-biased thin films in FY1988, we have applied our ferromagnetic resonance technique to NiMn-biased films provided by Seagate and to CoO-biased films prepared at NIST. We find that the presence of an unstable fraction is common to all these films. The NiO work was published in Phys. Rev. B, the CoO work has been submitted to J. Appl. Phys. and the NiMn work is in progress.

In collaboration with Mark Stiles (NIST, PL) the effects of stable and unstable ferromagnet-antiferromagnet interfacial interactions were modeled. These results were presented at the 42nd annual Conference on Magnetism and Magnetic Materials and at the Centennial Meeting of the American Physical Society. A paper has been published in Physical Review B, and a second paper on the temperature dependence of the effect is scheduled for publication November 1, 1999.

To control the magnetization in thin films, a possible alternative to exchange biasing is uniaxial anisotropy. We have discovered a technique for producing strong uniaxial anisotropy in thin films by oblique-incidence deposition of tantalum underlayers, and we have produced anisotropy fields on the order of 0.1 T (1 kOe) in thin films of NiFe and Co. These fields are an order of magnitude larger than the magnetocrystalline anisotropy fields in similar films. This work is in progress.

Our work in standard problems for micromagnetic modeling has continued to gain international attention. Three papers were published (one from NIST) in the J. Appl. Phys on standard problem #2 and one paper on standard problem #1. Another paper outlining an analytical solution and a more accurate computation has been submitted for publication. Three invited presentations have been given on micromagnetic standard problems in FY1999.

Impact:

Our work on exchange bias phenomena is part of a large community effort to understand and improve exchange bias materials to satisfy industrial demand for strong exchange bias fields in materials with high blocking temperatures and high thermal stability. Our development and publication of the ferromagnetic resonance method and model provide a more complete method of measuring exchange bias phenomena.

Published results on our micromagnetic standard problem #2 have been used by researchers and

Lawrence Livermore National Labs as a benchmark for their computational methods. Our recent collaborations with ITL have resulted in an analytical solution for the small-particle limit and enhanced accuracy computations that agree to within 0.01 %. The standard problems have also been receiving international attention as evidenced by our invitation to speak on standard problems to a European Community supported workshop.

Outputs:

Publications:

Stiles, M. D. and McMichael, R. D., "Temperature Dependence of Exchange Bias in Ferromagnet/antiferromagnet Bilayers," accepted for publication in Phys. Rev. B.

McMichael, R. D., Donahue, M. J., Porter, D. J., and Eicke, J. "Comparison of Magnetostatic Field Calculation Methods on 2-D Square Grids as Applied to Micromagnetic Standard Problem #2," J. Appl. Phys., **85** 5816, 1999.

Stiles, M. D. and McMichael, R. D., "Model for Exchange Bias in Polycrystalline Ferromagnet-antiferromagnet Bilayers," Phys. Rev. B., **59**, 3722, 1999.

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.

Presentations:

McMichael, R. D., "Experiences with Micromagnetic Standard Problems," Invited, NIST Workshop on Preisach Modeling, January 1999.

Eicke, J., "Element Shaping for Reduced Switching Field," Invited, NIST Workshop on Preisach Modeling, January 1999.

McMichael, R. D., "Micromagnetics -- Magnetism on the Mesoscale," Invited, poster component, APS Topical Group on Magnetism Display in the APS centennial meeting exhibits, Atlanta, GA, March 1999.

Stiles, M. D. (in collaboration with R. D. McMichael) "Hysteretic Effects in Exchange Biased Multilayers," Invited, APS Centennial Meeting, Atlanta, GA, March 1999.

McMichael, R. D., "Relaxation in Ferromagnetic Thin Films," Invited, Surface Science Lunch Bunch, NIST, May 3, 1999.

McMichael, R. D., "Standard Problems in Micromagnetics," Invited, DOE Computational Materials Sciences Network - Magnetism Workshop, Washington, DC, July 15, 1999.

McMichael, R. D., "Standard Problems in Micromagnetism," Invited, COST P3 Workshop - Simulation of Physical Phenomena in Technological Applications, Helsinki, Finland, September 1999.

McMichael, R. D., "Separation of Reversible and Irreversible Effects in Exchange-biased Films by Ferromagnetic Resonance," 43rd Annual Conference on Magnetism and Magnetic Materials, Miami, FL, November 1999.

Stiles, M. D. and McMichael, R. D., "Irreversible Effects in Exchange-biased Magnetic Layers," 43rd Annual Conference on Magnetism and Magnetic Materials, Miami, FL, November 1999.

McMichael, R. D. "Comparison of Magnetostatic Field Calculation Methods on 2-D Square Grids as Applied to Micromagnetic Standard Problem #2," 43rd Annual Conference on Magnetism and Magnetic Materials, Miami, FL, November 1999.

McMichael, R. D., "Contrasting the Temperature Dependence of Thin Films Biased by CoO," APS Centennial Meeting, Atlanta, GA, March 1999.

McMichael, R. D., "Element Shaping for Reduced Switching Field," MRS Spring Meeting, San Francisco, CA, April 1999.

Patents Pending:

Domain Wall Traps for Low Field Switching of Magnetic Elements

Robert D. McMichael

Disclosure Filed

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, and 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 dimensions have 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 of 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) and on 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 the Ba-Fe-Ti-O system, it has been found that in many of the compounds in the system the Fe is physically located into nanometer-sized regions of the crystal structure. However the magnetic character of these various structurally-related compounds has been found to change 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 and magnetic susceptibility. 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, when a non-magnetic species is added to that material, the magnetic coercivity will normally 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. Surprisingly, this year it was found that C60 inclusion in thin films of Fe and Co affects their coercivities differently. The relationship between coercivity and magnetocrystalline anisotropy in mechanically milled Fe-Al and Fe-Al-Ge nanocrystalline materials was also examined in a collaboration with Caltech.

Magnetic nanocomposites exhibiting 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. This year Dy-Al-Fe garnet nanocomposites were found to have enhanced magnetocaloric effects similar to those previously discovered in the Gd-Ga-Fe garnet nanocomposites.

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 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 addition, two students from the University of Toronto (J. McCrea and G. Hibbard) worked in our laboratory this summer examining the energy losses in these materials. 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 a collaboration with Caltech (B. Fultz and H. Frase) the magnetization behavior of a series of nanocrystalline materials was correlated with the magnetocrystalline anisotropy of the material, and the magnetic behavior of Co/Pt multilayers was examined in a collaboration with George Washington University (L. Bennett and R. Fry). A collaboration with Argonne National Laboratory (S. Bader and S. Jiang) was also successful this year in examining the remagnetization behavior of SmCo/Fe spring magnets; while a collaboration with the Johns Hopkins University (C.L. Chien and Kai Liu) was successful at examining the remagnetization behavior of wedge-shaped FM/AF materials. R. Shull was elected as the Chairman of the International Committee on Nanostructured Materials. A interagency group with R. Shull as one of the organizing members comprised of NIST, NSF, ONR, DOC/TA, AFOSR, NIH, and NASA organized a national workshop on the status and trends in research on nanomaterials and nanodevices.

Accomplishments:

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. Examination of materials prepared by depositing the magnetic species in the opposite order unequivocally showed that the asymmetry in remagnetization behavior is due to defects, like dislocations, in the antiferromagnet. Also, examination of a sample with a wedge-shaped ferromagnetic layer showed that the remagnetization behavior is dependent on the relative strengths of magnetostatic and exchange interactions on the ferromagnet.

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! It is felt this difference between Fe and Co films was due to differences in morphology caused by the addition of the C60.

SANS observations of nanocrystalline Ni resulted in a finding that the magnetic correlation length was not the same as the material's grain size. Since one of the big unanswered questions in nanocrystalline magnetic materials is the effect on the magnetic moment of the atoms near grain boundaries where the local atomic environment is significantly changed, these results have attracted great interest. Specifically, these results provide some of the strongest evidence to date that the grain boundary atoms' magnetic strength is not diminished.

Examination of the magneto-optic Kerr effect in layered Co/Pt films, envisioned for magneto-optical data storage, showed that the remagnetization behavior is accompanied by more than one magnetic phase reversal. In addition, significant time dependence effects were observed and modeled. In nanocrystalline Fe-Al and Fe-Al-Ge alloys, it was found that the major contribution to magnetic coercivity was residual stress in the material, not the magnetocrystalline anisotropy.

NIST was joined by NSF, ONR, DOC/TA, AFOSR, NIH, and NASA in organizing a national workshop to review of the status and trends in nanotechnology. A report of this workshop is in final review and will be used to justify a National Initiative in this area. 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.

Following the national workshop on nanomaterials organized by people (including R. D. Shull) from NIST, NSF, ONR, DOC/TA, AFOSR, NIH, and NASA, a document summarizing the activity and needs in this field was submitted to the White House and a National Initiative on Nanotechnology was developed for funding in FY2001.

Outputs:

Publications:

Weismuller, J., McMichael, R. D., Michels, A., and Shull, R. D., "Small Angle Neutron Scattering by the Magnetic Microstructure of Nanocrystalline Ferromagnets Near Saturation," J. Res. Natl. Inst. Stand. Technol. **104**, 261, 1999.

Nikitenko, V. I., Gornakov, V. S., Shapiro, A. J., Shull, R. D., Kai Liu, Zhou, S. M., and Chien, C. L., "Effect of Exchange Anisotropy on Elementary Events of the Magnetization Reversal Processes in Ferromagnetic/Antiferromagnetic Bilayers," J. Appl. Phys., in press.

Fry, R. A., Bennett, L. H., Della Torre, E., Shull, R. D., Egelhoff, W. F., Farrow, R. F. C., and Lee, C. H., "Magneto-optical Measurements of Co-Pt (111) Multilayers," J. of Mag. Magn. Materials **193** (1-3), 162, 1999.

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 **143**, 182, 1999.

Presentations:

Shull, R. D., "Magnetization Reversal in Exchange Spring Magnets Observed Directly with a Magneto-optical Indicator Film," International Symposium on Metastable, Mechanically Alloyed and Nanocrystalline Materials (ISMANAM-99), Invited Talk, Dresden, Germany, August 1999.

Shull, R. D., "Magnetic Domains in Nanocrystalline and Nanocomposite Materials," Materials Science Department Seminar Speaker, Darmstadt University, Invited Talk, Darmstadt, Germany, August 1999.

Shull, R. D., "Magnetization Reversal in Thin Film Bilayers With Exchange Anisotropy Observed Directly by the MOIF Technique," FIM-99 (Frontiers in Magnetism) Conference, Royal Institute of Technology, Invited Talk, Stockholm, Sweden, August 1999.

Shull, R. D., "Low Field, High Temperature Magnetic Refrigerants for the 21st Century," FIM-99 (Frontiers in Magnetism) Conference, Royal Institute of Technology, Invited Talk, Stockholm, Sweden, August 1999.

Shull, R. D., "Magnetic Properties of Nanostructured Films," NATO Advanced Research Workshop on Nanostructured Films and Coatings, Invited Talk, Santorini, Greece, June 1999.

Shull, R. D., "AC Susceptometry," Royal Institute of Technology, Invited Talk, Stockholm, Sweden, April 1999.

Shull, R. D., "Properties of Magnetic Nanocomposites," ICMAT-ICR, Invited Talk, Rome, Italy, April 1999.

Shull, R. D., "Magnetic Materials Group Programs," University of Bologna Seminar, Invited Talk, Bologna, Italy, April 1999.

Shull, R. D., "Magnetic Properties of Nanocomposites," Fourth International Conference on Metastable Phases (IWOMP-IV), Invited Talk, Bologna, Italy, April 1999.

Shull, R. D., "Domain Behavior in Magnetic Nanostructures as Revealed by MOIF Observations," Nanostructured Hybrid Materials Symposium, TMS Annual Meeting, Invited Talk, San Diego, CA, March 1999.

Shull, R. D., "Magnetic Nanocomposites," Seminar Speaker, Johnson Space Center, Invited Talk, Houston, TX, December 1998.

Shull, R. D., "New Directions in Magnetism: Magnetic Nanocomposites," Seminar Speaker, Department of Mechanical Engineering and Materials Science, Rice University, Invited Talk, Houston, TX, December 1998.

Shull, R. D., "Magnetic Activities in the NIST Magnetic Materials Group," Seminar Speaker, Patrick Air Force Base, Invited Talk, Melbourne, FL, November 1998.

Shull, R. D., "Direct Experimental Study of the Magnetization Reversal Process in Epitaxial and Polycrystalline Films with Unidirectional Anisotropy," 43rd Annual Conference on Magnetism and Magnetic Materials, Miami, FL, November 1998.

Shull, R. D., "Domain Behavior in Magnetic Nanostructures as Revealed by MOIF Observations," American Vacuum Society Annual Meeting, Baltimore, MD, November 1998.

Shull, R. D., "Magnetic Exchange Bias in a NiO/FeNi Antiferromagnetic/Ferromagnetic Bilayer," TMS Fall Meeting, Rosemont, IL, October 1998.

Shull, R. D., "Magnetic Dendrimers and Other Nanocomposites," American Chemical Society Annual Meeting, Invited Talk, Boston, MA, August 1998.

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 magnetic, electronic, optical, or other functional properties forming smaller but nonetheless critical markets. Whatever the application, satisfactory long term performance of metallic components demands microstructural stability and reliable performance. 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 for the Rockwell C scale, and blocks for additional scales are now being developed. These will facilitate the acceptance of a wide range of U.S. products in international markets, as well as minimizing product-acceptance disputes in domestic trade.
>
> Measurements of thermophysical properties such as thermal diffusivity and specific heat have been carried out, using NIST-developed techniques, to help engineers understand heat flow in systems ranging from integrated circuits to turbine engines. The measurements have extended from room temperature to over 2000 C and have been applied to pure metals, alloys of special interest, and thin film multilayer materials.
>
> Special microscopy techniques, including high resolution transmission electron microscopy and electron holography, are being used to reveal the finest details of atomic structure and interface reactions in advanced materials. The systems under study include novel phases with potential microwave applications, electronic devices and interconnects, and nanolaminate multilayers.

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 strongly on the conditions under which the materials are fabricated. These distributions are crucial in determining properties such as strength, ductility, homogeneity, conductivity, and others which are 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.

Project Title: ROCKWELL HARDNESS STANDARDS

Investigators: S. R. Low, D. J. Pitchure, C. D. Flanigan, 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), G. E. Hicho (Contractor), 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 many hardness scales 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. The consequence of this situation has been that U.S. hardness scales have shown significant variability between calibration 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 measurement industry alone is in the $10 M to $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 could 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 metallic materials, such as fasteners, automobiles, and aircraft. The value of goods affected will be in the billions of dollars.

The NIST Metallurgy Division, in collaboration with the Manufacturing Engineering Laboratory (MEL), the Information Technology Laboratory (ITL), the National Voluntary Laboratory Accreditation Program (NVLAP/TS), and the Standard Reference Materials Program (SRMP/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 the Manufacturing Engineering Laboratory.

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. The transfer standards are in the form of steel test blocks, which are sold to the public through the NIST Standard Reference Materials Program. International HRC scale intercomparisons with countries worldwide have been made to ensure compatibility with the Rockwell C hardness scales of other countries. Standardization of the Rockwell B hardness scale (HRB) has also been accomplished with HRB transfer standards expected to be available through SRMP in FY2000. Certification of Rockwell hardness indenters as NIST Standard Reference Materials is also currently under development in cooperation with MEL.

A research project is underway to develop an alternative material to the traditional brass and aluminum test blocks used commercially for HRB test-block transfer standards. Brass and aluminum test blocks have exhibited hardness instability over time. Rockwell measurements in these materials also produce relatively large areas of deformation surrounding the indentation, significantly limiting the number of indentations that can be made in the block. In collaboration with G. Hicho, the production of test blocks through consolidation of metal powders is being investigated.

A laboratory accreditation program for hardness calibration laboratories has been developed under the direction 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. The program is to be implemented in FY2000.

NIST is assisting ASTM in revising their current Rockwell hardness test method standard E18 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 U.S. 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 under the direction of NIST Technology Services and 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 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 implemented and 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 the ASTM Subcommittee on hardness and 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 30 test blocks at each of three levels of the Rockwell C scale (HRC) have been calibrated to replenish stock which was sold through the Standard Reference Materials Program in the previous year. Two workshops on Rockwell hardness standardization were presented in the past year; the first at the Measurement Standards Conference and the second at the National Conference of Standards Laboratories. Technical requirements were completed for use in the NVLAP accreditation program for hardness calibration laboratories. The program will be implemented early in FY2000. Standardization of the Rockwell B scale was completed. A contract was awarded to a hardness block producer to provide NIST with uncalibrated test blocks for the HRB scale. The NIST Small Business Innovative Research (SBIR) program awarded funding to a U.S. diamond indenter manufacturer to develop better processes for manufacturing Rockwell diamond indenters. This work will be applied to the development of the NIST SRM diamond indenters.

Impact:

With the release of the NIST SRMs for the Rockwell C scale, the U.S. national HRC hardness scale is now in-line with other countries throughout the world as evidenced by a worldwide intercomparison which was completed in FY1999. The previous U.S. HRC scale, maintained by industry, had for many years been in disagreement with countries in Europe and Asia. U.S. industries are now adapting to the new NIST scale; however, it may take a few years for it to be fully adopted. In an effort to accelerate the adoption of the new HRC scale, the ASTM is in the process of balloting a revision to the Rockwell test method standard that will require Rockwell calibrations to be made with respect to NIST standards, as they become available.

The NVLAP program for accrediting laboratories engaged in hardness calibrations has received requests from two companies requesting accreditation for Rockwell hardness calibrations. The accreditation process will begin in early FY2000.

Outputs:

Publications:

Liggett, W. S., Low, S. R., Pitchure, D. J., and Song, J., "Assessment of Error Sources in Rockwell Hardness Measurements," Proceedings of the IMEKO 99, Osaka, Japan, June 1999.

Song, J., Low, S. R., Pitchure, D. J., and Vorburger, T., "Measurement Traceability of NIST Standard Rockwell Diamond Indenters," Proceedings of the IMEKO 99, Osaka, Japan, June 1999.

Low, S. R., Gettings, R. J., Liggett, W. S., and Song, J., "Rockwell Hardness − A Method-Dependent Standard Reference Material," Proceedings of the National Conference of Standards Laboratories, Charlotte, NC, July 1999.

Presentations:

Low, S., "Hardness Standardization − Part 1: Traceability to NIST," Hardness Standardization Workshop at the Measurement Science Conference, Anaheim, CA, January 1999.

Low, S., "Hardness Standardization − Part 2: Uncertainty," Hardness Standardization Workshop at the Measurement Science Conference, Anaheim, CA, January 1999.

Low, S., "Standardization and Traceability of Rockwell Hardness," Hardness Standardization Workshop at the National Conference of Standards Laboratories, Charlotte, NC, July 1999.

Workshops Organized:

Hardness Standardization Workshop at the Measurement Science Conference, Anaheim, CA, January 1999.

Hardness Standardization Workshop at the National Conference of Standards Laboratories, Charlotte, NC, July 1999.

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

Objectives:

This main objective of this project is to improve the measurement process in magnetic materials in order to characterize these materials accurately and efficiently. This will enable industry to develop and produce new and better materials at lower cost.

Technical Description:

In collaboration with scientists from universities, industry, and other Divisions at NIST, magnetic materials important to the scientific and industrial communities are prepared and methods for the improved measurement of their properties are developed. Standard reference materials for the calibration of existing and planned instruments used in the measurement of magnetic properties are developed and produced. Methods for the improvement of flux pinning in superconducting materials are investigated in order to aid the industrial application of high temperature superconductors. Methods for the characterization of accommodation and aftereffect in magnetic recording and permanent magnetic materials are developed. Models are also developed for determining the most efficient methods to fully characterize magnetic materials, including their magnetostriction and time dependence.

Planned Outcome:

The expected results of this activity are fourfold: (1) improved characterization of magnetic recording media resulting in higher storage capacity and lower overall net cost per unit of storage, (2) improved characterization of permanent magnets, superconductors, and other industrial magnetic materials, resulting in more efficient and effective 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 at a lower cost.

Accomplishments:

Preparation, measurement, and analysis of a set of nickel spheres were completed. These spheres were issued as SRM 772a, a standard reference material intended for use in the calibration of magnetometers. A set of nickel disks was obtained for use as a standard reference material. Though they will not be as precise as the nickel spheres, the disks have the advantage that they are closer to the actual geometry used by a large number of laboratories who measure the magnetic properties of recording materials. They have the disadvantage that the user must measure the mass of the disk, whereas this is not necessary when using SRM 772a. Modifications to our absolute magnetometer that will enable the development of very low moment standards for use in high sensitivity instruments, such as alternating gradient magnetometers and SQUIDs, are planned. Critical currents were determined for a series of

$Bi_2Sr_2Cu_2O_{8+}$ high temperature superconducting tapes. The effect of Al_2O_3 and carbon nanotube additions on the flux-pinning was investigated.

The ability of the Preisach-Arrhenius model to predict the change in magnetic stability with changes in temperature was investigated. For a commercially prepared magnetic particle tape it was found that, above 150 K, good agreement with the model obtains. However, below 150 K the results are at variance with the theory. Modifications to the theory which will improve its predictive capability over the entire temperature range have been developed.

A series of measurements have been made on the alloy system $Zr_3(Rh_{1-x}Pd_x)_4$. This system is unique in that it exhibits rapid changes in its magnetic and superconducting properties over a narrow range of composition, the same range of composition in which incommensurate waves appear in the crystal structure. These results may have profound implications for theories of magnetism and superconductivity.

External Collaborations:

We are collaborating with several companies which produce magnetic measurement equipment and magnetic materials. We also collaborate with researchers at George Washington University, the State University of New York at Buffalo, and the University of Maryland.

Output:

Standard Reference Materials:

A nickel sphere for the calibration of magnetometers (such as vibrating sample magnetometers) was issued as SRM 772a.

Publications:

Della Torre, E., Swartzendruber, L. J., Bennett, L. H., and Rugkwamsook, P., "Experimental Test of the Preisach-Arrhenius Model with Temperature," accepted for publication in Physica B.

Della Torre, E. and Bennett, L. H., "A Preisach Model for Aftereffect," IEEE Trans. Magn. **34**, 1276, 1998.

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," Mat. Res. Soc. Symp. Proc., **517**, 355, 1998.

Della Torre, E., Bennett, L.H., and Swartzendruber, L. J., "Modeling Complex Aftereffect Behavior in Recording Materials using a Preisach-Arrhenius Approach," Mat. Res. Soc. Symp. Proc., **517**, 291, 1998.

Reimers, A., and Della Torre, E., "Fast Preisach Based Magnetostriction Model for Highly Magnetostrictive Materials," accepted for publication by the IEEE Trans. Magn. **34**, 3857, 1998.

Presentations:

Swartzendruber, L. J., "The Correlation between Magnetic and Mechanical Properties in Low

Alloy Sheet Steel," ASNT Spring Meeting, Orlando, FL, March 1999.

Project Title: MAGNETO-OPTICAL IMAGING

Investigators: A. J. Shapiro, R. D. Shull, V. I. Nikitenko (Guest Researcher), and V. S. Gornakov (Guest Researcher)

Objectives:

The primary goal of this project is one of the fundamental issues in magnetism - understanding of the microscopic mechanisms of magnetization reversal in quasi-two-dimensional nanocomposite magnetic materials. The advanced magneto-optical indicator film (MOIF) imaging technique developed by NIST and the Institute for Solid State Physics, Russian Academy of Sciences (ISSP RAS) is a simple, fast, illustrative, and sensitive tool for nondestructive and real-time visualization and characterization of materials magnetic microstructures at the micron scale. It opens perspectives for studies and solving practical and fundamental problems of materials science. In the last few years there has been a great deal of interest in studying the unique properties of nanocomposite materials. They may consist, for instance, of ultra thin layers. Thicknesses of such films are comparable to the domain wall width. In the films also a coexistence of ferromagnetic and antiferromagnetic exchange interactions is possible. This magnetic system is attractive for use as a memory element in future generation computers. For coupled magnetic systems, in particular, detailed knowledge of the magnetization reversal processes holds the key to unlocking the potential for practical applications. In addition, the advanced MOIF technique also can be used as a rapid non-destructive method for monitoring thin film quality during production.

Technical Description:

In the MOIF technique, a Bi-substituted yttrium iron garnet transparent film with in-plane anisotropy is placed on the top of a sample. Since the magneto-static field of the sample under study alters the magnetization of the film, it allows utilization of the film as an indicator of the magnetic field. When polarized light passes through the indicator film and is reflected back by an Al underlayer it undergoes the magneto-optic Faraday rotation which is proportional to a component of the magnetic stray field perpendicular to the indicator film plane. The interaction of the polarized light is imaged in a polarizing microscope. This allows visualizing, for example, the magnetization reversal processes, domain wall nucleation and motion, Bloch's lines, and crystal defects (e.g., dislocations, voids and sample edges) in magnetic materials.

The MOIF technique was applied to the investigation of the microscopic mechanisms in magnetization processes in three different types of materials: soft ferromagnet/hard ferro-magnetic, ferromagnet/antiferromagnetic (FM/AF) bilayers, and magnetic superlattices with nonmagnetic spacers.

In permanent magnets consisting of hard and soft magnetic phases coupled at the interfaces, the magnetization reversal limits the maximum achievable energy product. The hard magnetic phase provides the high anisotropy and coercive fields while the soft-magnetic phase enhances the magnetic moment. The soft-phase magnetization reversal occurs due to forming or unwinding of an exchange spring similar to the one which exists in a domain wall. Direct experimental studies of such phenomena were not available until now. The MOIF technique allows experimental investigation of the magnetization reversal process in exchange spring magnets such as thin film Sm-Co/Fe bilayer and Sm-Co/Co superlattice structures.

In the last few decades there has been a great deal of interest in studying the unique properties of exchange coupled ferromagnetic and antiferromagnetic ultra thin layers. Such a magnetic system is attractive for use as computer memory elements. For such an application, an understanding of the remagnetization process of these elements is mandatory. To date, the investigation of the microscopic magnetization reversal mechanisms in these systems has revealed drastic contradictions between theory and experiment in both the values of exchange bias field H_E and coercive force H_C. It is now well recognized that the understanding of the exchange-biased FM/AF thin film lies in the peculiarities of nucleation and motion of domain walls of both the constituent FM and AF layers. However, detailed experimental study of the domain wall dynamics of the FM/AF bilayers has been severely hampered by the complicated multi-domain structure which occurs during switching, occurring within a narrow field range, from one single-domain state to another with an opposite magnetization. Recently, macroscopic domain structures in an exchange-coupled bilayer of wedged-permalloy ($Py=Ni_{81}Fe_{19}$)/uniform-FeMn ($Fe_{50}Mn_{50}$), has been realized by exploiting the inverse dependence of the H_E on the FM layer thickness. The magnetization switching process involves only *two macroscopic* domains. Taking advantage of this unusually simple domain pattern, we have used the magneto-optical indicator film (MOIF) technique to investigate the macroscopic mechanisms of the domain wall nucleation and motion.

Magnetic superlattices with nonmagnetic spacers can exhibit the giant magnetoresistance (GMR) effect due to inversion of the magnetization direction in adjacent layers in an external magnetic field. Utilization of this effect allows developing new devices for noninductive reading of magnetically recorded information. Spin reorientation phase transformations are responsible for the magnetization processes in magnetic superlattices with nonmagnetic spacers. We studied the correlation between the magnitude of the GMR and the micromechanism of the magnetization reversal of electrodeposited Co/Cu superlattices for a range of Cu spacer thicknesses.

Planned Outcome:

This project will contribute to the fundamental understanding of the micromechanism of the magnetization reversal processes in quasi-two-dimensional nanocomposite magnetic materials. The MOIF imaging technique will be available for industrial applications: non-destructive quality magnetic materials control, research and development of new magnetic materials, domain wall behavior in ultra-thin layer structures, etc.

External Collaborations:

We conducted MOIF investigations as a part of collaborative studies of the following materials with the indicated companies and universities:

1. Epitaxial Sm-Co (35 nm)/Fe(50 nm) bilayer films grown on Cr (20 nm) buffered MgO (100) substrate by sputtering at the Argonne National Laboratory, Argonne, IL.

2. FeNi/FeMn bilayers with a linearly varying FeNi thickness (perpendicular and parallel to the

unidirectional anisotropy) and uniform FeNi/FeMn bilayers grown at Department of Physics and Astronomy, The Johns Hopkins University, Baltimore, MD.

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

4. Co/Cu magnetic superlattices prepared at NIST and studied jointly with Department of Materials and Nuclear Engineering, University of Maryland, College Park, MD.

Accomplishments:

For the first time the remagnetization process was observed directly using the MOIF technique in epitaxial Sm-Co (35 nm)/Fe(50 nm) bilayer films, grown on Cr (20 nm) buffered MgO (100) substrate by sputtering. The macroscopic parameters of magnetization reversal were measured in a SQUID magnetometer. It revealed characteristic exchange-spring behavior where the reversal of the soft Fe layer is pinned at the interface by the SmCo hard layer. In order to investigate the magnetic spin rotation process inside the bilayer during remagnetization, a 0.3 mm hole was made in the sample, and the magnetostatic field (H_{ms}) around the hole was visualized through the intensity changes of the double Faraday effect in a transparent indicator film with in-plane anisotropy. Black and white contrast on opposite sides of the microhole was observed, indicating the direction of magnetization in the sample around the hole. Analysis of the spin rotation processes in the soft ferromagnetic component during remagnetization have shown that spins rotate uniformly when the magnetic field was applied slightly off either side of the easy axis. When the field was aligned with the easy axis, no uniform spin rotation was observed. During rotational hysteresis, a unique spin behavior was observed: spin rotation was discovered to change sign without an accompanying change in the sign of the field rotation.

The features of the magnetization reversal processes in Permalloy (2 nm to 30 nm wedge)/ FeMn(30 nm)/Cu(30 nm)/Si bilayer system with the exchange anisotropy induced either perpendicular or parallel to the wedge direction were studied by an advanced MOIF technique and Vibrating Sample Magnetometry (VSM). When the exchange anisotropy is established perpendicular or parallel to the wedge direction, two macroscopic domains are observed. These domains are separated by a 180-degree wall in the perpendicular geometry and an intermediate band containing a large density of stripe-type microdomains in the parallel geometry. While the exchange field remains practically the same in both geometries, the coercivity and squareness of the loop are much less in the parallel geometry. Real-time magneto-optical indicator film images reveal distinct asymmetry in the motion of a single domain wall in a wedged-NiFe/uniform-FeMn bilayer due to the nucleation and behavior of an exchange spring in the *antiferromagnetic layer*. Magnetization reversal from the ground state begins at the thick end of the wedge where the exchange anisotropy field (H_E) is minimal and the magnetostatic field (H_{MS}) is maximal, whereas reversal into the ground state begins from the thin end where H_E is maximal and H_{MS} is minimal. We have directly observed macroscopic domain structures in a wedged- Permalloy / uniform-FeMn exchange-coupled bilayer with the anisotropy direction perpendicular to the wedge direction. Magnetization reversal from a fully magnetized state starts at the thick corners of the wedge where the exchange energy is minimal and the magnetostatic energy is maximal. The two edge domains then join and form a macroscopic reversal domain, separated from the original domain by a 180-degree macroscopic domain wall. The domain wall propagates toward and eventually vanishes at the thin end of the wedge where the exchange energy is maximal and the magnetostatic energy is minimal. The observed asymmetry in the domain wall motion, incompatible with a static AF spin structure, indicates the presence of a mobile domain wall (exchange spring) in the antiferromagnet.

We have investigated the elementary events of the magnetization reversal processes in anisotropic ferro- and antiferromagnetic superlattices $[Co(1.6 nm)/Cu(d_{Cu})]_{200}$ using MOIF and VSM techniques. Magnetization processes were analyzed through the intensity change due to the stray field at the edge of the multilayer, around domain walls and the deliberately created microhole. Specimens with different thicknesses of the non-magnetic spacer (d_{Cu} was varied in a range from 0.5 nm to 4 nm) were electrodeposited on the Si(001) substrates which were covered with a thin evaporated Cu seed layer. They were characterized by inplane fourfold symmetry of the magnetization and magnetoresistance. Peculiarities in the nucleation and motion of domain walls in superlattices with different types of interlayer exchange coupling between adjacent ferromagnetic layers were revealed. Nonuniform spin-reorientation transformations in the antiferromagnetic superlattice result in either a collinear or noncollinear magnetic phase, depending on the applied field direction. It was shown that the magnitude of the giant magnetoresistance effect (GMR) depends on the micromechanism of the magnetization reversal in electrodeposited Co/Cu superlattices.

Impact:

The advanced magneto-optical indicator film imaging technique developed by NIST and ISSP RAS is currently widely used in industrial and university laboratories in the USA and around the world for direct observation of the magnetization reversal processes in variety of magnetic materials. The results of our investigations have been transferred to our collaborators at the Argonne National Laboratory, Argonne, IL, Department of Physics and Astronomy, The Johns Hopkins University, Baltimore, MD, and Department of Materials and Nuclear Engineering, University of Maryland, College Park, MD.

Outputs:

Publications:

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magnetic Bilayer," PRL, in press.

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Kai Liu, Zhou, S. M., Chien, C. L., Nikitenko, V. I., Gornakov, V. S., Shapiro, A. J., and Shull, R. D., "Anisotropy-Dependent Macroscopic Domain Structure in Wedged-Permalloy / Uniform-FeMn Bilayers," JMMM, in press.

Presentations:

Shull, R. D., Shapiro, A. J., Nikitenko, V. I., and Gornakov, V. S., "Domain Behavior in Magnetic Nanostructures as Revealed by MOIF Observations," TMS Annual Meeting, San Diego, CA, February 1999.

Hilt, Z., Shapiro, A. J., Shull, R. D., Nikitenko, V. I., Gornakov, V. S., Jiang, J. S., Sowers, C.H., Inomata, A., and Bader, S. D., "Magneto-Optical Indicator Film Investigation of the remagnetization Behavior of Exchange Spring Magnets," MRS Spring Meeting, San Francisco, CA, April 1999.

Jiang, J. S., Fullerton, E. E., Sowers, C. H., Inomata, A., Bader, S. D., Shapiro, A. J., Shull, R. D., Gornakov, V. S., and Nikitenko, V. I., "Spring Magnet Films," INTERMAG 99, Kyongju, Korea, May 1999.

Nikitenko, V. I., Shapiro, A. J., Gornakov, V. S., Shull, R. D., Kai Liu, Zhou, S. M., and Chien, C. L., "Domain Wall Motion and Nucleation in the Wedge-Shaped FeNi/FeMn Bilayers with Unidirectional Anisotropy," APS Meeting, Atlanta, GA. March 1999.

Gornakov, V. S., Nikitenko, V. I., Shapiro, A. J., and Shull, R. D., "Magnetic Domain Formation on Dislocations in the Antiferromagnetic layer of Exchange Biased Bilayer Films," APS Meeting, Atlanta, GA, March 1999.

Shull, R. D., Shapiro, A. J., Brown, H. R., Nikitenko, V. I., Gornakov, V. S., Jiang, J. S., Inomata, A., Sowers, C. H., and Bader, S. D., "Magnetization Reversal In Exchange Spring Magnets Observed Directly With A Magneto-Optical Indicator Film," Dresden, Germany, August 1999.

Kai Liu, Zhou, S. M., Chien, C. L., Nikitenko, V. I., Shapiro, A. J., Gornakov, V. S., and Shull, R. D., "Anisotropy-Dependent Macroscopic Domain Structure in Wedged-Permalloy / Uniform-FeMn Bilayers," 44th Annual Conference on Magnetism and Magnetic Materials, MMM'99, San Jose, CA, November 1999.

Gornakov, V. S., Nikitenko, V. I., Shapiro, A. J., Shull, R. D., Gökemeijer, N. J., and Chien, C. L., "Direct Observation of Antiferromagnetic Domains and Magnetization Processes in an Exchange-Biased Permalloy/FeMn Bilayer," 44th Annual Conference on Magnetism and Magnetic Materials, MMM'99, San Jose, CA, November 1999.

Project Title: PERFORMANCE OF STRUCTURAL MATERIALS

Investigators: R. J. Fields, R. B. Clough, J. L. Fink, T. Foecke, R. E. Ricker, D. A. Shepherd, J. H. Smith, and M. R. Stoudt

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 materials failure is extremely large. Studies have shown that the annual costs of failures due to fracture and corrosion are each over $100 billion. 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 FY1999, work was conducted on several sub-projects:

Stress Rupture of Lead-Free Plumbing Solders

Stress rupture tests were conducted on soldered sleeve joints in copper tube for times up to one year at temperatures in the range 37.8 °C to 121.1 °C (100 °F to 250 °F). In addition to the previously studied Alloy Sb5 (95Sn-5Sb), two other lead-free solders were tested, namely Alloy E (4Cu-0.5Ag-bal.Sn) and Alloy HB (5Sb-0.3Ag-3.5Cu-1Ni-bal.Sn). This work was carried out in collaboration with the Copper Development Association (CDA) and with the B16 Committee of ASME, and was designed to establish permissible pressures for copper tubes joined by lead-free solders.

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.

Mechanical Properties of Orthorhombic Titanium Aluminides

Orthorhombic Ti-Al-Nb alloys are candidates for use as advanced propulsion and

airframe components in future Department of Defense and NASA aerospace programs. This study was undertaken to determine the origin of the improvement of the tensile and creep properties which results from additions of Mo.

Metallurgy of the R.M.S. Titanic

A forensic analysis of steel recovered from the wreck of the RMS Titanic generated a high level of interest in the news media. Tim Foecke continued to bring the metallurgical story of the Titanic to numerous audiences, generating widespread appreciation of how materials science can help us understand structural failures.

Corrosion of Aging Aircraft

The National Materials Advisory Board's Committee on Aging of U.S. Air Force Aircraft (NMAB-488-2) identified "the establishment of a link between laboratory tests and behavior in service" as one of their most important immediate R&D needs. In collaboration with the U.S. Air Force's Wright Laboratory, NIST fulfilled this need in the area of atmospheric crevice corrosion by developing a predictive model and a new test method that provided the kinetic data required by this model.

Corrosion of High Nitrogen Stainless Steels

New, high nitrogen, stainless steels developed by Crucible Materials Corporation and NIST, through a CRADA, are very resistant to corrosion and existing corrosion test methods and critical pitting temperature tests cannot evaluate the corrosion resistance of these alloys. To evaluate these alloys and make it possible to select the best compositions and processing conditions, NIST developed a new test method by modifying an existing standard test.

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 Compressed Gas Association) 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.

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 U.S. 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.

The predictive model for atmospheric crevice corrosion of aircraft alloys will contribute to understanding of the expected lifetime of aircraft under different exposure conditions.

The test for corrosion of high nitrogen stainless steel will make it possible to differentiate between the corrosion behavior of extremely corrosion resistant alloys.

External Collaborations:

The work on lead-free plumbing solders was 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 studies of orthorhombic Ti-Al-Nb alloys were 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).

The work on corrosion of aging aircraft was carried out in collaboration with the U.S. Air Force's Wright Laboratory.

The work on corrosion of nitrogenated stainless steels was carried out in collaboration with Crucible Materials Corporation.

Accomplishments:

In the work on stress rupture of lead-free solders, all 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.

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 FY1999.

The uniaxial tensile behavior of heat treated orthorhombic TiAl material without Mo additions has been determined from room temperature to 815 °C.

The metallurgical structure of the rivets of the RMS Titanic was identified as a possible contributing factor to their failure during the ship's collision with the iceberg. The theory advanced in 1994 that the "steel shattered like glass upon impact with the iceberg" has been largely discounted by our studies.

A predictive model for crevice corrosion was developed, and measurement methods for crevice corrosion and for corrosion evaluation of highly corrosion-resistant nitrogenated steels were developed.

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 U.S. 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 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.

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.

Crucible Materials Corp. is incorporating the test method developed for nitrogenated stainless steels into their alloy development program.

Outputs:

Media:

"Titanic: Answers from the Abyss," The Discovery Channel, aired April 25, 1999

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Foecke, T., "Metallurgy of the RMS Titanic," Sigma Xi Colloquium, Naval Research Laboratory, Washington, DC, February 1999.

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Foecke, T., "Metallurgy of the RMS Titanic," Notre Dame Chapter of ASM, Bosch Corporation, South Bend, IN, April 1999.

Foecke, T., "Metallurgy of the RMS Titanic," 3000 tele-linked students in 5 school districts in northern Indiana and southern Michigan, April 1999

Foecke, T., "Metallurgy of the RMS Titanic," Department Colloquium, Department of Materials Science and Engineering, Case Western Reserve University, Cleveland, OH, April 1999.

Ricker, R. E., "Influence of Aqueous Corrosion Reactions on the Propagation of Fatigue Cracks," Conference on Fatigue Damage of Structural Materials II, Cape Cod, MA, October 1998.

Ricker, R. E., "Evaluation of the Influence of Alloying Elements on the Pitting Resistance of Nitrogenated Alloyed Stainless Steels," Symposium on Damage Processes in Advanced Materials, ASM-Intl. and TMS, Chicago, IL, October 1998.

Ricker, R. E., "A Life Prediction Model for Atmospheric Crevice Corrosion in Aging Aircraft," MRS Fall Meeting, Boston, MA, December 1998.

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 characteristics 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 two 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 provides compositional analysis and an energy selecting imaging filter (IF) allows compositional mapping at atomic resolution. Several studies are underway with scientists of the Metallurgy and Ceramics Divisions.

Collaboration with the Chemical Science and Technology Laboratory (CSTL) enables 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. P. Searson (Johns Hopkins University) supplied nanoscale ZnO particles for surface morphology and structure measurements.

Accomplishments:

Atomic resolution imaging and compositional mapping was 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.

The amorphous zones revealed by high-resolution imaging of $BaTiO_3$/MgO photonic materials have 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.

Nanoscale particles of ZnO have been studied to determine the microstructural and particle size distributions. Particles with single atomic step facets and various morphologies were observed.

A new high precision polishing system has been deployed in the specimen preparation facility. This system allows materials to be thinned with an accuracy of +/- 1 μ m under various loads. Specimens may be loaded/unloaded reproducibly for optical inspection.

The precision ion polishing system has been upgraded with new magnets and a broad-beam operating mode. These upgrades allow for larger, electron transparent regions in specimens while preserving ion beam intensity.

The X-ray detection system for microanalysis has been improved on our EM430 300 kV TEM with a newer detector and modern pulse processing and computer control. This system provides 133 eV energy resolution.

Impact:

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

Outputs:

Publications:

Kaiser, D. L., Vaudin, M. D., Rotter, L. D., Bonevich, J. E., Armstrong, J. T., Roytburd, A. L., and Schlom, D. G., "Effect of Film Composition on the Orientation of (Ba,Sr)TiO_3 Grains in (Ba,Sr)yTiO2+y Thin Films," J. Mat. Res., in press.

Josell, D., Bonevich, J. E., Shao, I., and Cammarata, R. C., "Measuring the Interface Stress: Ag/Ni Interfaces," J. Mater. Res. **14**, 4358, 1999.

Bonevich, J. E., van Heerden, D., and Josell, D., "FCC Titanium: An Artifact in Ti/Al Multilayers," J. Mater. Res. **14**, 1979, 1999.

de Filipe, T. S., Murarka, S. P., Ajayan, P. M., and Bonevich, J. E., "Electrical Stability and Microstructural Evolution in Thin Films of High Conductivity Copper Alloys," IEEE Proc., 1999.

Fanesi, S., Pozzi, G., Bonevich, J. E., Kamimura, O., Kasai, H., Harada, K., Matsuda, T., and Tonomura, A., "Influence of the Core Misalignment and Distortion on the Fresnel and Holographic Images of Superconducting Fluxons," Phys. Rev. B **59**, 1426, 1999.

Bonevich, J. E. and Josell, D., "Comment on 'Dimensionally Induced Structural Transformations in Titanium-Aluminum Multilayers,'" Phys. Rev. Lett. **82**, 2002, 1999.

Josell, D., Carter, W. C., and Bonevich, J. E., "Stability of Multilayer Structures: Capillary Effects," NanoStructured Materials **12**, 387, 1999.

Wong, E. M., Bonevich, J. E., and Searson, P. C., "The Growth Kinetics of Quantum Size ZnO Particles," Proc. Mat. Res. Soc., Pittsburgh, PA, 1999, in press.

Bonevich, J. E., Pozzi, G., and Tonomura, A., "Electron Holography of Electromagnetic Fields," in: Electron Holography, eds. L. Allard et al., Plenum, New York, NY, pages 153-181, 1999.

Presentations:

Bonevich, J. E., "Materials Structure and Chemistry on the Atomic Scale," presentation to the Geophysical Laboratory of the Carnegie Institute of Washington, NIST, Gaithersburg, MD, June 1999.

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

Investigators: R. J. Schaefer, 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 1300 K to 4000 K.

Technical Description:

This project focuses on application of pulse-heating techniques to measure thermo-physical properties of materials at high temperatures (1300 K to 4000 K). 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 materials such as 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 with support from NASA in collaboration with Containerless Research, Inc. Collaboration is continuing in applying this technique to microsecond applications. Measurements were made in collaboration with Stratonics, Inc., to identify emissivity measurements which will increase the accuracy of two-color pyrometry.

Accomplishments:

Experiments were performed to study the effect of heating rate and grain size on the melting behavior of alloys. These experiments have helped us understand how to better interpret the temperature vs. time profile during melting to extract useful information. These plots were compared to those generated from a diffusion-model of the melting process and shown to agree within reasonable limits. Thermophysical properties of a simple binary alloy, 53Nb-47Ti, were determined with the millisecond system. The properties thus determined were compared to the values calculated from a thermodynamic description of the Nb-Ti system, accounting for the non-equilibrium initial condition, with good agreement (about 2 %). The understanding gained from these experiments will be valuable in studying other alloys in the future.

Recently, experiments were done to determine the feasibility of using non-conventional specimens in the millisecond system. In one case, a coating of a material with a lower melting point is deposited on the substrate of a higher melting metal, e.g., Ti on Mo. The initial success achieved with these experiments will allow the co-deposition of two metals to form an alloy of the desired composition, especially for alloys that are difficult to fabricate. In another variation of the same idea, a metal of a higher melting point is deposited over a lower melting metal, e.g., Mo on Cr. This configuration would be useful for materials that evolve gases when heated.

A three-step calibration and validation procedure for the Stratonics two-color pyrometer was proposed. As a first step, the two-color pyrometer was calibrated against a tungsten-filament lamp across a broad range of temperature.

As the second step, preliminary experiments are being done on the alloy, 90Ti-6Al-4V, to determine the normal spectral emissivity as a function of wavelength at several temperatures up to its melting temperature. These experiments were done by simultaneously using the six-wavelength pyrometer, the two-wavelength pyrometer and laser polarimeter covering a broad spectral range, 600 nm to 1500 nm. Data determined from these experiments form the basis of the temperature corrections for the error due to the assumption of gray-body behavior of the target material. Such experiments will be repeated for the alloys of industrial importance so that ratio-pyrometry can be applied more effectively on these alloys.

The last step would consist of comparison of the ratio-temperature, as determined by the two-color pyrometer with the true temperature as determined from the radiance temperature and

normal spectral emissivity. These experiments will be done on specimens held at a constant temperature and would serve as an independent means of validating the instrument.

Impacts:

Experiments done on alloys with the millisecond system have demonstrated the use of a high-speed transient technique for the determination of reliable thermophysical properties of alloys. The study of melting behavior of alloys has consolidated our understanding of the heating rate dependence of the temperature profile in the melting region. Demonstration of the use of coated specimens has extended the existing capabilities to work with materials which are otherwise difficult to measure. The potential also exists to extend the technique to non-conducting materials, e.g., ceramics. The knowledge gained from the above mentioned experiments will form the basis for developing a successful program on the measurement of several properties of alloys, e.g., specific heat capacity, enthalpy, heat of fusion, solidus temperature, liquidus temperature, electrical resistivity, which are of necessity to the industry.

Wavelength dependence of emissivity data will form the basis of improving the accuracy of ratio-pyrometers which are gaining popularity in industrial operations. This would reduce the uncertainties in measurements made with such instruments, benefiting both the manufacturer and the end user.

Output:

Publications:

McClure, J. L., Boboridis, K., and Cezairliyan, A., "Radiance Temperatures (in the Wavelength Range 521 to 1500 nm) of Rhenium and Iridium at Their Melting Points by a Pulse-Heating Technique," *Int. J. Thermophys.* **20**: 1137, 1999.

McClure, J. L., Cezairliyan, A., and Kaschnitz, E., "Radiance Temperatures (in the Wavelength Range 527 to 1500 nm) of Palladium and Platinum at Their Melting Points by a Pulse-Heating Technique," *Int. J. Thermophys.* **20**: 1149, 1999.

Boboridis, K., Pottlacher, G., and Jäger, H., "Determination of the Critical Point of Gold," *Int. J. Thermophys.* **20**: 1289, 1999.

Basak, D., Boettinger, W. J., Josell, D., Coriell, S. R., McClure, J. L., Krishnan, S., and Cezairliyan, A., "Effect of Heating Rate and Grain Size on the Melting Behavior of the Alloy Nb-47 mass % Ti in Pulse-Heating Experiments," *Acta Mater*., **47**, 3147, 1999.

Matsumoto, T., Cezairliyan, A., and Basak, D., "Hemispherical Total Emissivity of Niobium, Molybdenum, and Tungsten at High Temperatures Using a Combined Transient and Brief Steady-State Technique," *Int. J. Thermophys.* **20**, 943, 1999.

Krishnan, S. and Basak, D., "Application of High-Speed Laser Polarimetry to Non-Contact

Detection of Phase Transformations in Metals and Alloys at High Temperatures," *Int. J. Thermophys.,* in press.

Kaschnitz, E., McClure, J. L., and Cezairliyan, A., "Radiance Temperatures (in the Wavelength Range 530 to 1500 nm) of Nickel at its Melting Point by a Pulse-Heating Technique," *Int. J. Thermophys.* **19**: 1637, 1998.

Posters:

Seifter, A., Boboridis, K., Krishnan, S., and Pottlacher, G., "Absolute Temperature Measurements using Laser Polarimetry and Spectral Radiometry on Microsecond Pulse-Heated Materials", 7th International Symposium on Temperature and Thermal Measurements in Industry and Science, Delft, The Netherlands, June 1999.

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 thin films and materials containing high densities of interfaces for the power generation and electronics industries is the major goal of the thermal transport studies. Evaluating the effect of high densities of interfaces on the stability, creep and yield behaviors of multilayer materials is the goal of the studies of mechanical properties.

Technical Description:

The thermal and mechanical properties of thin films can differ significantly from those of the bulk materials from which they are fabricated. The source of these differences is both modified properties within the volume of the film and effects arising specifically from the interface. Taken together, these effects can lead to thermal conductivities that are substantially decreased below values predicted by analyses that use bulk properties. We have been working to evaluate the influence of both these effects, including quantification of the interface contribution. This has been accomplished by measuring the thermal diffusivities of multilayer materials containing various densities of interfaces (different layer thickness). The experimental apparatus is based on the photothermal deflection technique and, with appropriate modeling, the data yields thermal transport properties for heat flow both normal to and parallel to the layers of the film.

In a related effort, we have been studying the mechanical properties of multilayer materials. This work is closely linked to the thermal transport studies as the high temperature and large thermal gradient environments in which layered materials are frequently utilized directly affect the structural integrity of layered structures. Our work in this area includes studies of the thermodynamic properties of interfaces, particularly the interface stress and interface free energy. These quantities influence strains within the materials adjacent to the interface and the extent to which polycrystalline thin films degrade by capillary instabilities. Both of these effects become larger as layers become thinner, making them more relevant as electronic devices continue to shrink.

Planned Outcome:

The thermal transport studies will establish a value for the interface thermal resistance as well as quantify the changes of the properties within the layers themselves. This information assists our industrial partners in accurately predicting heat flow and temperature fields within structures containing layered materials. The mechanical properties will help to establish stability issues pertinent to finely layered materials.

External Collaborations:

D. Josell collaborates with Professor T. Weihs of Johns Hopkins University (JHU) in Baltimore, Maryland studying interfacial free energies and the stability of multilayer materials. He also collaborates with Professor R. Cammarata of JHU measuring interface stresses in materials containing many thin layers. A jointly held grant from the U.S.-Israel Binational Science foundation, which funded work with Professor D. Shechtman of the Technion, Israel, ended early in the fiscal year. A collaboration with a consortium consisting of the Electric Power Research Institute (EPRI), Battelle, Howmet and Solar Turbine studying the thermal transport properties of multilayer thermal barrier coatings ended in the first half of the fiscal year.

Accomplishments:

The thermal transport properties of thin films and multilayer thin films were measured. As a result of these measurements the interface thermal resistance was measured for alumina/zirconia and titanium/aluminum interfaces.

X-ray diffraction experiments on freestanding silver/nickel multilayers of varying layer thickness were used to measure the interface stress. This work was the first to demonstrate that freestanding films could be used in such studies. By removing the substrates on which interface stress measurements had previously been conducted, the need for wafer curvature measurements to determine substrate induced strains was eliminated, a significant simplification.

Impact:

As a result of the measurements provided by NIST on industry-provided multilayer thermal barrier coatings, the EPRI led consortium concluded that the claims of a high interfacial thermal resistance were erroneous, and therefore they stopped studying multilayer alumina/zirconia thermal barrier coatings.

Outputs:

Publications:

Bonevich, J. E., van Heerden, D., and Josell, D., "FCC Titanium: An Artifact in Titanium/Aluminum Multilayers," Journal of Materials Research **14**, 1977, 1999.

Bonevich, J. E. and Josell, D., "Comment on 'Dimensionally Induced Structural transitions in Titanium-Aluminum Multilayers,'" Physical Review Letters **82**, 2002, 1999.

Josell, D., Heerden, D. van, Shechtman, D. and, Read, D., "Mechanical Properties of Multilayer Materials," NanoStructured Materials, **12**, 405, 1999.

Josell, D., Carter, W. C., and Bonevich, J. E., "Stability of Multilayer Structures: Capillary Effects," NanoStructured Materials, **12**, 387, 1999.

Josell, D., and Spaepen, F., "Surfaces, Interfaces and Changing Shapes in Multilayer Materials," MRS Bulletin **24**, #2, 39, 1999.

Josell, D., Heerden, D. van, Read, D., and Shechtman, D., "Tensile Testing Low density Multilayers: Aluminum/Titanium," Journal of Materials Research **13**, 2902, 1998.

Josell, D., Bonevich, J. E., Shao, I., and Cammarata, R. C., "Measuring the Interface Stress: Silver/nickel Interfaces," Journal of Materials Research, in press.

Foecke, T., "New Geometry for Controlled In Situ TEM Fracture Experiments in Brittle Materials," Scripta Materialia, in press.

Anderson, P. M., Foecke, T., and Hazzledine, P., "Dislocation-Based Deformation Mechanisms in Metallic Nanolaminates," MRS Bulletin **24**, #2, 27, 1999.

Gavens, A. J., van Heerden, D., Foecke, and T., Weihs, T. P., "Evaluation of Vapor Deposited Nb/Nb_5Si_3 Microlaminates," Materials Science and Engineering A **261**, 212, 1999.

Gavens, A. J., van Heerden, D., Foecke, T., and Weihs, T. P., "Fabrication and Evaluation of Nb/Nb_5Si_3 Microlaminate Foils," Metallurgical and Materials Transactions **A,** in press.

Weihs, T. P., van Heerden, D., Gavens, A. J., Shang, C. H., and Foecke, T., "Metal/Silicide Microlaminates: Stress, Strength and Stability," Proceedings of the Bi-National Conference on High-Temperature Materials, Kona, Hawaii, in press.

Presentations:

Foecke, T., "Dislocation-Based Deformation Mechanisms in Layered Metallic Nanomaterials," invited talk at Ohio State University, April 1999.

Foecke, T., "Deformation Mechanisms in Nanolayered Metallic Materials," Invited Talk at 7th International Conference on Plasticity and its Applications, Cancun, Mexico, January 1999.

Foecke, T., "Deformation Mechanisms in Nanolayered Metallic Materials," Invited Talk at University of Connecticut, December 1998.

Foecke, T., "Strength of and Slip Propagation in Metallic Multilayered Thin Films," Talk at TMS Fall Meeting, October 1998.

Josell, D., "Thermal Transport Through Multilayer Materials: Quantifying the Interfacial Thermal Resistance," invited talk at Technion, Haifa, Israel, November 1998.

Josell, D., "Microstructure and Mechanical Properties of Aluminum/Titanium Multilayer Thin Films," invited talk at Tel Aviv University, Tel Aviv, Israel, November 1998.

Josell, D., "Thermal Transport Through Multilayer Coatings," Invited Talk at Materials Research Society Fall Meeting, November 1998.

Josell, D., "The Thermal Resistance of Aluminum/Titanium Multilayer Thin Films and Their Interfaces," Talk at Materials Research Society Spring Meeting, April 1999.

Josell, D., "Determination of Interface Stress from Transmission X-ray Diffraction of Freestanding Silver/Nickel Multilayers," talk at Materials Research Society Spring Meeting, April 1999.

Josell, D., "Multilayer Materials: Balancing Mechanical Enhancement and High Temperature Stability," Invited Talk at 44th Sagamore Conference on Nanostructured Materials, August 1999.

METALS PROCESSING

Major successes in applying measurements and modeling to processing applications have been achieved through NIST's interactions with the powder metallurgy, electroplating, electronics and aerospace 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. Through studies of the mechanistic, chemical and process variables controlling the structure/properties of electrodeposited coatings and thin films, rational approaches are being developed for the optimization of electrochemical processing conditions to obtain the desired deposit characteristics.

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

> Measurements are made under dynamic conditions to monitor, in real time, materials characteristics during metals processing operations. Special fast-response sensors, simulations and imaging techniques have been developed for application to powder atomization, thermal spray, and welding processes. These sensors are used in conjunction with dynamic models of the process both for design of manufacturing procedures and for applications of real time feedback and control.
>
> The physical characteristics of electrodeposits are related to electrolyte chemistry and deposition conditions. This work includes measurements of the deposition characteristics of corrosion-preventing aluminum alloys deposited from room temperature molten salts, measurements of the mechanical properties of chromium alloys deposited from environmentally friendly trivalent chromium electrolytes, and measurement of the effects of organic additives on recrystallization of electrodeposited copper used in on-chip interconnects.
>
> Understanding of metals processing relies on models which relate the behavior of the metal to physical property data. Models are developed describing solidification and solid-state transformations in terms of basic thermodynamic and kinetic properties of industrially important alloy systems.

Project Title: SOLIDIFICATION MODELING

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

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. Phase field models are being extended to describe the motion of grain boundaries.

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.

The onset of convective instabilities during the growth of in-situ composites in the monotectic aluminum-indium system was calculated in collaboration with Prof. J. B. Andrews of the University of Alabama at Birmingham.

NIST continues to collaborate 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 continued.

Phase field calculations of grain boundary motion are being conducted with Prof. R. Kobayashi, Sapporo University.

Modeling activities on multicomponent dendritic solidification were conducted in collaboration with M. Rappaz of EPFL in Lausanne, Switzerland.

Accomplishments:

Accomplishments are divided into three areas: 1) fluid flow and dendritic growth, 2) diffusion couples and 3) grain boundary motion.

1) Oscillatory flows can be used to prevent instabilities, such as the bunching of elementary steps, during the growth of crystals from solution. Solution growth is used to prepare non-linear optical materials (potassium dihydrogen phosphate) for laser fusion applications. Numerical calculations using Floquet theory have determined the optimal values of modulation frequency and amplitude to prevent step bunching.

Approximate solutions have been found for dendrites with four-fold axial symmetry (cubic materials) which provide a relationship between the bulk undercooling and a dimensionless product (the Peclet number) of the growth velocity and tip radius of the dendrite. The calculated results are in general agreement with the observed measurements of the undercooling/Peclet number relationship by Glicksman and colleagues for growth of succinonitrile dendrites. The dendrite shape has also been calculated by comparing it with the portion of the equilibrium shape of a cubic crystal.

2) Under certain conditions, nonunique (multiple) similarity solutions (propagation proportional to the square root of time) are possible for 1-D free boundary problems that require simultaneous diffusion of heat and solute, as occurs when hot liquid is brought into contact with a cold solid during soldering. Similar difficulties arise during simultaneous diffusion of two solutes, as occurs during isothermal diffusion in ternary alloys. This loss of uniqueness is quite disturbing, as it complicates our ability to predict microstructure evolution.

For the heat/solute case, there are three similarity solutions under certain conditions, some where the solid may melt and others where the liquid may freeze. Calculations have shown that one solution is always unstable and that the inclusion of non-equilibrium effects at the solid-liquid interface select the applicable solution from the remaining two solutions.

For the isothermal ternary case, three solutions were also found for similarity solutions when one end member of the diffusion couple is composed of single-phase material (α) and the other end member is composed of two-phase material ($\alpha + \beta$). The conditions under which the two-phase region grows or dissolves are determined in terms of the nature of the jumps in concentration and phase fraction at the boundary between the two materials. The conditions for the occurrence of virtual and/or unique solutions were established. Such theoretical investigations can be applied to diffusion in thermal barrier layers and/or oxidation.

3) A new phase field model is being 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, the model predicts grain coarsening with simultaneous rotation of

closely oriented grains. Validation of this model, and its connections with microscopic (dislocation based) models of grain boundaries remains an area of intense focus.

Impact:

Several criteria have been established to determine the physically relevant solution to diffusion problems where multiple solutions exist for the same initial conditions. These criteria eliminate a major roadblock in the formulation of correct processing models of solidification and other diffusion problems of practical importance such as soldering and solid state diffusion bonding.

A phase field model of grain growth has been formulated which should stimulate broad scientific interest as did our former research on phase field models of solidification.

In collaboration with five other scientists in the field of alloy solidification, two of us (SRC and WJB) have reviewed recent advances in the understanding and application of solidification microstructures, and have suggested future directions for research in a special millennium issue of Acta Materialia.

Outputs:

Publications:

Boettinger, W. J., Coriell, S. R., Greer, A. L., Karma, A., Kurz, W. Rappaz, M., and Trivedi, R., "Solidification Microstructures: Recent Developments, Future Directions," Acta Materialia, accepted for publication.

Boettinger, W. J. and Warren, J. A., "Simulation of the Cell to Plane Front transition During Directional Solidification at High Velocity," J. Crystal Growth, **200,** 583, 1999.

Boettinger, W. J., Coriell, S. R., McFadden, G. B. and Campbell, C. A., "On the Properties of α /α +β Diffusion Couples," Acta Materialia, in press.

Coriell, S. R., Murray, B. T., Chernov, A. A. and McFadden, G. B., "The Effect of a Shear Flow on the Morphological Stability of a Vicinal Face: Growth from a Supersaturated Solution," Adv. Space Res. **22**, No. 8, 1153-1158, 1998.

Coriell, S. R., McFadden, G. B., and Sekerka, R. F., "Selection Mechanisms for Multiple Similarity Solutions for Solidification and Melting," J. Crystal Growth **200**, 276-286, 1999.

McFadden, G. B., Coriell, S. R., and Sekerka, R. F., "Analytic Solution for a Non-Axisymmetric Isothermal Dendrite," J. Crystal Growth, accepted for publication.

Rappaz, M. and Boettinger, W. J., "On Dendritic Solidification of Multicomponent Alloys with Unequal Liquid Diffusion Coefficients," Acta Mat. **47**, 3205, 1999.

Warren, J. A., Carter, W. C., and Kobayashi, R., "A Phase Field Model of the Impingement of Solidifying Particles," Physica A **261,** 159-166, 1998.

Warren, J. A., Kobayashi, R., and Carter, W.C., "Modeling Grain Boundaries using a Phase Field Technique," in the Hokkaido University Technical Report Series in Mathematics, Series #58, March 1999.

Presentations:

Boettinger, W. J., "Phase Field Modeling of Solidification," Hume-Rothery Symposium, TMS Annual Mtg., San Diego, CA, March 1999.

Boettinger, W. J., "Phase Diagrams," EPFL/Calcom Short Course on Solidification, Les Diablerets, April 1999.

Boettinger, W. J., "Solidification Path in Multicomponent Alloys," EPFL/Calcom Short Course on Solidification, Les Diablerets, April 1999.

Coriell, S. R., "Multiple Similarity Solutions for Solidification and Melting," 1999 TMS Annual Meeting, San Diego, March 1999.

Coriell, S. R., "Selection Mechanisms for Multiple Similarity Solutions for Solidification and Melting," Eleventh American Conference on Crystal Growth & Epitaxy, Tucson, AZ, August 1999.

Warren, J. A., "Phase Field Modeling of Grain Boundary Formation," TMS Symposium in Honor of John Cahn's 70th Birthday, Rosemont IL, October 1998.

Warren, J. A., "Phase Field Modeling of Grain Boundaries," Department Colloquium, McGill University, Montreal, November 1998.

Warren, J. A., "Phase Field Modeling of Grain Boundaries," Conference on Anisotropic Effects in Crystal Growth and its Mathematical Analysis, Sapporo, Japan, January 1999.

Warren, J. A., "Phase Field Modeling of Grain Boundaries," APS March Meeting, March1999.

Warren, J. A., "Phase Field Modeling of Grain Boundaries," Presentation at Argonne National Lab, April 1999.

Warren, J. A., "Incorporating Crystallography into Phase Field Models," Gordon Research Conference on Thin Films and Crystal Growth, Plymouth, NH, June1999.

Warren, J. A., "Incorporating Crystallography into Phase Field Models," American Conference on Crystal Growth & Epitaxy-11, Tucson AZ, August 1999.

Project Title: SENSORS AND DIAGNOSTICS FOR THERMAL SPRAY PROCESSES

Investigators: S. D. Ridder, F. S. Biancaniello, P. A. Boyer, R. D. Jiggetts, S. P. Mates, R. L. Park, and R. J. Schaefer

Objectives:

The primary focus of this project is to improve the reliability and reproducibility of thermal spray coatings by developing tools for the measurement and control of process conditions for thermal 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 feasibility is examined of obtaining more reproducible coating quality based on feed-back from sensors directly monitoring particle temperatures and velocities, as well as substrate and deposit characteristics.

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. Process conditions are monitored by an Infra-Red (IR) thermal imaging sensor, capable of measuring either the temperature of rough, variable emissivity surfaces or particle temperature and velocity distributions within a thermal spray plume. New technology is under development to apply a ripple technique (modulation reflectometry) to the measurement of surface emissivity. This work is targeted at providing quantitative data regarding the quality of thermal spray coatings. It should also provide a similar evaluation of substrate surface quality prior to coating.

Planned Outcome:

Robust process sensors will be developed and provided to industry for monitoring and control of atomizers and thermal 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 has included 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, a 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 DC plasma thermal spray equipment. Discussions are ongoing with Ford Motor Company on the use of thermal spray technology for automotive body panel seam-filling. 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 Dr. Levi of the University of California at Santa Barbara on the reliability of TBC's and with Dr. Shechtman at the Technion University in Haifa and Dr. Lang at the University of Capetown, South Africa on the powder production, thermal spraying, characterization and wear properties of stable quasi-crystals coatings.

Accomplishments:

The NIST thermal spray system, provided 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, is now operated under computer control to establish coating "repeatability" and to provide better spatial resolution of the data generated by the process sensors.

A broad bandwidth spectrometer (for electromagnetic wavelengths from 200 nm to 1100 nm) is now in use to measure emission spectra in the thermal spray plasma plume generated by DC plasma torches. This sensor provides emission spectrum data for calibration of the thermal imaging sensor and for monitoring plume chemistry.

The Particle Imaging Pyrometer (PIP) for measuring temperature, velocity and size of thermal spray particles in flight, developed in a collaborative effort between the Cooke Corporation and Stratonics, Inc., has been tested extensively. Simultaneous measurements by the PIP and the spectrometer system have provided insights into the influence of light from different sources, such as the incandescent particles and the plasma, on radiometric measurements.

A Phase I SBIR with Stratonics, Inc. on developing a new modulation reflectometry technique to evaluate substrate and coating surface qualities has been initiated. A computer controlled, three-axis gonio-reflectometer with a modulated diode laser light source has been constructed. Coupling the motion control system to the light intensity measurement software is now underway. A series of properly and improperly grit-blasted spray substrates have been sent to NIST by Praxair Surface Technologies to serve as the initial test samples to be measured by the gonio-reflectometer and other techniques for evaluating surface roughness are being applied to the same samples.

A new process model for DC plasma thermal spray has been tested using the PIP. Results indicate a good correlation between process parameter settings and particle velocities and temperatures. This work will be expanded to include measurements of anode wear using a recently purchased high bandwidth, two channel, oscilloscopic data acquisition system designed to measure time domain voltage signals from direct measurements of the anode voltage and from acoustic sensors. These results will be used to provide control strategies for the motion and gun parameter controllers.

A portable schlieren system suitable for analysis of the gas flow in thermal spray systems was designed and constructed. When applied to the twin-wire arc spray system, this system revealed low-frequency oscillations in the flow which may lead to inhomogeneities in the deposited material.

Impact:

NIST SBIR funded research has resulted in dramatic improvements to a new imaging pyrometer with wide applicability in the materials processing area. This technology, available from Stratonics, Inc. of Laguna Hills, CA, can be configured as either a "Surface Imaging Pyrometer" or as a "Particle Imaging Pyrometer." These sensors use special IR optics to produce a high-resolution two-color image of the material under test. In the surface configuration, this system 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.

Outputs:

Publications:

"Thermal Spray Coatings Workshop: Sensors, Modeling and Control Strategies," Summary of a Workshop held at NIST, Physics Building, Room B165, Gaithersburg, MD, November 19, 1998

Presentations:

Craig, J. E., Parker, R. A., Lee, D. Y., Biancaniello, F. S., and Ridder, S. D., "A Two-wavelength Imaging Pyrometer for Measuring Particle Temperature, Velocity and Size in Thermal Spray Processes," International Symposium on Advanced Sensors for Metals Processing, Quebec, Canada, August 1999.

Project Title: PROCESSING OF ADVANCED MATERIALS

Investigators: F. S. Biancaniello, R. D. Jiggetts, U. R. Kattner, 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, data, 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 (gas atomization, planar flow casting, e-beam welding, vacuum melting and casting, thermal spray coating, etc.) 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 on-going 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 the automotive, aerospace, powder producer, and 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 metallic systems. Having an in-house NIST fabrication facility allows us to explore processing-structure and property relationships in a meaningful way.

External Collaborations:

Collaborations have been conducted with Crucible Materials Corporation through a CRADA on (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 HIP consolidation. A CRADA project with Carpenter Technology Corporation was completed on NIST nozzle design optimization techniques via gas flow diagnostics and modeling. 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 FY2000. Collaborative studies have been initiated with Dr. Shechtman at the Technion University in Haifa and Dr. Lang at the University of Capetown, South Africa on the powder production, thermal spraying, characterization and wear properties of stable quasi-crystals coatings. A dialogue was initiated with processing researchers from the Knolls Atomic Power Laboratory in Schenectady, New York. This collaboration will involve the exchange of ideas and joint research projects in various areas of spray processing of metals including gas atomization and thermal spray coatings.

Accomplishments:

The gas jet diagnostic flow bench system (gas mass flow rates up to 1 kg/s) has been equipped with a new computer controlled pitot-static tube manipulator and the gas flow imaging system has been modified to produce color still or video schlieren pictures.

Inconel 1481 has been produced by rapid solidification of gas atomized powders and HIP consolidation for a new standard reference material. Characterization and validation are currently underway.

Aluminum alloy sheet was prepared under carefully controlled conditions for automotive body panel property measurements.

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.

Characterization of industrial atomization equipment will lead to higher yields of desirable powder sizes. This will lead to a generalized improvement in process efficiency (less atomizing gas consumed, less scrap, less remelting, etc.).

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

Outputs:

Publications:

Lang, C. I., Biancaniello, Ridder, S. D., and Shechtman, D. "Characterization of an $Al_{70.9}Cu_{9}Fe_{10}B_{0.1}$ Stable Quasiperiodic Material as a Wear Resistant Thermal Spray Coating," Proceedings of TMS Fall Meeting 1999, Symposium on Powder Materials: Current Research and Industrial Practices, TMS, Warrendale, PA, 1999.

SRMσ Under Development:

SRM #861Aerospace Nickel Alloy

Project Title: LIGHTWEIGHT MATERIALS FOR AUTOMOTIVE APPLICATIONS

Investigators: R. J. Fields, R. B. Clough, T. J. Foecke, L. E. Levine, J. L. Fink, R. E. Ricker, M. R. Stoudt, G. G. Long (852), and R. Thomson (850)

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 the United States Council for Automotive Research (USCAR) and Partnership for a New Generation of Vehicles (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 conventional 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. These equations will form the basis for 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 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 the United States Automotive Materials Partnership (USAMP) meets quarterly and the efforts are coordinated at these meetings. The industrial consortium consists of the automotive Big Three, Valimet, Stackpole, Mascotech, Hoeganaes, Norton, and Kennametal. In addition, staff from Ames Laboratory, Oak Ridge National Laboratory, 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 commercialization of the modeling.

Formability research has largely been carried out in conjunction with the ATP project participants: Chrysler, Ford, General Motors, Budd, Alcoa, U.S. Steel, Livermore Software Technology Corporation, and the Autobody Consortium, consisting of 60 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. We have finalized the details of a large multi-institution collaboration that is working on developing a physically based model for the plastic deformation of metals. Our partners include: The Aluminum Company of America (ALCOA), MARC Analysis Research Corporation, Pacific Northwest National Laboratory (PNNL), and Washington State University (WSU). Each of these institutions has committed internal funding to this project. This collaboration heavily leverages NIST's work in this area by providing experimental, theoretical, and computational resources that NIST lacks.

Accomplishments:

Extensive measurements of green strength and sintered strength have been made to compare the effects of reinforcement concentration, different size ratios, and forms of SiC. The effect of size is most distinct and a predictive model was developed. The effect of concentration is more complex and critical experiments are underway to distinguish between various possible theoretical approaches. A data base of elevated temperature compressibilities has been developed for most of the powders of interest. This will be used to predict the consolidation behavior of reinforced powders under conditions most applicable to those used by industry. All modeling developments by Cambridge University have been completed under the cooperative research agreement that ended on July 12, 1999. These models have been transferred to MatSys, Inc. A guest scientist from MatSys has been appointed who will use the computing facilities at NIST and work with NIST staff to incorporate the NIST validated models and database into an existing commercial software package for powder consolidation. The Matsys effort is being supported through an agreement with USAMP. It will result in a demonstration predicting the fabrication of both the gerotor and the connecting rod of interest to the USAMP program.

We have used our previously completed (FY1998) theoretical work on small-angle-scattering (SAS) from dislocation structures to analyze ultra-small-angle X-ray scattering (USAXS) data we obtained from single-crystal Al samples deformed *in situ* at NIST's materials science beam-line (X23A3) at the National Synchrotron Light Source (Brookhaven National Laboratory). All of the data are consistent with our theoretical predictions, and the theory allowed several physical parameters to be quantified. The experiments have probed positional correlations between dislocations, measured the changing interface width of the dislocation walls, detected the presence of dislocation dipoles, examined the inhomogeneity of the microstructure, and measured changes in the dislocation structures during room-temperature creep. Papers describing these results have been submitted to Phys. Rev. B and J. Appl. Cryst.

In preparation for experiments at the new USAXS facility on UNICAT sector 33 at the Advanced Photon Source (Synchrotron Radiation Analysis Program, Ceramics Division Annual Report, 1999), we are building a new *in situ* tensile stage. The mechanical assembly is nearly completed and the electrical work will commence shortly. The new tensile stage will allow use of a wider range of sample sizes and shapes, and will provide improved rotational stability. The construction of the new USAXS facility is nearly completed and commissioning is in progress. It is expected that the USAXS facility will become operational in FY2000. Dislocations USAXS experiments at the APS will begin as soon as this occurs.

The sample control programs for the USAXS experiments were adapted for use in synchrotron X-ray diffraction imaging experiments. These codes enable us to orient the samples for stereo X-ray imaging of the dislocation structures within Al single-crystal samples during deformation. Additional work is required to determine which sample orientations will provide the best data. Sample preparation continues to be a bottleneck. A technician was trained how to make shaped single-crystal samples using previously worked-out techniques. Work on an improved method of producing these samples (higher through-put) using a graphite mold heated in vacuum is in progress. At present, each sample represents approximately one person-week of effort.

On a theoretical front, we have continued work on our strain percolation model which describes the transport of mobile dislocations through dislocation wall structures. Computer simulations of this transport process are currently being conducted in collaboration with researchers at WSU and PNNL. The strain percolation model uses information from the experiments and dislocation simulations described above and makes connection with the mechanical properties of the metal. During FY1999, it was determined that the universality class of the model is the same as standard percolation for the first of two possible cases. Work on case 2 is in progress.

Planning is underway for "Dislocations 2000: An International Conference on the Fundamentals of Plastic Deformation, to be held at NIST on June 19-22, 2000. Funding for this conference is being provided by the CTCMS, the Metallurgy Division, and PNNL. Up-to-date information on this conference may be found on the conference web page: http://www.metallurgy.nist.gov/D2000/D2000.html.

To obtain a better understanding of the factors influencing surface roughness and the functional form of the relationship between surface roughness and strain, analytical tools that would enable extraction of the maximum possible information from surface profiles were sought. Time series analysis and spectral analysis were thought to be prime candidates because distance and wavelength form a conjugate pair suitable for analysis by Fourier transform similar to time and frequency and would enable the evaluation of periodic components in the roughness profile that might be caused by grain size or sample thickness effects. As a result, initial evaluations were conducted with a fast Fourier transform (FFT) macro written for use in a commercial spreadsheet and graphing software package. Analysis of the surface profiles obtained on the Al alloy 7050 tensile samples indicated that grain size influenced the roughness spectrum. As a result, a series of artificial roughness profiles were created with different periodic conditions to emulate grain boundaries and also were analyzed. These models indicated that grain boundary periodicity can be readily lost in the spectrum as the variance in the grain boundary spacing increases or the variance in the roughness profile increases. To evaluate the influence of tensile strain on the roughness of an Al alloy, tensile samples of a typical Al alloy used for deformation processing, Al alloy 5052, with a thickness close to that expected for use in automotive body panels, were strained to different strain levels in uniaxial tension at two different heat treatment conditions. The resulting surface roughness was then measured in the tensile axis and transverse to the tensile axis. The most common measure of surface roughness used by industry is R_a. This quantity is essentially the standard deviation of the residuals left after fitting the measured surface profile to a straight line. Each measured surface profile was reduced to a single R_a value and then the average of 5 such profiles for each strain increment and heat treatment was determined and plotted against plastic tensile strain. The resulting plot indicated that a straight line could be used to represent the relationship between tensile strain and R_a with the slope of this line varying with heat treatment and orientation of the profile with respect to the tensile axis (also the rolling direction of the sheet).

Impact:

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 is used to improve the mass uniformity of pressed powder parts by a factor of four with a corresponding reduction in part distortion at higher production rates.

The USAXS experiments were the first success 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 as described above to develop an improved model of metal deformation, and coupled with our work on surface roughening and data from standard test methods, this research could save the automobile industry at least 50 to 100 million dollars per year.

Outputs:

Publications:

Campbell, G. T., Raman, R., and Fields, R. J., "Optimum Press and Sinter Processing for Aluminum/SiC Composites, in Proc. of the First Int. Conf. On Powder Metallurgy Aluminum and Light Alloys for Automotive Applications, ed. by W. F. Jandeska and R. A.Chernenkoff, pub. by Metal Powder Industries Federation, 1998.

Munitz, A., Livne, Z., Rawers, J. C., Adams, J. S., and Fields, R. J., "Effect of Nitrogen on the Mechanical Properties and Microstructure of Hot Isostatically Pressed Nanograined Fe," Nanostructured Materials **11**, 159, 1999.

Rawers, J. C., Biancaniello, F., Jiggetts, R. D., Fields, R. J., and Williams, M. E., "Warm-HIP Compaction of Attrition-Milled Iron Alloy Powders, Scripta Materialia **40**, 227, 1999.

Thomson, R., and Levine, L. E., "Theory of Strain Percolation in Metals, PRL **81**, 3884, 1998.

Thomson, R., Levine, L. E., and Long, G. G., "Small-angle Scattering by Dislocations," Acta Cryst. A**55**, 433, 1999.

Presentations:

Levine, L. E., Thomson, R., Long, G. G., and Zbib, H., "How to Develop a Microstructure-Based Model of Plastic Deformation," Materials Research Society Fall Meeting, Invited, Boston, December 1998.

Thomson, R. and Levine, L. E., "Theory of Strain Percolation in Metals," Materials Research Society Fall Meeting, Invited, Boston, MA, December 1998.

Long, G. G., Levine, L. E., and Thomson, R., "Observation of Ultra-Small-Angle X-ray

Scattering by Dislocations," University of Illinois, Champagne-Urbana, IL, Dept. of Mat. Sci. Colloquium, Invited, December 1998.

Levine, L. E., "*In Situ* Synchrotron X-ray Studies of Plastic Deformation," American Physical Society Centennial Meeting, Invited, Atlanta, GA, March 1999.

Levine, L. E. and Thomson, R., "How To Develop a Microstructure-Based Model of Plastic Deformation," Pacific Northwest National Laboratory, Invited, Richmond, WA, April 1999.

Long, G. G., Levine, L. E., and Thomson, R., "*In Situ* Observation of Small-Angle Scattering by Dislocations," SAS-99, Brookhaven National Laboratory, Invited, Upton, NY, May 1999.

Levine, L. E., "Strain Percolation During the Plastic Deformation of Metals," Ninth Conference on Computational Research on Materials, Invited, Morgantown, WV, May 1999.

Levine, L. E., Long, G. G., and Thomson, R., "Ultra-Small-Angle X-Ray Scattering by Single-Crystal Al Deformed *In Situ*," 1998 Annual Meeting of the Society of Engineering Science, Pullman, WA, September 1998.

Thomson, R. and Levine, L. E., "A Statistical Approach to the Problem of Deformation in Metals," 1998 Annual Meeting of the Society of Engineering Science, Pullman, WA, September 1998.

Levine, L. E., Long, G. G., and Thomson, R., "*In Situ* Measurements of Dislocation Structure Evolution Using Ultra-Small-Angle X-Ray Scattering," Conference on the Integration of Material, Process and Product Design, Champion, PA, October 1998

News Releases and Popular Press Reports:

"NIST Advance Aids Metal-Forming Industry," Federal Technology Report, July 30, 1998.

"Advance Could Save Big Bucks in Metal Forming," American Machinist, August 1998.

"Bent Metal Under Scrutiny," Huntsville Times, August 4, 1998.

"Ultra-small Angle X-ray Scattering," AIP Bulletin of Physics News, July 28, 1998.

"NIST Scientists Use *In-Situ* Ultra-Small-Angle X-ray Scattering to Study Defects," JOM, September 1998.

"Advance Could Lead to Savings in Metal-forming Industry," Materials Performance, September 1998.

"Scientists at the National Institute of Standards and Technology are the first to succeed," ASTM Standardization News, October, 1998.

"Big Benefit Seen for Car Makers From Research in Die Making," Design News, October 5, 1998.

"New Technology Shows Metal Shape As It Deforms," Business & Industry, September, 1998.

"Advance Could Lead to Big Savings in Metal-forming Industry," Manufacturers' Mart, New England Edition, October 1998.

Automatic Machining, October 1998.

ASTM Standardization News, October 1998.

"New Technique Helps Manufacturers Cast Better Dies," Business & Industry, October 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 restock SRM Coating Thickness Standards 1358a, 1359b, 1361b, 1362b, 1363b, and 1364b 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 μ m to 2 mm, which has been electrodeposited onto low carbon steel substrates. The uniform coatings are then overplated with a thin protective later 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:

Certification of all the 1273 units produced in FY1998, plus the production and certification of an additional 155 units for FY1999.

Accomplishments:

The production and certification of the Coating Thickness Standards became fully operational this year. From the 1428 units of standards owed to OSRM from work orders dating back to FY1995, 1313 units were delivered by September 30, 1999. The outstanding 115 units are near completion and will be delivered in the first quarter of FY2000.

Impact:

The depleted inventory for this family of SRMs has been replenished and is available for purchase.

Outputs:

To date, 496 out of 553 units of SRM 1358a and 466 out of 524 units of SRM 1362b have been delivered to OSRM in addition to all of the units for SRMs 1359b (109 units), 1361b (75 units), 1363b (114 units), and 1364b (53 units).

SRMs in production:

SRM#1358aCu & Cr Coating on Steel

SRM#1359bCu & Cr Coating on Steel

SRM#1361bCu & Cr Coating on Steel

SRM#1362bCu & Cr Coating on Steel

SRM#1363bCu & Cr Coating on Steel

SRM#1364bCu & Cr Coating on Steel

Project Title: ELECTRODEPOSITION OF ALUMINUM ALLOYS

Investigators: G. R. Stafford, V. Jovic (Guest Researcher), and T. P. Moffat

Objectives:

This project seeks to develop an understanding of aluminum-transition metal alloy electrodeposition from organic halide and alkali halide-based chloroaluminate molten salt electrolytes. Two approaches are taken. The first attempts to correlate the deposition potential of several binary alloys with the free energy of alloy formation using thermodynamic data taken from the phase diagram literature. The second attempts to understand the earliest stages of alloy formation by examining the underpotential deposition (UPD) of aluminum onto single crystal copper electrodes.

Technical Description:

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 and Al-Ti have been electrodeposited at potentials negative of the aluminum reversible potential while aluminum-transition metal alloys such as Al-Ni, Al-Co and Al-Cu 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 viewpoint since the composition of alloys formed by UPD phenomena should depend exclusively on the electrode potential. Our activities over the past year have focused on the energetics associated with the electrodeposition of aluminum-transition metal alloys as well as the UPD of aluminum onto Cu(111), Cu(110), and Cu(100) single crystal surfaces. Our initial observations of aluminum UPD by *in-situ* scanning tunneling microscopy (STM) in the room-temperature molten salt electrolyte are also reported.

Planned Outcome:

The electrodeposition of alloys at underpotentials is driven by the free energy of alloy formation. Consequently, one should be able to predict deposition potentials from thermodynamic data which appear in the literature. We also expect to better understand alloy formation by examining the underpotential deposition of aluminum onto single crystal surfaces.

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:

The free energy - composition curves for several binary aluminum alloys were calculated from thermodynamic descriptions found in the literature. The aluminum activity for each alloy was estimated from the partial molar free energy as a function of composition. Equilibrium potentials as a function of alloy composition were then calculated using the Nernst equation for the aluminum deposition reaction with the estimated aluminum activities. This treatment correctly predicts the onset of alloy deposition for Cu-Al, Co-Al, Fe-Al and Ni-Al. It also correctly predicts that no alloy formation is expected in Zn-Al since addition of aluminum to the hexagonal close packed (hcp) Zn lattice results in a free energy increase.

Cyclic voltammograms recorded on Cu(111), Cu(100) and Cu(110) surfaces clearly indicate that aluminum UPD commences at about 0.3 V vs. an aluminum reference electrode. On the Cu(111) surface, UPD takes place through two sharp and separate peaks, indicating that two distinct surface processes occur prior to the formation of a complete aluminum monolayer. Preliminary STM experiments indicate that an ordered adlayer appears on the copper surface at potentials positive of the first UPD wave but negative of copper dissolution. We have tentatively identified the adsorbed species on Cu(111) to be $AlCl_4$- where three of the four Cl atoms in the tetrahedra occupy approximately every third three-fold lattice site on the Cu(111) surface. The first UPD wave is then associated with the desorption of $AlCl_4$- from the copper surface, likely through the elimination of Cl^- . $AlCl_4$- is not generally considered to be electroactive in these melts since its reduction potential is negative of the decomposition potential of the imidizolium cation.

Impact:

Electrodeposition may offer an inexpensive method for producing homogeneous and fine-grained aluminum-based thin films but a fundamental understanding of the co-deposition process does not currently exist. We present a method by which one can predict deposition potentials of aluminum-transition metal binary alloys. We also present evidence which suggests that the earliest stages of alloy formation may involve the reductive deporption of a species which otherwise is not electrochemically active in this electrolyte.

Outputs:

Publications:

Stafford, G. R. and Haarberg, G. M., "The Electrodeposition of Al-Nb Alloys from Chloroaluminate Electrolytes," Plasmas and Ions 1, 35, 1999.

Stafford, G. R., Jovic V., and Hussey, C. L., "Electrodeposition of Cu-Al Alloys and UPD of Al onto Cu Single Crystals from a Room-Temperature Chloroaluminate Molten Salt", Proc. of the Third Yugoslav Materials Research Society Conference, Herceg Novi, Yugoslavia, September 20-24, 1999.

Presentations:

Stafford, G. R., "The Electrodeposition of Aluminum Alloys From Chloroaluminate Molten Salt Electrolytes," Ben-Gurian University, Beer-Sheva, Israel, October 1998.

Stafford, G. R., "The Electrodeposition of transition Metal-Aluminum Alloys From Room Temperature Chloroaluminate Molten Salts," Gordon Research Conference on Molten Salts and Liquid Metals, New England College, Henniker, NH, July 1999.

Jovic, V., "Aluminum Alloy Deposition from Chloroaluminate Electrolytes," Third Yugoslav Materials Research Conference, Herceg Novi, Yugoslavia, September 1999.

Project Title: GOLD MICROHARDNESS STANDARDS

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

Objectives:

The objective of the proposed 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:

Gold is widely used as an electrochemically applied coating for interconnects in the electronics industry (0.12 million troy ounces per year) and by the general plating industry for decorative applications such as jewelry. The measurement of microhardness is used by these industries as an indication of process control for Au electrolytes with and without grain refining addition agents. The development of the Au microhardness standard resulted from the request from industry for a standard in the range of 60 to 100 Knoop or Vickers microhardness when measured at loads of 0.098 N and 0.245 N.

Planned Outcome:

The expected availability of the new Au microhardness standard is mid-year 2000. The 24 K gold standard reference material (SRM) will have a nominal Knoop hardness of 70 with an uncertainty less than 10 % when measured at a load of 0.098 N or 0.245 N. The uncertainty in the certified hardness value of the Au standard is greater than the <5 % uncertainty of the NIST copper and nickel standards, due to the larger grain size of the pure Au deposit.

Accomplishments:

The Electrochemical Processing Group has produced twenty-five 24 K gold, low load microhardness standards. The surface area is 2.25 cm^2 and the deposit thickness is a minimum of 200 μ m. At its certified load of 0.245 N, more than 1,000 indentations can be made on its surface.

The fabrication production scale-up of the Au electrodeposition process, a means to cut the material uniformly, accurately and without embedding abrasive, a system to uniformly mount the samples and a mounting jig that allows the diamond turning of 10 samples at a time were all successfully completed. The single-point diamond turning of the 24 K Au results in a mirror finish having a surface roughness of 63.5 nm, peak to valley. With this operation, no further processing steps are required. The determination of the uncertainty of the certified hardness values is in progress with the statistical evaluation of the material uniformity.

Impact:

The 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 twenty-five 24 K gold, low load microhardness standard reference materials with an average hardness of 70 Knoop with an expected uncertainty of less than 10%.

SRMs Under Development:

SRM # 1870 Gold Microhardness Standard

Project Title: ELECTRODEPOSITED CHROMIUM AND CHROMIUM ALLOYS FROM TRIVALENT ELECTROLYTES

Investigators: C. E. Johnson, J. L. Mullen, and J. Tesk (854)

Objectives:

The program has two primary focus areas. The first seeks to develop a non-toxic trivalent (Cr^{+3}) electrolyte for the deposition of thick chromium coatings as a replacement for the present commercial process of depositing chromium from a toxic hexavalent (Cr^{+6}) electrolyte. The structure and properties of the chromium coatings from the trivalent electrolytes are compared to coatings from hexavalent electrolytes to identify the conditions which may lead to fully functional coatings.

The second focus area is involved with an investigation into the use of amorphous alloy coatings for biomedical applications. This focus area is divided into three subgroups: 1) wear-resistant coatings, Cr-C, for Surgical tools, 2) potential bearing surfaces, Co-Cr-C, for orthopaedic implants, and 3) tissue engineered coatings, Co-Cr-P or Co-Cr-P-C, for bone attachment to 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 trivalent 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.

With the resurgence of interest from industry, academia, clinical practice and regulatory and standards communities in 1) the development and utilization of alternative bearing surfaces to mitigate wear debris in the present cobalt-based alloy and ultra high molecular weight polyethylene coupe, and 2) a tissue engineered coating alternative to calcium phosphate for bony attachment to implants, this year's work focussed on the electrodeposition of amorphous alloys for biomedical applications. 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. An adaptation of the trivalent chromium electrolyte allows one to electrodeposit metal-carbon alloys (U. S. Patents 5,672,262 and 5,759,243) such as Co-Cr-C and Co-Cr-C-P. These alloy coatings are being evaluated as alternative bearing surfaces for implants and as tissue engineered coating alternatives to calcium phosphate coatings on implants.

Planned Outcome:

There are unique mechanical properties that can be attained with glassy alloys that make them attractive for consideration as orthopaedic implant bearing surfaces. The Co-Cr-C system glassy alloy described appears to offer a good basis for further investigation and compositional modification because of its proximity to the composition of Co-Cr-Mo alloys currently used in orthopaedics.

Amorphous Co-Cr-P and/or Co-Cr-P-C alloy coatings have the potential for use as an implant coating to induce bony apposition instead of the numerous approaches that have been tried for applying calcium-phosphate coatings to implant surfaces for the purpose of more rapidly and firmly anchoring them to bone.

Accomplishments:

The potential applicability of metallic glasses for improving the wear resistance of orthopaedic joint bearing couples is being investigated with the electrodeposition of amorphous Cr-C and Co-Cr-C alloy coatings and Co-C/Cr-C multilayer coatings on cast Co-Cr-Mo implant material substrates. Wear-resistance and adhesion evaluation for both the as-deposited and heat treated coatings are in progress.

A tissue engineered coating alternative to calcium phosphate depends on a stable phosphorus-enriched surface layer for bone attachment. An earlier attempt using amorphous Co-P was found unsuitable due to the lack of passivity which resulted in the deterioration of the surface phosphorus oxide film. The incorporation of chromium into the phosphorus-containing coatings was pursued to enhance passivation. Two electrolytes were developed that incorporated chromium in the amorphous Co coatings. Trivalent chromium was added to the amorphous Co-P coating electrolyte with limited passivation enhancement due to the low chromium content (1 to 5 mass percent) in the coating. However, the second electrolyte, a modification of the trivalent chromium process with cobalt and phosphorus additions, resulted in significant enhancement in passivity due to the greater chromium content (15 to 20 mass percent in the coating). Both alloy and multilayer coatings of Co-Cr-C-P were investigated for enhanced passivity. These same coatings are presently being evaluated for chromium reaction with the phosphorus enriched surface layer to determine if calcium phosphate compound can be formed.

Outputs:

Presentations:

Tesk, J. A., Johnson, C. E., Hsu, S., Skrtic, D., and Tung, M., "Amorphous Alloys Containing Cobalt for Orthopaedic Applications," ASTM Symposium on Cobalt-Base Alloys for Biomedical Applications, Norfolk, VA, November 1998.

Publications:

Tesk, J. A., Johnson, C. E., Hsu, S., Skrtic, D., and Tung, M., "Amorphous Alloys Containing Cobalt for Orthopaedic Applications," Cobalt Base Alloys for Biomedical Applications, ASTM STP 1365, J. A. Disegi, R. L. Kennedy, R. Pilliar, Eds., American Society for Testing and Materials, West Conshoken, PA, 1999.

Project Title: ELECTROCHEMICAL PROCESSING OF NANOSCALE MATERIALS

Investigator: T. P. Moffat

Objectives:

This work develops an understanding of physical processes and parameters required for the synthesis of novel materials via electrochemical processing.

Technical Description:

A variety of nanostructured materials may be synthesized by electrochemical deposition. Currently, our effort is focused on producing low dimensional structures, such as strained-layer superlattices, with an eye towards possible application in magnetic and mechanical devices. Producing these materials requires an understanding of the deposition of copper and iron group metals on a variety of different substrates ranging from metal and semiconductor single crystals, to highly oriented thin films. Understanding the linkage between processing parameters and the dynamics of nucleation, growth, and morphological stability is central to providing well-defined materials. In order to develop a deeper understanding of some of these issues in-situ characterization of the structure and dynamics of solid/electrolyte interfaces is being pursued using scanning probe microscopy (SPM). Specifically, the role of inorganic and organic adsorbates on the evolution of thin film microstructure and morphology during homo- and heteroepitaxial deposition is being closely examined.

Planned Outcome:

This work will lead to a detailed understanding of the engineering requirements for producing well-defined strained-layer superlattices for magnetic and mechanical property measurements.

The commercial success of many electroplating technologies stems largely from the remarkable influence of electrolyte additives on the physical properties of the deposited films. Our SPM studies promise to provide considerable insight into the way these adsorbates influence microstructural evolution.

Controlled alloy formation via underpotential deposition is a topic of considerable interest ranging from semiconductors to metallic alloys as well as novel two-dimensional alloys all of which have a wide range of potential applications.

External Collaborations:

We have been working with Prof. L. Slamanca-Riba to explore the magnetic properties of electrodeposited strained-layer superlattice. During the past year Dr. Matsuhiro Shima received his Ph.D. from the University of Maryland for work involving the synthesis and characterization of Cu/Co multilayers.

We have begun a collaboration with Rosa A. Lukaszew of the University of Michigan, Department of Physics examining the use of carefully grown molecular beam epitaxy Cu seed-layer on Si(100) for studying defect evolution in electrodeposited multilayer films.

We are just beginning collaboration with Prof. L. Bennett and Dr. R. Fry to examine the evolution of the magnetic properties of electrodeposited ultrathin magnetic films.

Accomplishments:

Highly oriented copper seed layers on Si(100) and Si(111) have been used as substrates for electrochemically growing oriented Cu/Co strained-layer superlattices which have potential application as magnetic sensors. In collaboration with the Magnetic Materials Group, and the University of Maryland, a series of $[Cu/Co]_N$ Si(100) films were shown to exhibit a dependence of the GMR on in-plane orientation due to magnetocrystalline anisotropy of the epitaxial structure. In the films examined to date, oscillatory antiferromagnetic/ferromagnetic coupling as a function the thickness of the copper spacer layer has not been observed. XTEM studies reveal that this is due to significant grain-boundary grooving during growth which gives rise to strong magnetostatic coupling between the neighboring layers.

The evolution of the magnetic behavior of thin cobalt films deposition onto a Cu(100) surface have been examined in collaboration with the Magnetic Materials Group, and the University of Maryland. The films are observed to undergo a series of transitions as a function of film thickness; from superparamagnetic to isotropic to fourfold anisotropic ferromagnetic behavior. The first transition occurs between 1 ML to 2 ML (monolayer equivalents) of Co while the onset of four-fold anisotropy appears at 3 ML. Comparison with chronoamperometric data suggests that the last transition corresponds to coalescence of the Co islands.

A continuing effort is underway to study the direct deposition of metals onto a variety of semiconductor substrates. Studies to date have focused on copper and cobalt deposition onto n-GaAs(100). A series of symmetric Cu/Co spin valves have been fabricated which exhibit a magnetic field sensitivity of 2 %/mT.

In situ STM is being 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 dealt with anion adsorption (Cl^-, Br^-, SO_4^{2-} and ClO_4^-) and lead underpotential deposition on Cu(100), Cu(111) and Cu(110). Step faceting due to the formation of an ordered, commensurate adlayer has been demonstrated for Cu(100). While a sequence of compression structures have been observed for halide on Cu(110). A chloride-induced faceting or reconstruction of Cu(110) is observed at saturation chloride coverage. Studies of Pb upd on Cu(100) reveal an alloying-dealloying transition as a function of lead coverage. Importantly, potential manipulation during copper deposition allows these 2-D phase transitions to be used to affect morphological evolution. This work not only suggests new possibilities for synthesis but also helps rationalize some of the previously reported beneficial effects of pulse plating.

Room temperature molten salts are being used as a model system for examining the utility of reactive alloy formation via underpotential deposition. STM studies have been initiated examining the nature of chloroaluminate adsorption and reduction on copper surfaces.

Impact:

Electrodeposition is a convenient, inexpensive, low temperature process for producing thin films for a variety of technological applications ranging from metallization of semiconductor devices to the synthesis of magnetic materials. Our studies using STM to characterize metal deposition processes promise to contribute valuable information on the relevant physical processes, kinetics and morphological evolution during film growth. 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 information to the subject. This is likely to be of some importance as submicron copper metallization is introduced into the fabrication of semiconductor devices. Our specific findings are that the surface of the copper electrode is covered by a layer of oxidatively adsorbed chloride at electrode potentials typically associated with copper deposition and dissolution. The adlayer exerts a strong influence on the adatom binding, the activation energy for interlayer versus intralayer transport, etc, and thus plays a dominant role in determining the evolution of surface morphology.

Outputs:

Publications:

Moffat, T. P., "STM Studies of Halide Adsorption on Cu(100), Cu(110) and Cu(111)," in Electrochemical Processing in ULSI Fabrication II, to be published by The Electrochemical Society, 1999.

Moffat, T. P., "STM Studies of Metal Electrodes," Electroanalytical Chemistry: ed. A.J. Bard and I. Rubinstein, V. 21, 211-316, Marcel Dekker, N.Y., N.Y., 1999.

Shima, M., Salamanca-Riba, L., and Moffat, T. P., "Dissolution Dynamics of Artificially Structured Alloys," Electrochemical and Solid-State Letters, 2, 271, 1999.

Shima, M., Salamanca-Riba, L., Moffat, T. P., and McMichael, R. D., "Magnetic Four-Fold Anisotropy of Co/Cu Films Electrodeposited on Cu/Si(001) and GaAs(001) Substrates," Magnetic Materials, Processes and Devices V, The Electrochemical Society, 1999.

Moffat, T. P., "Oxidative Chloride Adsorption and Lead upd on Cu(100): Investigations into Surfactant-Assisted Epitaxial Growth," J. Phys. Chem. B, 102, 10020, 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., 198-199, 52, 1999.

Nikitenko, N. I., Gornakov, V.S., Dedukh, M., Khapikov, A. F., Moffat, T. P., Shapiro, A. J., Shull, R. D., Shima, M., and Salamanca-Riba, L., "Direct Experimental Study of the Microscopic Remagnetization Mechanism in Co/Cu Magnetic Superlattices," J. Mag. Magn. Matls., 198-199, 477, 1999.

Presentations:

Moffat, T. P., "Electrodeposition: Novel Materials and New Methods," MTM-IMEC, Leuven, Belgium, September 1999.

Moffat, T. P., "Electrodeposition: Novel Materials and New Methods," Max-Planck-Institut fur Mikrostrukturphysik, Halle, Germany, September 1999.

Moffat, T. P., "Electrodeposition of Metallic Multilayers," International Society of Electrochemistry 50th Meeting, Bicentenary of A. Volta's Pile, Pavia, Italy, September 1999.

Moffat, T. P., "Electrodeposition: Novel Materials and New Methods," Workshop to Develop a Research Roadmap for Atomic Scale Manufacturing, University of Virginia, Charlottesville, VA, July 1999.

Moffat, T. P., "Electrodeposition: Novel Materials and New Methods," The Electrochemical Society, Inc., Metropolitan New York Local Section, Iselin, NJ, May 1999.

Moffat, T. P., "Electrodeposition: Novel Materials and New Methods," The Electrochemical Society, Inc., Wisconsin Local Section, Milwaukee, WI, May 1999.

Moffat, T. P., "ECSTM Studies of Copper Surfaces," 2nd Symp. on Electrochemical Processing in ULSI Fabrication, 195 th Electrochemical Society Meeting, Seattle, WA, May 1999.

Moffat, T. P., "Electrodeposition of Metallic Multilayers," E. B. Yeager Center for Electrochemical Sciences Microsymposium, Case Western Reserve University, Cleveland, OH, December 1998.

Moffat, T. P., "Electrodeposition of Strained-Layer Copper-Cobalt Superlattices," Chemical Engineering Department Seminar, University of Virginia, Charlottesville, VA, October 1998.

Moffat, T. P., "STM Studies of the Role of Adsorbates in Cu Electrodeposition," MRS Fall Meeting, Boston, MA, December 1998.

Moffat, T. P., "Pb upd on Cu(100) and its Application in Copper Deposition," 194th Electrochemical Society Meeting, November 1998.

Shima, M., Salamanca-Riba, L., Moffat, T. P., and McMichael, R. D., "Evidence for Superparamagnetism in Electrodeposited Co/Cu Multilayers," 194th Electrochemical Society Meeting, November 1998.

Shima, M., Salamanca-Riba, L., Moffat, T. P., and McMichael, R. D., "Correlation Between Structural Imperfection and Giant Magnetoresistance Effect in Electrodeposited Co/Cu Multilayers," 194th Electrochemical Society Meeting, November 1998.

Project Title: REACTIONS OF ZINC VAPOR WITH ZIRCALOY

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

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 U.S. Nuclear Regulatory Commission (NRC) and the electric utility companies that operate nuclear power plants 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 tests to identify metallurgical reactions and diffusion processes that might arise between this zinc vapor and Zircaloy-4, which is a zirconium-based alloy with a small fraction of alloying elements. On the basis of the initial studies, the NRC saw the need for further reaction measurements at low temperature, as well as tests to evaluate the effect of the reaction on the mechanical properties of the Zircaloy. The new measurements are intended to provide data which can be used to estimate the response of the Zircaloy during long-term exposure. In addition, in order to aid in interpretation of the reaction rate measurements, the reaction of zinc vapor with pure (nuclear grade) zirconium has been studied.

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, and to develop kinetic models of the reaction process which can be used to estimate long-time behavior. Mechanical tests of Zircaloy tubing exposed to zinc vapor will provide an indication of how severely the reaction with zinc may influence the strength of the cladding material.

External Collaborations:

This project was planned during discussions with the U.S. Nuclear Regulatory Commission and was funded by them. Progress and results were discussed periodically with the NRC and their consultants.

Accomplishments:

Reactions of zinc vapor with pure (nuclear grade) zirconium and Zircaloy-4 tube reduced extrusion (TREX) were analyzed over a range of temperatures (650 °C to 800 °C). Individual samples were encapsulated with α brass filings (Cu-30 wt.% Zn) as a source of Zn vapor in quartz tubes. An important conclusion from the observations was that the eutectoid temperature of the beta zirconium to alpha zirconium plus ZnZr was lower than shown on the published phase diagram. The growth kinetics of the reaction layer were analyzed and an activation energy of 131 kJ/mole was measured for Zircaloy-4 in the temperature range of 650 °C to 700 °C. No evidence of enhanced low-temperature growth due to grain boundary diffusion was seen, but TEM measurements would be needed to completely rule it out.

For a new series of tests, started at the request of the Nuclear Regulatory Commission, samples have been prepared to measure the low-temperature reaction of Zn vapor with Zircaloy-4, and with oxide-coated samples of Zircaloy-4. Mechanical test samples of Zircaloy-4 tubing were also prepared and a set of special grips was designed to test the tubing in uniaxial tension.

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. Emphasis is placed on modeling the diffusion mechanisms associated with the transient liquid phase bonding of Ni-based superalloys, including 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 joint then solidifies isothermally through rapid interdiffusion of an element, such as boron. However, difficulties arise when applying TLP bonding to multicomponent commercial Ni-based superalloys: brittle precipitates may form during the bonding processing 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. 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 Siemens 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.

A discussion with engineers at BWX Technologies confirmed the difficulties with the precipitation of intermetallic phases in the base material.

Accomplishments:

For the ternary Ni-Al-B system, the results of the TLP bonding experiments of a Ni-5 wt.% Al substrate with a Ni-1.9 wt.% B filler composition at 1315 °C for 0.25 h, 0.5 h, 1 h, and 5 h were compared with the simulated predictions. The observed and predicted microstructures qualitatively agreed, both showing the precipitation and dissolution of the $Ni_{20}Al_3B_6$ (τ) intermetallic in the base material. The experiments were more quantitatively assessed by the comparison of the measured and predicted Al profiles across the joint, the width of the frozen quenched liquid, and the fraction of τ as a function of distance.

As Ni-Cr-B filler materials are more commonly used by industry than Ni-B fillers, TLP bonding experiments were also performed using a Ni-15 wt.% Cr-3 wt. % B filler. These experiments were performed at 1200 °C for 0.167, 0.3, and 0.5 hours. To compare the experimental results with model predictions required further thermodynamic and mobility assessment work. Assessment of the Ni-Al-Cr-B system used the previously assessed Ni-Al-B system and required the revision of the Cr-B system to treat boron as an interstitial element and the assessment of the Ni-Cr-B and Al-Cr-B ternary systems. The mobility database was constructed using the Ni-Al-Cr assessment of Engström and the limited available literature data for Ni-B and Cr-B. The comparison of the experimental results and simulation predictions are currently being evaluated.

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:

Publications

Campbell, C. E., and Kattner, U. R., "A Thermodynamic Assessment of the Ni-Al-B System," J. Phase Equilibria, **20**, 485, 1999.

Boettinger, W. J., Coriell, S. R., Campbell, C. E., and McFadden, G. B., "On the Properties of α/α+β Diffusion Couples," in press *Acta Metall.*

Presentations

Campbell, C. E., "DICTRA and Transient Liquid Phase Bonding in the Ni-Al-B System," Steel Research Group Meeting, Evanston, IL, March 1999.

Campbell, C. E., and Boettinger, W. J., "Time-dependent Diffusion Paths Associated With Transient Phases in Ternary Systems," TMS Annual Meeting, San Diego, CA., March 1999.

Campbell, C. E., "Transient Liquid Phase Bonding in Ni-Based Superalloys," Poster Session for Manhattan Project, November 1998.

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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.

In the last half century, a rather complete body of literature has been developed describing phase equilibrium in simple systems. Although many of these systems could still benefit from additional refinement, most of the current effort in MSEL is directed toward analysis of more complex systems of importance in specific emerging technologies. Several of the main projects in MSEL's Phase Equilibria program, therefore, provide the underlying thermodynamic framework for projects in other program areas such as Electronic Packaging, Interconnection, and Assembly.

MSEL phase equilibrium work includes the following main projects:

- High Temperature Superconductors. Experimental studies are conducted 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.

- Dielectrics for Wireless Communications. Advanced ceramics with high dielectric constant, low dielectric loss, and reliable temperature stability are needed for components of cellular communications circuits with improved performance and lower cost. This research activity emphasizes experimental determination of selected ternary (or higher) oxide phase diagrams, and the correlation of chemical composition, crystal structure, and dielectric performance within each system.

- Computational Studies of Ferroelectrics and Dielectrics. Using first-principles phase diagram calculation tools, including the Ising model and Monte Carlo methods, this project models the atomic structure of ferroelectric ceramics. These materials have unique properties that are widely exploited to produce multilayer capacitors and transducers, but their electronic properties are strongly dependent upon the exact ordering patterns adopted by the atoms.

- NIST-ACerS Phase Equilibria Diagrams Database. This project prepares and publishes critically evaluated phase equilibria data for the industrial and academic communities, in collaboration with the American Ceramic Society.

- Data for Lead-Free Solders. The phase equilibria in the Sn-Ag-Bi-Cu quartenary system have been assessed and used to predict alloy characteristics such as liquidus temperature, melting range, and phase content. Industrial partners are using these data to down-select compositions for further study as possible lead-free solders.

- Metallurgy of the Electrical Contacts to Gallium Nitride Semiconductors. Stable, low resistance metal-to-semiconductor contacts are needed to take full advantage of the properties of gallium nitride for optoelectronics and high-temperature microelectronics. This project investigates phase equilibria in the Ti-Al-Ga-N system and applies the results to analysis of reactions at the metal-to-semiconductor interface.

- Reactive Bonding in Metals. The joining of superalloys by transient liquid phase bonding requires carefully planned processing cycles to avoid the formation of unwanted intermetallic phases which can lead to failure in the joints. Phase diagram data are combined with mobility data to produce a model describing the distribution of phases formed in the joints.

Project Title: THERMODYNAMIC DATABASES AS THE BASIS OF PREDICTION OF INDUSTRIAL PROCESSES

Investigators: U. R. Kattner, A. V. Davydov, C. E. Campbell, and W. J. Boettinger

Objective:

The objective of this project is to develop thermodynamic databases for the calculation of phase equilibria in multicomponent alloys such as solders, Ni-base superalloys, and Group III nitride compound semiconductors.

Technical Description:

The experimental determination of phase diagrams is a time-consuming and costly task. This becomes even more pronounced as the number of components increases. The calculation of phase diagrams reduces the effort required to determine equilibrium conditions in a multi-component system and can provide numerical information that is frequently needed in other modeling efforts. Even though phase diagrams alone do not describe systems which deviate from thermodynamic equilibrium, it is well established that the phase equilibria can be applied locally (local equilibrium) to describe the interfaces between the phases. Phase equilibrium calculations not only give the phases present and their compositions, but also provide numerical values of enthalpy content, temperature and concentration dependence of phase boundaries.

New solder compositions are being sought by the electronics industry for several specialized applications. It is imperative for candidate solder alloys to have the appropriate melting temperature and freezing range. The thermodynamic database can be used to predict these properties and also show the effects of non-equilibrium solidification.

The calculation of phase equilibria provides a method to predict the fraction solid and heat content vs. temperature relationship during the solidification of multicomponent superalloys. The thermodynamic database will be used with commercial software code developed by UES for the simulation of casting processes.

Knowledge of the phase diagrams for the semiconductor systems will be helpful in understanding such processes as thin film and bulk crystal growth, conventional and rapid thermal annealing, and contact formation.

Planned Outcome:

Thermodynamic databases for solders, Ni-base superalloys and Group III nitride semiconductors will be developed. These databases can be used with commercial software packages, such as casting simulation software or phase equilibria software.

External Collaborations:

The assessment of the Co-Ti description was performed in collaboration with the Royal Institute of Technology (KTH), Stockholm, Sweden. The description of the Ni-Hf binary system for use in the superalloy database was provided by QuesTek, Evanston, IL. Group III - N systems were evaluated in collaboration with the University of Florida. Potential implementation of the thermochemical data for nitride compound semiconductors into the commercial crystal growth modeling code, CFD-ACE+, was discussed with the CFD Research Corporation, Huntsville, AL, and reflected in their SBIR proposal submitted to NSF.

Accomplishments:

Calculations for commercial alloy compositions were carried out using the existing 9 component database for superalloys. The predictions for the liquidus and solidus temperatures are reasonable, but the descriptions of the $\gamma'(L1_2)$ and $\beta(B2)$ phases need to be refined. The descriptions of these two phases were analyzed in detail in all 28 Ni-base ternary subsystems.

A thermodynamic description of the binary Al-Hf system was developed and used with descriptions of the Ni-Al and Ni-Hf systems for the extrapolation of the ternary Ni-Al-Hf system.

Thermodynamic descriptions of the binary Cr-B and the ternary Ni-Cr-B systems were developed for the transient liquid phase bonding project.

A preliminary description of the Co-Ti system was developed and experiments to clarify the melting point of the intermetallic compound CoTi have been initiated.

The construction of the thermodynamic database for solders was initiated and the description of the Sn-Bi-Pb system included.

The semiconductor Ga-N system has been critically assessed, and the Al-N and In-N systems were tentatively evaluated. Phase diagrams permitted the evaluation of pressure-temperature stability regions for the three nitride compound semiconductors, GaN, AlN and InN. Predicted thermal instability of gallium and indium nitrides should be taken into account in annealing experiments at elevated temperatures.

Impact:

The thermodynamic databases developed in this project enable industry to reduce the required number of experimental test procedures. For solder alloys, the results can be used to eliminate candidate solder alloys for which the calculation revealed unsuitable freezing temperature and range from further testing. For Ni-base superalloys, the detailed solidification behavior can be predicted. This results in improved quality of simulation of investment castings by providing more reliable prediction of casting defects, thus allowing industry to reduce the number of test castings to reach an acceptable design. For the Group III nitride semiconductors, evaluated thermochemistry and phase diagrams allow reasonable estimates of missing properties, including the melting and sublimation temperatures of compound semiconductors and the equilibrium component partial pressures. This information can further be used to optimize conditions for the semiconductor growth and device processing.

Output:

Publications:

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Kattner, U. R., Eriksson, G., Hahn, I., Schmid-Fetzer, R., Sundman, B., Swamy, V., Kussmaul, A., Spencer, P. J., Anderson, T. J., Chart, T. G., Costa e Silva, A., Jansson, B., Lee, B.-J., and Schalin, M., "Use of Thermodynamic Software in Process Modeling and New Applications of Thermodynamic Calculations," CALPHAD, in press.

Presentations:

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Davydov, A. V., Kattner, U. R., Sundman, B., and Ozaki, K., "Critical Evaluation and Thermodynamic Assessment of the Co-Ti System," CALPHAD XXVIII Conference, Grenoble, France, May 1999.

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Davydov, A. V., "Application of Phase Diagrams for Selected Compound Semiconductors to the Electronic Materials Processing," Seminar at the National Renewal Energy Laboratory, Golden, CO, June 1999.

Kattner, U. R. "Construction of a Thermodynamic Database: A Case Study of Ni-base Superalloys," CALPHAD XXVIII Conference, Grenoble, France, May 1999.

Kattner, U. R. "Application of Computational Thermodynamics to Problems in Materials Science," Workshop on Computational Materials Science, Hsinchu, Taiwan, July 1999.

Project Title: MICROSTRUCTURAL STUDIES OF COMPLEX PHASES

Investigator: L. A. Bendersky

Objectives:

Wireless communication technology needs better ceramic materials with higher dielectric constant, lower losses and zero thermal coefficient for use in a wide range of frequencies. The most suitable materials candidates are complex metal oxides. The main objective of this project is to fully determine the structure of such oxides and correlate this information with the technologically relevant dielectric properties. The structural study involves high-resolution transmission electron microscopy (TEM) as well as x-ray and neutron diffraction. It is focused on determination of: (1) atomistic details of structures, (2) possible phase transformations, and (3) microstructure of ordered domains. The structural information obtained will provide the necessary bridge between the chemistry and the properties of these materials.

Technical Description:

Four $Ca_4Nb_2O_9$ polymorphs with perovskite-related $A(B'_{1/3}B''_{2/3})O_3$ structures and different arrangements of B-site cations were identified. The B-cation ordering in three of these phases is combined with *a+b-b-* octahedral tilting. Two high-temperature forms of $Ca_4Nb_2O_9$ were shown to be separated by a displacive phase transition, which involves octahedral tilting and occurs between 1500 °C and 1600 °C. Above this transition, the structure is either disordered or exhibits chemical 1: 1 ordering (ordering vector $1/2[111]_c$*) of Ca and Nb cations on the B-sites; the correct structural model is being determined. Below the transition, the structure exhibits 1: 1 ordering combined with octahedral tilting. Upon cooling, the 1: 1 ordered structure transforms to a metastable P1 triclinic structure with ordering vector $1/4[111]_c$ *. This transformation occurs by reordering of cations on $\{111\}_c$ planes. The metastable P1 structure transforms upon annealing to a stable P21/c structure with ordering vector $1/3[111]_c$ *. This first-order transition occurs by precipitation and growth of the 2: 1 ordered phase, which is stable below 1400 °C. The effect of the different orderings on dielectric properties is being determined.

The main features of the $Ca_4Nb_2O_9$ - $CaTiO_3$ phase diagram were established. The system represents a diagram where ordering and phase separations occur on a disordered B-site of a perovskite structure. Accordingly, a complex sequence of transformations involving displacive rotation of $(Ca,Ti,Nb)O_6$ octahedra, ordering on B-sites between Ca, Nb and Ti, and phase separation were identified. This system, though hitherto unstudied, offers a rich variety of order/microstructure states. These states can be well controlled and are expected to have a significant effect on the dielectric properties of interest. One of the compositions, $Ca_5Nb_2TiO_{12}$, has dielectric properties (permutivity and temperature coefficient) which warranted a patent application by Lucent. In collaboration with Prof. R. Cava from Princeton University we were able to explain the effect of sintering temperature on the changes in dielectric constant and temperature coefficient through complete characterization of ordering and microdomain state of this material.

Experimental work on characterization of microstructure and properties of ferroelectric

$PbZr_{0.2}Ti_{0.8}O_3$ (PZT) oxide thin films was completed. The study has been focused on the effect of different heterostructure parameters on the domain formation in a PZT layer.

The heterostructure consists of strontium titanate (STO) and lanthanum aluminide (LAO) substrates, PZT capacitors of different thickness and La-Sr-Co-O (LSCO) electrodes. The work was in collaboration with Profs. Roytburd and Ramesh from University of Maryland.

Planned Outcome:

This work establishes a correlation between the materials structure (ordering, atomic displacements, mixture of phases) and the physical properties (dielectric constant, thermal coefficient and losses) of the studied compounds. It elucidates the structural principles of ordering in perovskite-based complex oxides.

External Collaborations:

Collaboration with Professor J. Cohn at the University of Miami on fabrication, by pulsed laser deposition (PLD), and characterization of novel Ba-Fe-Ti-O magnetic phases.

Collaboration with Professors A. Roytburd and R. Ramesh at the University of Maryland on fabrication (PLD) and characterization of ferroelectric PZT thin films for memory applications.

Collaboration with Professor M. Greenblatt at Rutgers University on lanthanum manganates (La-Ca-Mn-O), produced by the citrate-gel process, that exhibit colossal magnetoresistance.

Collaboration with Professor R. Cava at Princeton University on finding correlations between the structural details and dielectric properties of Ca-Nb-Ti oxides.

Accomplishments:

Phase equilibria in the $Ca_4Nb_2O_9$ - $CaTiO_3$ section of the phase diagram were established. In addition, the crystallography, phase transformations and microstructures of four $Ca_4Nb_2O_9$ polymorphs were established in great detail.

The effect of the electrode layer on the polydomain structure of epitaxial $PbZr_{0.2}Ti_{0.8}O_3$ thin films was established experimentally and explained theoretically.

Impact:

This study has resulted in substantial clarification of the atomic structure and phase equilibria of $Ca_4Nb_2O_9$ - $CaTiO_3$ compounds. As such it is an important element in the NIST effort to develop phase diagrams of metal oxides that are of potential interest to U.S. industries involved in wireless communications. It has also contributed to fundamental understanding of the physics of ordering in complex compounds.

Outputs:

Publications:

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Microscopy," Phil. Magazine A. **78**, 1299, 1998.

Levin, I., and Bendersky, L. A., "Crystal Structure of the Layered Perovskite-Like $Sr_n(Nb,Ti)_nO_{3n+2}$ Compounds. Part I: Symmetry Classification of the $A_nB_nO_{3n+2}$ Structures" Acta Cryst., in press.

Levin, I., Bendersky, L. A., and Vanderah, T. A., "Crystal Structure of the Layered Perovskite-Like $Sr_n(Nb,Ti)_nO_{3n+2}$ Compounds. Part II: TEM Study of the $Sr_n(Nb,Ti)_nO_{3n+2}$ Structures," Phil. Magazine A, in press.

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Levin, I., Bendersky, L. A., Vanderah, T. A., and Roth, R. S., "Polymorphic Phase transitions in $Ca_4Nb_2O_9$" Proceedings of International Conference on Solid-Solid Phase Transformations '99, in press.

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Bendersky, L. A., "Magnetic Multilayers in a Series of BaO: TiO_2: Fe_2O_3 Compounds," Invited Seminar, University of Negev, Israel, November 1998.

Bendersky, L. A., Roth, R. S., and Levin, I., " Phase Separation and Ordering in $Ca_{(4-3x)}Nb_{(1-x)}TiO_{(9-6x)}$ Compounds," talk at International Conference on Solid-Solid Phase Transformations '99, Kyoto, Japan, 1999.

Levin, I., Roth, R. S., Bendersky, L. A., and Vanderah, T. A., "Combination of Octahedral Tilting with Two Different Types of Cation Ordering in $Ca_4Nb_2O_9$," talk at Materials Research Society Fall Meeting, 1998.

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Grey, I.E., Roth, R. S., Mumme, G., Bendersky, L. A., and Minor, D., "Crystal Chemistry of New Calcium Tantalate Dielectric Materials," MRS Symposium *Solid-State Chemistry of Inorganic Materials*, December 1998.

Levin, I., Roth, R. S., Bendersky, L. A., and Vanderah, T. A., "Combination of Octahedral Tilting with Two Different Types of Cation Ordering in $Ca_4Nb_2O_9$," poster, International Conference on Solid Solid Phase Transformations '99, Kyoto, Japan, 1999.

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 and Craniofacial 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 and Craniofacial Research, the National Heart, Lung and Blood Institute, the U.S. 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 with a metallic restorative without the use of mercury that can be hand consolidated while maintaining critical mechanical properties and satisfying the biocompatibility criteria.

Technical Description:

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 for more than one hundred years, 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 of 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, resulting in powders ranging in size from 0.2 Φ m to 2.0 Φ m. 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.

A series of *in vitro* biocompatibility tests, for cytotoxicity, hemolysis, Ames' and Styles' cell transformation, were used in the evaluation of hand-consolidated and machine-pressed silver-based alternative restorative material.

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:

The development of a mercury-free metallic alternative to conventional dental amalgams, which was the subject of a four-year long program supported by the National Institute of Dental Research, has concluded. The current technology is based on the ability of silver surfaces to adhere (cold weld) to each other after being treated with dilute fluoboric acid. Silver particles that have been immersed in such acid can be hand-consolidated into cohesive solids (78 % theoretical density) using conventional dental tools at applied pressures of 35 MPa to 50 MPa.

Over the course of the program, several forms of silver powder were evaluated and it was determined that the best source of silver was obtained from a two solution chemical precipitation process (patent pending). Silver powder properties to best promote hand consolidation were also determined. One of the most important parameters is the agglomerate size and individual particle size of the silver powder. Dramatic increase in both the transverse rupture strength and density of hand consolidated samples can be achieved as the maximum agglomerate size of the silver powder is decreased. The precipitation process was optimized for agglomerate size less than 40 Φ m (80 % < 25 Φ m). Another important parameter is the annealing of the silver powder prior to consolidation. Transverse rupture strength and density are improved dramatically when the precipitated silver powder is annealed at 750 °C. This has been attributed to a reduction in yield strength of the powder prior to consolidation. Minimal sintering and agglomeration occurs as a result of the 750 °C anneal. Acid-assisted consolidation (three patents, one issued and two pending) was the major finding which allows us to put forth a mercury-free metallic restorative. Surface spectroscopy and electrochemical measurement results supported the assumption that the function of the fluoboric acid is to remove the silver surface oxide and thereby promote cold welding.

Using the current technology, hand consolidated silver equals or exceeds the transverse rupture strength, shear strength, creep, toughness, corrosion resistance, microleakage, cyclic contact fatigue, and wear properties of conventional silver amalgam. The alternative silver restorative placement time is twice that for amalgams which warrants further study with emphasis on reducing the placement time.

In vitro biocompatibility tests which included cytotoxicity, hemolysis, and Ames' and Styles' cell transformation were completed on the component (precipitated silver powder and fluoboric acid), hand-consolidated and machine-pressed samples of the alternative restorative, and corrosion products resulting from immersion of hand-consolidated material into an artificial saliva solution. The 7 d, 21 d and 90 d corrosion products did not reach the threshold level in any of these tests to be considered non-biocompatible. Under the conditions employed by the Ames' and Styles' tests, silver powder, fluoboric acid and hand-consolidated restorative samples showed no mutagenic potential. The hemolysis examination indicated that silver powder and fluoboric acid (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, silver powder is quickly consolidated and the bioavailable surface area is quickly reduced. Most of the consolidated Ag would be surrounded by hard tissue. Initial cytotoxicity tests showed the powder and consolidated material to be severely cytotoxic while the dilute fluoboric acid is not cytotoxic. Subsequent testing of consolidated silver disk extracts were found to be severely toxic in tissue culture medium. The cytotoxicity was exacerbated by 30 % with cell to metal contact. However, all extracts in artificial saliva were not cytotoxic. Thus it appeared that the majority of the cytotoxicity was an artifact of the corrosive properties of the tissue culture medium, not likely to be present in the oral cavity. Furthermore, the cytotoxicity rapidly decreases upon dilution. Dilution of released silver within the oral cavity is very likely to occur with salivary flow. Thus there may be little or no cytotoxic effect under clinical conditions.

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 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:

Electrochemical Fluidized Bed Coating of Powders, U.S. Patent No. 5,603,815, February 18, 1997.

C. E. Johnson, D. R. Kelley, *et. al*.

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Method for the Chemical Precipitation of Metallic Silver Powder Via a Two Solution Technique, NIST Docket No. 98-027US, U.S. Patent Application No. 09/256,073.

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(301) 975-5121	Ferromagnetic resonance
	Nanocomposites
	Magnetocaloric effect
Shapiro, Alexander J.	Mössbauer effect
alexander.shapiro@nist.gov	Scanning electron microscopy (SEM)
(301) 975-5970	X-ray microanalysis
	Image analysis
	MOIF method microscopy
Shull, Robert D.	Nanocomposites
robert.shull@nist.gov	Magnetic susceptibility
(301) 975-6035	Mössbauer effect
	X-ray and neutron diffraction
	Magneto-caloric and magneto-optical effects
	Magnetic domain imaging
Swartzendruber, Lydon J.	Magnetic susceptibility
(retired)	Magnetic methods, NDE
	Mössbauer spectroscopy
	Barkhausen effect

Materials Performance Group

Clough, Roger C.	Micromechanical modeling
roger.clough@nist.gov	Acoustic emission
(301) 975-6143	Mechanical properties
deWit, Roland	Fracture mechanics
(retired)	Dislocation theory
	Finite element analysis
Fields, Richard J.	Mechanical properties
richard.fields@nist.gov	Mechanical testing
(301) 975-5712	Powder consolidation
	Metal forming
Foecke, Timothy J.	Nanostructured materials
tim.foecke@nist.gov	Experimental fracture physics
(301) 975-6592	SEM, TEM, SPM
	Micro- and nano-mechanics of materials
	Dislocation-based deformation mechanisms
	Historical metallurgy
Hicho, George E.	Mechanical properties
(retired)	Failure analysis
	Mechanical testing
Levine, Lyle E.	Diffraction theory
lyle.levine@nist.gov	Dislocation-based deformation

(301) 975-6032	Synchrotron x-ray technique
	Percolation theory
	TEM, SEM, SPM
Low, III, Samuel R.	Hardness standards
samuel.low@nist.gov	Hardness testing
(301) 975-5709	Mechanical properties of materials
	Mechanical testing of materials
Ricker, Richard E.	Corrosion and electrochemistry
richard.ricker@nist.gov	Deformation and fracture
(301) 975-6023	Prediction of materials performance
Shepherd, Dominique A.	Titanium alloys
dominique.shepherd@nist.gov	Mechanical testing
(301) 975-4798	Mechanical properties
	SEM, TEM
Smith, John H.	Mechanical properties of materials
jhsmith@nist.gov	Fracture of materials
(301) 975-5160	Pressure vessel technology
Stoudt, Mark R.	Metal fatigue
mark.stoudt@nist.gov	Thin films
(301) 975-5961	Mechanical properties
	Environmentally assisted cracking

Materials Structure and Characterization Group

Bendersky, Leonid A.	Functional ceramics
leonid.bendersky@nist.gov	Analytical and high-resolution TEM
(301) 975-6167	High-temperature intermetallics
	Order-disorder
	Thin film oxides
Bonevich, John E.	Electron holography
john.bonevich@nist.gov	High resolution/analytical electron microscopy
(301) 975-5428	Magnetic materials
Claggett, Sandra W.	Specimen preparation for electron microscopy
sandra.claggett@nist.gov	Digital imaging
(301) 975-6406	
Drescher-Krasicka, E.	Development of scanning acoustic microscopy
(deceased)	Stress measurement in electronic packaging
Gayle, Frank W.	Structure/property relationships
frank.gayle@nist.gov	Transmission electron microscopy
(301) 975-6161	Aluminum metallurgy
	Solder science
Josell, Daniel	Thermal diffusivity measurement and theory
daniel.josell@nist.gov	Modeling of grain boundary effects on multilayer equilibria
(301) 975-5788	Modeling of solder joint geometries
	Creep of thin films

Powell, IV, Adam C.	Electron beam melting and evaporation
(resigned)	Modeling of liquid free surface shape and capillary force
	Lattice gas automata models
Smith, Leonard	Solder joint failure analysis
(retired)	Optical microscopy and microstructure characterization
Warren, James A.	Computer simulations of solidification
james.warren@nist.gov	Dendrite pattern formation
(301) 975-5708	Modeling of solder/substrate wetting processes
	Modeling grain boundaries

Metallurgical Processing Group

Biancaniello, Frank S.	Spray deposition measurements and diagnostics
frank.biancaniello@nist.gov	Inert gas atomization: metal powder measurements and consolidation
(301) 975-6177	Nitrogenated steels, standard reference materials
	Special alloys, heat treating, melt- spinning
Boettinger, William J.	Relation of alloy microstructures to processing conditions
william.boettinger@nist.gov	Casting and solidification
(301) 975-6160	Solder spreading
Campbell, Carelyn E.	Transient liquid phase bonding
carelyn.campbell@nist.gov	Multicomponent diffusion simulations
(301) 975-4920	Alloy design methodology

Coriell, Sam R.	Modeling of solidification processes
sam.coriell@nist.gov	Interface stability
(301) 975-6169	Convection and alloy segregation during solidification
Elmer, Christopher E.	Applied mathematics
christopher.elmer@nist.gov	Numerical analysis
(301) 975-6146	Microstructure (lattice) effects in materials
	Analytical and numerical solutions to functional differential equations of mixed type
Jiggetts, Rodney D.	Hot isostatic pressing
rodney.jiggetts@nist.gov	Electron beam welding
(301) 975-5122	Quantitative metallography
Kattner, Ursula R.	Alloy phase equilibria calculations
ursula.kattner@nist.gov	Solder alloy evaluations
(301) 975-6157	Casting of aerospace alloys
Manning, John R.	Metals processing
(retired)	Diffusion kinetics
	Interface reactions
Mates, Steven	Compressible fluid flow
steven.mates@nist.gov	Metal sprays
(301) 975-8114	Fluid flow visualization

Napolitano, Ralph E.	Solidification
(post-doc completed)	Defects in single crystal castings
	Computational physical metallurgy
Ridder, Stephen D.	Spray dynamics and deposition
stephen.ridder@nist.gov	Thermal spray processes
(301) 975-6175	Process modeling and control
Williams, Maureen E.	Differential thermal analysis
maureen.williams@nist.gov	Powder x-ray diffraction
(301) 975-6170	Solder wettability