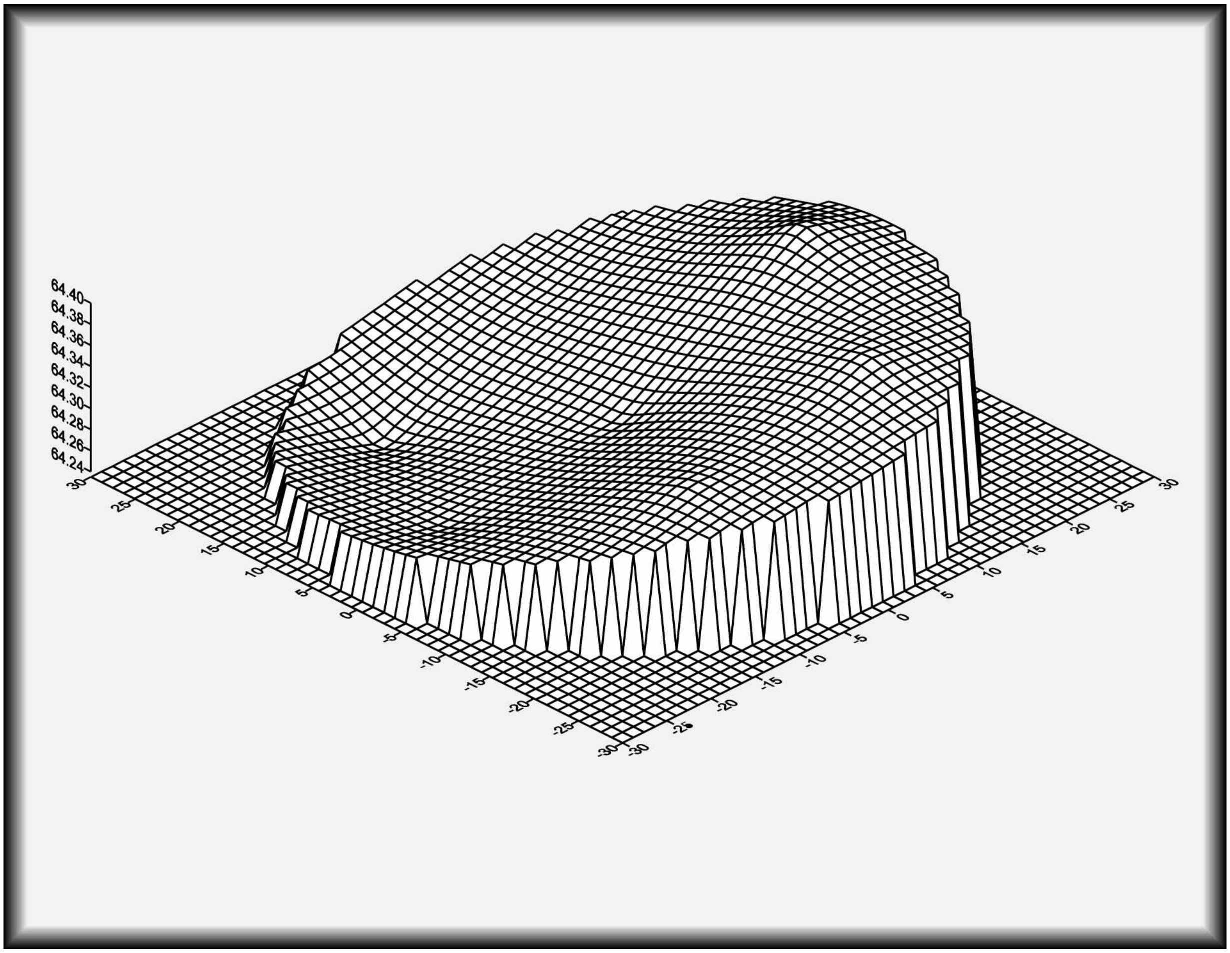
Materials Science and Engineering Laboratory

METALLURGY



NISTIR 6066
U.S. Department of Commerce
Technology Administration
National Institute of Standards
and Technology

Technical Activities 1997

METALLURGY DIVISION

CHIEF

Carol A. Handwerker
Phone (301) 975-6158

DEPUTY CHIEF

Robert J. Schaefer
Phone (301) 975-5961

GROUP LEADERS

Electrochemical Processing
Gery R. Stafford
Phone (301) 975-6412

Magnetic Materials
Robert D. Shull
Phone (301) 975-6035

Materials Performance
E. Neville Pugh
Phone (301) 975-4679

Materials Structure and Characterization
Frank W. Gayle
Phone (301) 975-6161

Metallurgical Processing
John R. Manning
Phone (301) 975-6157

TABLE OF CONTENTS

Page

INTRODUCTION 1

ELECTRONIC PACKAGING, INTERCONNECTION AND ASSEMBLY 7
Lead-Free Solders 8
High-Temperature Solders for Microelectronics 10
Solderability Measurements for Microelectronics 12
Solder Interconnect Design 14
Stress Measurements in Electronic Packaging 16
Solder Jet Printing for Microelectronics Applications 18

INTELLIGENT PROCESSING OF MATERIALS 21
Solidification Path Modeling for Casting of Multicomponent Aerospace Alloys 22
Generation of Grain Defects Near Corners and Edges in Castings 24
Porosity in Castings 26
Thermophysical Data for Castings 29
Magnetics for Steel Processing 31

MAGNETIC MATERIALS 33
Giant Magnetoresistance Materials 34
Processing and Micromagnetics of Thin Magnetic Films 39
Magnetic Properties of Nanomaterials 42

METALS DATA AND CHARACTERIZATION 47
Thermophysical Properties 48
Microstructural Studies of Complex Phases 51
Mechanical and Thermal Properties of Multilayered Materials 54
Hardness Standards 58
Magnetic Properties and Standard Reference Materials 62
Lightweight Materials for Automotive Applications 63
Performance of Structural Materials 68
Performance of Materials in Corrosive Media 73
Magneto-Optical Imaging 77
Development of Scanning Acoustic Microscopy 79
Electron Microscopy 81

METALS PROCESSING 84
Processing of Advanced Materials 85
Solidification Modeling 88

Sensors and Diagnostics for Thermal Spray Processes 91
Electrodeposition of Alumium Alloys 94
Electrodeposited Coating Thickness Standards 97
Gold Microhardness Standards 98
Electrogalvanzied Coatings on Steel 99
Electrodeposited Chromium from Trivalent Electrolytes 100
Electrochemical Processing of Nanoscale Materials 102

DENTAL AND MEDICAL MATERIALS 106
Advanced Restorative Dental Materials 107

EVALUATED MATERIALS DATA 110
NACE-NIST Corrosion Data Program 111

HIGH TEMPERATURE SUPERCONDUCTIVITY 113
Magnetic Properties of Superconductors 114

ADDITIONAL OUTPUT 116

RESEARCH STAFF 117

ORGANIZATIONAL CHARTS . . . .
Metallurgy Division 123
Materials Science and Engineering 124
National Institute of Standards & Technology 125

INTRODUCTION

Carol A. Handwerker, Chief

This report describes the major technical activities and accomplishments of the Metallurgy Division in 1997, and, therefore, reflects the research priorities established after extensive consultation and collaboration with our customers in US industry. It also reflects the Program planning and management structure that we have developed within the Materials Science and Engineering Laboratory (MSEL) to meet the identified needs of the Nation's measurement and standards infrastructure. The Division is organized administratively 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 science and engineering, 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. We hope that this report provides insight into how our research programs meet the objectives of our customers, how the capabilities of the Metallurgy Division are being used to solve problems important to the national economy and the measurements and standards infrastructure, and how we interact with our customers to establish new priorities and programs. We welcome advice and suggestions from our customers on how we can better serve their needs.

The NIST Metallurgy Division mission is to provide measurement methods, standards, and a fundamental understanding of materials behavior to aid US industry in the more effective production and use of both traditional and emerging materials. As part of this mission we are responsible not only for developing new measurement methodologies with broad applicability across materials classes and industries, but also for working with individual industry groups to develop and integrate measurements, standards, and evaluated data for specific, technologically important applications.

The Metallurgy Division philosophy is that the development of measurement methods must be coupled with a fundamental understanding of the relationship among materials structure, processing, and properties in order to have a lasting impact in measurement science and the industries we serve. Two examples of this philosophy are:

- Beginning in 1990, NIST set up a major new research program specifically aimed at providing the scientific understanding and measurement capability needed to enable U.S. industry to make the best GMR materials in the world. This program was centered on a new facility, known as the Magnetic Engineering Research Facility (MERF), which is one of the most advanced magnetic thin-film production plants ever constructed. From the beginning, NIST researchers have developed the measurement techniques, clarified the scientific issues, and established the manufacturing processes needed to produce the highest quality GMR materials. Once again this year, research at MERF is defining the state-of-the-art in magnetic thin film fabrication. NIST researchers at MERF set a new record for the largest value ever recorded in the type of material (a spin valve with one Cu layer) best suited to commercial products, discovered that increasing specular electron scattering at the top and bottom surfaces of a spin valve plays a key role in achieving the largest possible GMR values, and found two processing methods for increasing specular electron scattering. These NIST discoveries were transferred to U.S. industry as quickly as possible for implementation in its manufacturing facilities.

- Thermal barrier coatings protect engine parts from the elevated temperatures of the combustion process. It had been proposed that the presence of the numerous interfaces in multilayer thermal barrier coatings decreases their thermal conductivity, making multilayer coatings more effective thermal barriers than the materials from which they are manufactured. High-temperature measurements using NIST's pulsed laser heating system established that the upper bound for the interface thermal resistance in industry-supplied coatings is orders of magnitude below the postulated value driving industrial multilayer thermal barrier coatings research. An industrial consortium will decide by the end of 1997, based, in part, on these measurements, whether to continue its program on multilayer thermal barrier coatings for engine applications.

In 1997, outstanding achievements by Metallurgy Division staff to measurement science and technology transfer were recognized in the areas of high-temperature thermophysics and national hardness standards. Ared Cezairlian was awarded the Yeram S. Touloukian Award of the American Society of Mechanical Engineers (June 1997) in recognition of his novel systems for the high-speed, high precision measurement of thermophysical properties of materials at high temperatures. His recent designs of computer-controlled high-speed optical techniques allowed measurement of thermal and related properties at high temperatures for complex alloys important to the aerospace industry. Sam Low and David Pitchure of the Metallurgy Division, Walter Liggett of the Information Technology Laboratory, and Jun Feng Song and Ted Vorburger of the Manufacturing Engineering Laboratory were awarded the NIST Rosa Award in recognition of their development and the international acceptance of their method for the more accurate determination of the Rockwell C Hardness, a measured materials property of great importance in manufacturing and commerce. Sam Low's leadership of this NIST program and of the American delegation to ISO 9000 hardness committee has been critical to the establishment of a new dimensional-metrology-based approach to the measurement of hardness.

The Division uses most of its resources to meet specific, high priority measurement-related needs identified by the aerospace, automotive, magnetic recording, microelectronics, and stationary power generation industries. Industrial priorities were established through formal and informal means: industrial roadmapping activities, workshops, technical meetings, standards committee participation, and individual visits with our customers. In order for us to undertake a new program or project within an existing program, several criteria must be met: (1) there must be a clear research need; (2) the NIST role must be consistent with the NIST and Metallurgy Division missions; (3) the industrial and NIST resources must be sufficient to accomplish the goals; and (4) there must be a clear path for technology transfer of NIST results, whether the results are a fundamental understanding of materials behavior, measurement techniques, standards, evaluated data, software, or sensors. The list of research accomplishments that follows provides an indication of the scope and quality of programs in the Metallurgy Division.

METALLURGY DIVISION
SIGNIFICANT ACCOMPLISHMENTS AND IMPACT

Electronic Packaging, Interconnection and Assembly

- ***Solder Interconnect Design for Microelectronics*** - The Solder Interconnect Design Team, organized by the Metallurgy Division and the NIST Center for Theoretical and Computational Materials Science, is developing software that will facilitate the design of electronic packaging. The Design Team, which includes Motorola, DEC, Ford, Susquehanna University, and others, has used this software to determine equilibrium shapes of solder joints and resulting forces on the electronic package leads. Industrial application of the software is spreading rapidly. At Motorola, the software has allowed electronic packaging engineers to redesign circuit boards in production; as a result of the calculations, component "fall off" while soldering the second side of a two-sided production circuit board was virtually eliminated, changing the manufacturing yield from 20 percent to over 90 percent. In another soldering challenge, a product suffered from "floating and twisting" of every battery contact during soldering, requiring each contact to be repositioned by hand, a serious manufacturing failure. Using the software and insights gained at the semi-annual NIST Solder Interconnect Design Team meetings, Motorola solved this problem as well.

- ***High Temperature Fatigue-Resistant Solder Alloys*** - NIST has taken a leadership role in the NCMS Consortium for the Development of High Temperature Fatigue-Resistant Solders, whose members include Delco Electronics, Ford Motor Company, AlliedSignal, Indium Corporation of America, Heraeus Cermalloy, Johnson Manufacturing, Ames Laboratory , and Rensselaer Polytechnic Institute. NIST’s role is to provide a fundamental knowledge of materials processing and the physical metallurgy of solder joint formation. In FY 1997, NIST, in collaboration with Indium Corporation, discovered a new class of alloys with promising wetting characteristics and thermal fatigue behavior; these alloys were the subject of a patent disclosure by NIST and Indium Corporation.

- ***Measurements of Residual Stresses in Electronic Packaging*** - Measurements of residual stresses in chip packages using a scanning acoustic microscopy technique developed at NIST demonstrated that significant levels of residual stresses remain even after delamination has occurred between the chip and the mold compound. The acoustic microscope measurements, performed in collaboration with Texas Instruments, demonstrated that these residual stresses can be detected over a wide frequency range (15-150 MHZ). It was also shown that the observed gradual phase shift is frequency independent in agreement with the model for scanning acoustic imaging of stress.

Intelligent Processing of Materials

- ***Solidification Path Modeling in Multicomponent Aerospace Alloys*** - The NIST software for computation of enthalpy-temperature relationships appropriate for multicomponent alloy solidification has been incorporated into ProCAST™, a commercial software code, as part of the NIST Consortium on Casting of Aerospace Alloys. Such data will be used by the investment casting industry to shorten design cycles for production of turbine engine parts.

- ***Modeling Grain Nucleation in Superalloy Castings*** - Single crystal superalloy castings enable aircraft turbine engines and, more recently, industrial gas turbines, to operate at higher temperatures and thus at higher efficiencies. Defects such as stray grains or regions of crystallographic misalignment degrade the high-temperature performance of superalloys and thus cause a high reject rate in these castings. NIST scientists have developed a method to predict when conditions in the casting will be favorable for spurious grain nucleation. This time-efficient computational method incorporates thermal simulation results and the anisotropic growth kinetics of a dendritic front to compute the complete time-temperature history of a three-dimensional casting and time-minimized path to any given location in the casting. Experimental nucleation data or an analytical nucleation rate expression can then be used to quantify the nucleation tendency along the path. This method is being linked to ProCAST™.

Magnetic Materials

- ***Measurements of the Thermal Stability of Spin Valves*** - A method has been developed for characterizing the reversible and irreversible temperature dependence of spin valve magnetoresistance that involves measurement of magnetoresistance (R vs. applied field) at increasingly elevated temperatures and at room temperature following each heating. The measurements at high T reflect both reversible and irreversible changes, while the room T measurements reflect only irreversible changes as a function of annealing temperature.

- ***Thermal Stability of Spin Valves Improved -*** The thermal stability of thin magnetic film spin valves with the highest value of giant magnetoresistance (GMR) ever recorded has been improved from 250°C to 325°C by adding a 5 nm thick capping layer of tantalum. This 75°C improvement is particularly significant since lithographic practices used in circuit construction (including these devices) generally use photoresists which need baking at temperatures close to 250°C.

Metals Data and Characterization

- ***International Hardness Intercomparison*** **-** As a result of NIST development of national hardness standards, agreement on international hardness scales is developing. An intercomparison study using the new NIST Rockwell C Scale SRM test blocks, conducted by NIST and the National Research Laboratory of Metrology in Japan, showed agreement within +/- 0.1 HRC at all three levels of hardness for which the NIST standards are produced. An intercomparison of the HRB scale was also conducted with Japan and agreement to +/- 0.15 HRB was found at four levels of hardness. This unprecedented agreement is a direct result of NIST research in identifying and quantifying the individual uncertainties associated with the variability of diamond indentors, the standard test blocks, the load cycle, and the testing machine.

- ***New Corrosion Test Method Supports Alloy Development*** **-** Crucible Materials Corporation is developing new corrosion-resistant high nitrogen stainless steels produced by gas atomization and HIP consolidation, with sponsorship from the Advanced Technology Program and through a CRADA with the NIST Metallurgy Division. Since existing corrosion test methods were unable to induce pitting corrosion of these highly resistant alloys, differences in the corrosion resistance of these alloys could not be measured. A new pitting corrosion test technique that employs more aggressive conditions was developed at NIST. The technique has been adopted by Crucible to support their alloy development program.

- ***New Measurement Methods for Fundamental Studies of Formability*** **-** NIST is working with ATP awardees in the automobile industry to develop constitutive models for metal deformation which can be used in modeling sheet metal formability. Using neutron scattering and synchrotron X-ray measurements, combined with analyses of X-ray and neutron scattering by dislocations, the NIST work is leading to methods for the determination of dislocation content and arrangement in bulk samples of materials. This information is needed to predict the changes in deformation behavior which develop continuously during the forming process.

- ***High-Speed Laser Polarimeter is Commercialized*** **-** The high-speed (millisecond resolution) laser polarimeter, developed jointly by NIST and Containerless Research Incorporated (CRI) to enhance the NIST facilities for measurement of fundamental thermophysical properties, has been commercialized by CRI and has been successfully marketed internationally. This innovative instrument will significantly simplify the accurate measurement of high temperatures by directly determining the normal spectral emissivity of a specimen surface without the requirement of a blackbody configuration.

Metals Processing

- ***Materials Processing for Non-linear Optical Materials*** - Bunching of the elementary steps during layerwise growth of crystals for optical applications causes impurity segregation, inhomogeneous optical properties, and decreased damage thresholds in the crystals. Analytic and numerical calculations have been used to determine the fluid flow conditions required to avoid step bunching during crystal growth of KDP, large crystals of which are required for laser fusion applications. Realistic modeling of the growth process required extension of a previous theory to include nonlinear anisotropic interface kinetics. In addition, optimized growth conditions identified in the NIST research can now be used to produce higher quality lead bromide-silver bromide crystals as non-linear optical materials.

- ***Imaging Pyrometer for Spray/Atomization Processes*** - NIST/SBIR-funded research has resulted in a new imaging pyrometer with wide applicability to materials atomization processing. This "Thermal Spray Imaging" sensor, developed by Stratonics, Inc. of Laguna Hills, CA, uses special IR optics to produce a high resolution two-color image of the material under test. This approach provides both temperature and emissivity data with spatial resolution as high as 15 µm. Equipped with a standard video CCD array, this device can measure real-time accurate surface temperatures (±10 K), emissivity, and roughness of such objects as plasma spray coatings, spray deposition substrates, and the surface of hot or molten materials. An image intensifying camera is currently under development that will provide similar results from thermal spray and atomization droplets in flight.

- ***Gold Microhardness Standard*** - A 24K gold, low load microhardness standard prototype has now been developed. The surface area is 2.25 cm^2 and the deposit thickness is 200 µm. At a load of 25 grams, more than 1,000 indentations can be made on its surface. The average Knoop hardness is 75.5 +/- 10%. The request for this standard has come mainly from the electronics industry where gold is electrodeposited on printed circuit boards. Also, the general plating industry for precious metals has requested the standard for process control of addition agents to Au electrolytes. This microhardness standard is expected to fill a void in the low hardness, low load SRMs presently offered.

Dental and Medical Applications

- ***Consolidation of Mercury-Free Dental Restoratives*** -The American Dental Association has obtained an exclusive license for a NIST patent on silver-based filling materials. The patent resulted from developmental work at NIST supported by the National Institute of Dental Research to find an alternative to mercury-containing dental restoratives and a technique to place or consolidate the restorative using normal dental hand tools.

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.

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 effort led to the development of an interdivisional MSEL program committed to addressing industry's most pressing materials measurement and standards issues. These issues are central to the development and utilization of advanced materials and material processes for new product technologies, as outlined in 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 - will 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 metal and polymer thin films; solders, solderability and solder joint design[2]; interfaces and adhesion; electromigration and stress voidage; and built up stress and moisture in plastic packages. These projects are always conducted in concert with partners from industrial consortia, individual companies, academia, and other government agencies. The program is strongly coupled with other microelectronics programs within government and industry, including the National Semiconductor Metrology Program (NSMP)[2]. 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, is contained in *Electronics Packaging, Interconnection and Assembly at NIST: Guide and Resources*, NISTIR5817 (http://www.msel.nist.gov/epia1996/contents.htm). Copies may be obtained by contacting Michael Schen at (301) 975-6741 or michael.schen@nist.gov.

----

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

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

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

Project Title: LEAD-FREE SOLDERS

Investigators: C. A. Handwerker, U. R. Kattner, W. J. Boettinger, J. R. Manning, F. W. Gayle, M. E. Williams, L. Smith, and J. Adams

Objectives:

The objectives of this program are to develop environmentally friendly solders as replacements for tin-lead near-eutectic alloys, the workhorses of the microelectronics industry, and to evaluate the impact of such solders on industrial practice.

Technical Description:

Scientists from NIST, working with a broad-based industrial consortium organized through the National Center for Manufacturing Sciences (NCMS), have established critical tests and provided materials property data to evaluate Pb-free solder alloys with respect to a wide range of manufacturing, performance, and environmental standards.

NIST and NCMS had a multi-year CRADA ending in FY97 describing NIST participation in this $11M research and development program, which is supported almost entirely by in-kind contributions from each of its members. In addition to NIST, members include AT&T/Lucent Technologies, Rockwell, Texas Instruments, Ford, GM-Hughes, GM-Delco, Hamilton Standard/United Technologies Research Center, Rensselaer Polytechnic Institute, and Sandia National Laboratories. NIST contributions to this industry-led program included phase diagram determinations, materials fabrication, and test development for manufacturing performance and mechanical failure assessments.

The project was successfully completed this year, resulting in a comprehensive report.

Planned Outcome:

Lead-free solder alloys will be evaluated for their potential to replace Sn-Pb eutectic alloys for various applications. Guidelines for testing alloys for use in microelectronics interconnects will be provided. At the end of the NCMS project, the data will be made publicly available.

External Collaborations:

Throughout this project, NIST staff have worked closely with the members of the NCMS Lead-Free Solder Project, including AT&T, Rockwell, Delco Electronics, Ford Motor Company, Texas Instruments, GM-Hughes, Hamilton Standard/United Technologies Research Center, as well as with Sandia National Laboratories, Ames Laboratory, and Rensselaer Polytechnic Institute.

Accomplishments:

In FY 1997 the Metallurgy Division took the responsibility for leading the team in critically analyzing the data, incorporating the results into a final report, and recommending applications for the candidate solders.

Impact:

The final report has been written and made publicly available through NCMS. Replacements have been identified for various applications, particularly for surface mount technology, although there is no universal drop-in replacement for Pb-Sn eutectic solder. The work has revealed that the design of through-hole joints using high-tin solders must consider a new failure mode which was identified.

Outputs:

Publications:

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

Presentations:

Handwerker, C. A., “Fillet-Lifting in Plated-Through-Hole Geometries: An Issue for Lead-Free Solders,” IPC Printed Circuits Expo ‘97, San Jose, CA, March 11, 1997.

Handwerker, C. A., “Fillet-Lifting in Plated-Through-Hole Circuit Boards,” TMS Annual Meeting, Orlando, FL, February, 1997.

Boettinger, W.J., “Through-hole Solder joint Fillet Lifting Phenomenon and its Possible Remedies,” TMS Materials Week ‘97 Conference, Indianapolis, IN, Sept 15, 1997.

Project Title: **HIGH TEMPERATURE SOLDERS FOR MICROELECTRONICS**

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

Objectives:

The objective of this program is to identify and develop high temperature fatigue-resistant solders for microelectronics applications in harsh environments, especially in the automotive, telecommunications, and avionics industries.

Technical Description:

In this project, scientists from the Metallurgy Division are working with a broad-based industrial consortium organized through the National Center for Manufacturing Sciences (NCMS) to develop critical tests and evaluate performance of candidate microelectronics solder alloys for applications at high temperatures. The need for these new solder alloys is being driven by the automotive, telecommunications, and avionics industries, all of which have new demands for the performance of interconnects beyond the current capabilities of lead/tin eutectic alloys. There is a particular focus on thermal fatigue of the alloys since this is regarded as the primary failure mechanism for solders in high temperature applications.

In addition to NIST, members of the consortium include Delco Electronics, Ford Motor Company, AlliedSignal, Indium Corporation of America, Heraeus Cermalloy, Johnson Manufacturing, Ames Laboratory, and Rensselaer Polytechnic Institute. NIST's role is to provide fundamental knowledge of materials processing and physical metallurgy of solder joint formation. NIST contributions to this industry-led program have included phase diagram calculations, materials fabrication for testing and measurements, metallographic analysis and metallurgical evaluation of alloy performance, and test development for manufacturing performance and mechanical failure assessments.

Planned Outcome:

Guidelines for alloy testing will be established for development of new alloys with high thermal fatigue resistance, and new high temperature alloys will be identified with improved thermal fatigue performance for demanding applications. During this three year program results will be available to the High Temperature Solder Consortium, and the results will be released to the electronics industry in general after the end of the program.

External Collaborations:

The High Temperature Solder project is aligned with the NCMS High Temperature Fatigue Resistant Solder Project, an industry-academia-government laboratory collaboration. NIST is working closely with the consortium members Delco Electronics, Ford Motor Company, AlliedSignal, Indium Corporation of America, Heraeus Cermalloy, Johnson Manufacturing, Ames Laboratory, and Rensselaer Polytechnic Institute to determine measurement needs in this area and to conduct the research program to meet those needs.

Accomplishments:

In FY 1997 the Metallurgy Division led the Materials Task Group, which is responsible for one of two technical aspects of the NCMS High Temperature Fatigue Resistant Solder Consortium. In addition to chairing the weekly conference calls, the Division has conducted several technical activities within the consortium and led the evaluation of candidate alloys. We have conducted a metallographic measurement and evaluation of solidification behavior of 52 candidate solder alloys. We have also managed the data base for alloy downselection for the Consortium which lead to the final 12 tin-based and 10 lead-based alloys used for Thermo-mechanical Fatigue Test Vehicle evaluation. These alloys have been used to assemble components to printed wiring boards and ceramic substrates and will be the subject of thermal cycling testing to evaluate fatigue behavior.

Impact:

A promising new concept in thermal fatigue management through special modification of alloy composition has been proposed and evaluated and is the subject of a patent disclosure by NIST and Indium Corporation.

Outputs:

Presentations:

Gayle, F.W., “New High Temperature Solders: A Phase Diagram Approach” October, 1996, TMS Fall Meeting, Cincinnatti, OH

Gayle, F.W., “Novel Means to Improve Wettability and Fatigue Life of Pb-rich Solders,” National Center for Manufacturing Sciences, Nov. 12, 1996, Ann Arbor, MI

Gayle, F.W., “ Measurement and Testing Criteria for High Temperature Solders,” NCMS High Temperature Fatigue Resistant Solder Consortium Meeting, Orlando, FL, February, 1997.

Gayle, F.W., "Solder Alloy Selection For High Temperature Fatigue Reliability," at Heraeus Cermalloy, W. Conshohocken, PA, Sept. 23, 1997.

Patents Pending:

Lead-based Solders for High Temperature Applications
Frank W. Gayle (NIST) and James A. Slattery (Indium Corporation)
disclosure filed

Project Title: **SOLDERABILITY MEASUREMENTS FOR MICROELECTRONICS**

Investigators: J. R. Manning, U. Bertocci, W. J. Boettinger, F. W. Gayle, C. A. Handwerker, S. C. Hardy, K. W. Moon, G. R. Stafford, J. A. Warren 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. manufacturers can use to evaluate solders and components for solderability before committing them to the production line.

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 produced a need for improved solderability measurements and standards.

To aid in the interpretation and improvement of the frequently used wetting balance test for solderability, studies are being made of wettability and interactions between solders and substrates under conditions similar to those in dynamic wetting balance tests, where a component is dipped into a solder bath and dynamic wetting occurs. In particular, effects of solder temperatures and wetting balance atmospheres have been investigated. Through interactions with the Institute for Interconnecting and Packaging Electronic Circuits (IPC), the national packaging standards development organization, results from these studies are being incorporated in national standard test methods.

The growth of oxides on surfaces is a frequent cause of loss of solderability of printed wiring boards and components during storage. Electrochemical tests, especially sequential electrochemical reduction analysis (SERA), are being applied to measure the chemical nature of the species produced by oxidation, the structure and thickness of the surface layer, and their role in the degradation of solderability on copper electrodes. The electrochemical data are being supplemented by glancing angle x-ray analyses. Similar tests on copper treated with imidazole oxidation inhibitors seek to determine the effectiveness of these compounds in preventing or slowing down surface oxidation.

Planned Outcome:

Improved solderability test methods will lead to increased manufacturability and reliability in microelectronic devices. Such increased reliability and predictability for solder joints will be essential for U.S. industry in producing surface mount and ball grid array interconnects, where small size scales and limits on visual inspection of the solder joint make rework of improperly soldered connections difficult or impossible. Electrochemical tests will allow evaluation of accelerated aging treatments as well as the effectiveness of organic protective coatings.

External Collaborations:

On an industry-wide basis, collaborations are on-going with industry-led national standards development organizations, especially the IPC Solderability Committee. NIST scientists serve as mentors for projects in universities funded by the industry-supported Semiconductor Research Corporation.

Accomplishments:

Processes determining limits on reproducibility of wetting balance tests for solderability have been evaluated and the results were used in development of improved tests by standards groups with which NIST is collaborating, such as ANSI and the IPC Solderability Committee.

Measurements made at NIST under controlled atmospheres showed that the measured forces and solder profiles in wetting balance tests are very sensitive to the condition of the solder surface as well as to the condition of the surface to be soldered.

From application of the SERA method, the three main constituents of the surface film formed upon exposure of copper to certain electrolytic solutions have been identified, the thicknesses of the films have been measured by analysis of the electric charge passed, and the sequence of oxidation and reduction reactions has been described.

Modeling of reactive wetting using a diffusion/fluid flow approach has lead to prediction of the rate of solder spreading as a function of alloy composition. This research establishes for the first time the fundamental coupling between the metallurgy of solder/substrate interaction and wetting.

Impact:

Results from NIST measurements have been incorporated into testing criteria for ANSI/J-STD-002 (Joint Industry Standard on Solderability Tests for Component Leads, Terminations, Lugs, Terminals and Wires) in the revision currently being completed by the Institute for Interconnecting and Packaging Electronic Circuits (IPC).

Outputs:

Publications:

Warren, J. A., Boettinger, W. J., and Roosen, A. R., "Modeling Reactive Wetting," in The Design and Reliability of Solders and Solder Interconnections, edited by R. K. Mahidhara, D. R. Frear, S.M.L. Sastry, K. L. Murty, P. K. Liaw, and W. L. Winterbottom, The Minerals, Metals, and Materials Society, Warrendale, PA (1997), pp. 155-157.

Liggett, W., Moon, K. W., and Handwerker, C. A. "An Experimental Method for Refinement of Solderability Measurement," Soldering and Surface Mount Technology, Vol. 9, July 1997, 8 pp.

Presentations:

Handwerker, C. A., "Solder Science: What Do We Really Know About Reactive Wetting and

Spreading?" The Johns Hopkins University, Baltimore, MD, January 29, 1997.

Handwerker, C. A., "Scientific Issues in Soldering," University of Maryland Chapter of the Materials Research Society Technical Conference, College Park, MD, Sept. 12, 1997.

Project Title: **SOLDER INTERCONNECT DESIGN**

Investigators: J. A. Warren and C. A. Handwerker

Objectives:

The main objective of this program is to develop modeling tools for predicting the geometries of small-scale solder joints with a wide range of starting configurations of interest to industry. Implicit in the development of such tools is the necessity of developing the computational methods for importing solder geometries 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/WWW. In addition, the SIDT also holds workshops and symposia to promote collaboration and bring the community toward a consensus on the features required for a useful solder modeling system.

Technical Description:

The NIST Solder Interconnect Design Team, with support from NIST's Center for Theoretical and Computational Materials Science, has been formed to address several pressing issues in the design and fabrication of circuit board assemblies. This multibillion dollar industry is highly dependent on solder interconnects as the dominant method for attaching components to a circuit board. Having met frequently over the past four years, in partnership with both academic and industrial researchers, the Team has established an agenda for solving modeling problems concerning equilibrium solder joint shape, and the consequential thermal and mechanical properties of the formed joints.

Our ultimate goal is to provide the industrial community with a suite of useful software tools for solder interconnect design, and to provide solved test problems (available electronically on the World Wide Web). With this in mind we are actively supporting the development of software that will interface the public domain program Surface Evolver, which has been shown to be quite capable at computing equilibrium solder meniscus shapes.

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

Planned Outcome:

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

External Collaborations:

The SIDT is an industry-academia-government laboratory collaboration. Participants over the past few years have included many people and companies. Attendees at workshops include: Edison Welding Institute, DEC, Motorola, BOC Gasses, Ford Motor Co., Lucent Technology, AMP, Rockwell, Delco, Texas Instruments, 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, Sandia, and, of course, NIST.

The CTCMS currently provides support to several SIDT members. The author of the Surface Evolver, Ken Brakke (Susquehanna), is an essential member of the SIDT. Ken has attended all of the SIDT meetings, modified his code to meet our needs, and continues to collaborate on relevant problems. Recently, the CTCMS has begun to support research at the University of Greenwich (Chris Bailey) to examine the buildup of stress during the solidification of optical interconnects, as well as the dynamics of the melting and fluid flow of solder-flux paste under reflow conditions.

Finally, a CRADA with Boeing has been established this year in conjunction with the ATP program in optoelectronics assembly. 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:

This year saw a very successful workshop June 9-11, 1997. Work on a variety of topics was presented spanning the industrial concerns of AMP, TI, Ford, Motorola, and Lucent, as well as exciting new scientific work from many of our academic and government partners.

A new modeling technology is being developed by SIDT member U. Greenwich, to describe the stresses which develop during the solidification of solder interconnects. This effort also should improve the ease of use of the Surface Evolver, which currently requires substantial specialized expertise.

Impact:

The SIDT's impact on the solder community is getting harder to measure as we become more successful at disseminating software via the Internet. Most academic groups who work in the area of solder interconnect issues in electronic packaging are now aware of the Surface Evolver, thus the word is out. In concrete terms, perhaps the most spectacular impact is at Motorola, where designers, using the software and insights gained at the semi-annual NIST Solder Interconnect Design Team meetings, were able to prevent component "fall off" while soldering side two of a two-sided board, changing the yield from 20 percent to 90 percent. In another soldering challenge, a product suffered from "floating and twisting" of every battery contact during soldering, requiring each contact to be repositioned by hand. Motorola solved this problem as well, using the Surface Evolver. More material can be found at (http://www.ctcms.nist.gov/programs/solder)

Outputs:

Publications:

Warren, J. A., Boettinger, W. J., and Roosen, A. R., “Modeling Reactive Wetting,” The Design and Reliability of Solders and Solder Interconnections, TMS Proceedings, February (1997).

Warren, J. A. and Handwerker, C. A., “The Solder Interconnect Design Team,” The Design and Reliability of Solders and Solder Interconnections, TMS Proceedings, February (1997).

Presentations:

Warren, J. A., “The Solder Interconnect Design Team," TMS, Orlando, FL, February, 1997.

Warren, J. A., “Modeling Reactive Wetting," TMS, February, Orlando, FL, 1997.

Warren, J. A., “The Solder Interconnect Design Team," Interpack, Honolulu, HI, June, 1997.

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

Investigator: Eva Drescher-Krasicka

Objectives:

The objective of this project is to improve acoustic microscopy methods of measuring delamination and stresses preceeding delaminations in electronic packages.

Technical Description:

Accumulated stress in electronic packages creates cracks and delaminations. Delamination at the die surface can lead to wire-bond degradation, thin film cracking at the die surface and metal-conductor displacement during temperature cycling. The failure of one chip in an electronic device frequently causes failure of the device.

Scanning acoustic microscopy (SAM) is used to detect “popcorn” cracks and delamination in electronic packages. Routine tests are available for on-line control of hidden mechanical defects. However the latent damage due to absorbed moisture that occurs during the solder reflow, but without measureable cracking and delamination, can have a dramatic effect on the long term performance of the package during subsequent temperature cycling, yet be undetectable by conventional acoustic microscopy techniques. Industry needs a fast and reliable method for detecting the undesirable accumulation of residual stresses in electronic and microelectronic components and also for accurate measurement of the delamination which has already occurred. This need has lead to the proposal of new techniques for in situ assessment of stress in electronic packaging. The existing phase inversion technique for delamination measurement works well when there is complete debonding between the die and plastic mold, i.e., a significant air gap exists between the surfaces. However, when the die is not completely debonded, the phase inversion technique shows a gradual transition of phase shift with degree of delamination which cannot be explained based on an ideal plane wave model. Ambiguities in interpretation make conventional SAM insufficient for characterizaion of delamination sizes in many cases, as reported by our industrial collaborators.

Several factors may cause this apparent phase shift, and an understanding of its origin may allow faster and more reliable assessment of package reliability. Metallurgy Division work on scanning acoustic imaging of stress has led us to the conclusion that the most plausible cause of intermediate phase shifts in delaminated electronic components is stress induced elastic anisotropy in the mold. Delaminated samples were imaged by use of an acoustic microscopy of stress at two different frequencies: 75 MHz for the shear wave and 150 MHz for the longitudinal wave. The measured values arise from the state of stress around the delamination in the mold and can be well understood using the theory of acoustoelasticity for stress induced anisotropy. We have performed independent shear and longitudinal imaging of the delaminated components giving results consistent with our model.

Planned Outcome:

This program will develop models of stress imaging in electronic packaging and modes of imaging by scanning acoustic imaging for more accurate measurement of delaminations in electronic packaging based on the NIST patent on stress imaging.

External Collaborations:

This work was done in cooperation with Dr. Thomas Moore from Texas Instruments who created the phase inversion technique that is used for the routine acoustic microscope control of defects in electronic packaging. He has also supplied the delaminated samples which were milled to the desired thickness of the mold compound necessary for the high frequency tests. We also interact with Dr. James Sweet from Sandia National Laboratory, and with the producers of the acoustic microscopes at SONIX, our CRADA partners.

Accomplishments:

Delamination in electronic components was previously believed to completely relieve stresses. We have proved that there are significant levels of residual stresses in the compound mold above the delaminated area, which can cause gradual phase shifts. The acoustic microscope inspection demonstrates these residual stresses at every tested frequency (150 MHz, 75 MHz, 50 MHz, 25 MHz and 15 MHz). This understanding should allow improved measurement of delamination sizes.

Impact:

This research has provided measurements to Texas Instruments in their analysis of stresses in packages, leading to a new approach in their models.

Outputs:

Publications:

Moore, T., Drescher-Krasicka, E., "Moisture/Thermal Induced Stress in Packaged IC's by Acoustic Imaging," Proceedings of the Fourth International Conference on Composites Engineering, Big Island of Hawaii, July (1997).

Drescher-Krasicka, E., Willis, J. R., "Mapping Stress with Ultrasound," *Nature*, Vol. **384**, No. 6604, November (1997).

Presentations:

Moore, T., Drescher-Krasicka, E., “Moisture/Thermal Induced Stress in Packaged IC’s by Acoustic Imaging,” ICCE/4 Fourth International Conference on Composites Engineering, Hawaii, July, 1997.

Project Title: **SOLDER JET PRINTING FOR MICROELECTRONICS APPLICATIONS**

Investigators: F.W. Gayle, L.C. Smith, and M.E. Williams

Objectives:

The main objective of this program is to develop measurement techniques to solve materials compatibility issues in a high temperature droplet printer capable of printing patterns of solder alloys. Resolution of these problems will bring the commercialization of solder jet technology closer to reality. A number of microelectronics companies have determined that this tecnology is needed to improve flexibility of manufacturing.

Technical Description:

The printing of solder patterns onto chips or circuit boards using ink jet printer technology is a novel means to avoid cumbersome screening techniques and environmentally unfriendly electroplating methods. In addition, "solder jet" technology is flexible (patterns can be input by keyboard) and capable of very fine pitch between solder deposits (< 100 µm), providing much needed capabilities for the next generation of microelectronic packaging.

The NIST Metallurgy Division has worked closely with ATP Awardee MicroFab Technologies, of Plano, Texas, and an industrial consortium including Delco Electronics, AMP, Universal Instruments, Texas Instruments, Eastman Kodak, and Motorola, to bring solder jet technology closer to commercial reality. NIST scientists have focused on materials compatibility issues involving the liquid solder and the jetting apparatus, and reactions between the jetted solder and the various substrate materials used in microelectronic interconnects.

This project was successfully completed in FY 1997.

Planned Outcome:

This project was designed to resolve materials compatibility problems associated with containing and jetting liquid metals, and to provide guidance for a set of deposition conditions which are appropriate for producing solder joints with good integrity.

External Collaborations:

Throughout this project the Metallurgy Division has worked closely with ATP awardee MicroFab Technologies, with whom we have a CRADA, and the various companies of the Solder Jet Consortium, including Delco Electronics, AMP, Universal Instruments, Texas Instruments, Eastman Kodak, and Motorola. Through interactions with the Consortium, NIST scientists have been able to keep abreast of industry needs and have direct technology transfer to major players in microelectronics assembly.

Accomplishments:

The Metallurgy Division has collaborated with MicroFab and its customers in determining system requirements for reliable solder jet operation and for product (solder joint) performance. The Metallurgy Division has also provided guidance to MicroFab regarding metallization of nozzles for improved performance of solder jet devices.

Impact:

Processing windows for substrate temperature, jet height, etc., were found which allow necessary wetting of substrates but without excessive interfacial reaction. Certain conditions unfavorable to reflow were also found.

Analysis of reliability problems and recommendations by Metallurgy Division staff have contributed to an increase in solder jet lifetimes from less than 8 hours to more than one month, bringing the solder jet reliability into a commercially useful regime. The research by the Division has contributed directly to the commercialization of solder jet technology by MicroFab Technologies.

Outputs:

Presentations:

Gayle, F.W., "Solder Jetting - from Development to Application," presented to U.S. Senate Task

Force on Manufacturing, November 1, 1996

INTELLIGENT PROCESSING OF MATERIALS

Research activities in the Intelligent Processing of Materials (IPM) Program investigate the conversion of materials into value added products using model-based control of processing variables. The central elements of IPM are (1) process understanding expressed in terms of an advanced process model, (2) sensors capable of monitoring the condition of the processed material, not just its environment, (3) accurate thermophysical properties as needed for input to the process model, and (4) a model-based sensing and control strategy to achieve the desired characteristics in the finished product.

Many advanced materials have microstructures, and hence properties, which are highly sensitive to the conditions under which they are produced. While it is possible to construct process models on the basis of empirical correlations between processing conditions and microstructures, such models will be unable to account for conditions or material compositions which lie outside the range of the empirical data. If, instead, the models are based on a detailed analysis of the development of material microstructure during processing, the models can be applied to a very wide range of compositions and processing conditions.

In the Metallurgy Division, a large IPM effort has been devoted to work with the aircraft engine industry under the NIST-led Consortium on Casting of Aerospace Alloys. Members of this Consortium include the leading aircraft engine manufacturers (GE Aircraft Engines and United Technologies - Pratt & Whitney), their suppliers of high-quality castings (Howmet Corp. and PCC Airfoils) and the producer (UES, Inc.) of ProCAST™ software for the modeling of casting, as well as several universities. This Consortium's activity is closely coordinated with that of the DARPA-sponsored Investment Casting Cooperative Arrangemant (ICCA), which has also promoted the use of modeling to improve casting quality. The Casting Consortium activity includes four porjects in the Metallurgy Division, described below, as well as a project on X-ray Diffraction Sensing of Solid-Liquid Interfaces in the Materials Reliability Division and a project on Low-sulfur Standards for Superalloys in the Analytical Chemistry Division of the Chemical Science and Technology Laboratory. Each of these projects is closely coordinated with the activities of one or more of the industrial members of the Consortium. The central goal of the Consortium's activities is to greatly increase the capacity of modeling software to predict critical microstructural features of aerospace castings, and to make this enhanced capacity available to the industrial users by incorporating it into the ProCAST™ software.

The fifth Metallurgy Divison IPM project develops magnetic sensor technology which can be used on-line for measurement of mechanical properties of sheet steel. By detecting variations in the mechanical properties of the steel without the need for actual mechanical tests, such sensors can provide warning of possible formability problems.

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

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

Objectives:

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

Technical Description:

This project provides a method to predict the fraction solid (and heat content) vs. temperature relationship for multicomponent superalloys. This information is necessary for accurate macroscopic heat flow modeling of castings used to determine soundness. The information and solidification models produced in this project also predict the identity and volume fraction of all phases present in the casting microstructure. For ease of application, the solidification models are provided in a form compatible with software used by the aerospace industry. A combination of multicomponent phase diagram calculations with a kinetic analysis of solidification microsegregation is being applied to superalloys to predict the phases that will form, and these predictive models are being implemented into a commercial software code for castings as part of the NIST Consortium on Casting of Aerospace Alloys.

Planned Outcome:

This project will result in the availability of a thermodynamic data base for Ni-base superalloys, which can be used for the calculation of phase equilibrium information required for the solidification models. These will be coupled with solidification kinetic models for multicomponent superalloys to treat the dendritic aspects of solidification. To make these models available to industrial users, they will be integrated into commercial casting software.

The data bases and models produced by this project are planned to provide a comprehensive system that industry can use for design of aerospace castings. Availability of alloy phase diagram and solidification path information, especially in commercial software used by the aerospace industry, aids in casting design and promotes manufacturing efficiency. Improved quality of simulation of investment castings by industry will provide more reliable prediction of casting defects and reduce casting reject rates, thus reducing manufacturing costs.

External Collaborations:

The phase diagram data are being developed in collaboration with the University of Wisconsin-Madison and the University of Florida. Integration of the models into commercial software is being carried out in collaboration with UES, Inc. Howmet Corp. has interacted strongly on the choice of important alloy systems and evaluation of the output from the models. Data generated by this project has served as input to models of macrosegregation and fluid flow processes being developed at the Universities of Arizona and Iowa.

Accomplishments:

As part of the Consortium on Casting of Aerospace Alloys, NIST developed phase diagram subroutines that are being used within commercial casting simulation software. These sub-routines have been modified to predict the enthalpy vs. temperature relation during solidification and to utilize existing commercial thermodynamic databases for Al, Fe, Ti and Ni-base alloys. An additional thermodynamic database for Ni-base superalloys that contain elements such as Ta and Re is also being constructed. Such a data base is required to treat single-crystal alloys now favored by industry for blades and vanes in aero- and land-based turbines. This work combines NIST, University of Florida, and University of Wisconsin-Madison research. Current progress includes a treatment of the elements Ni-Al-Cr-Ta-Re. Next year the elements Ti, Co, W, Mo, Nb, and Hf will be added to the data base. Use of these data bases is reducing the quantity of alloy specific data that a simulation software user must either find or guess in order to model a casting.

Outputs:

Publications:

M.C. Schneider, J.P. Gu, C. Beckermann, W. J. Boettinger and U.R. Kattner,"Modeling of Micro-Macrosegregation and Freckle Formation in Single-Crystal Nickel-Base Superalloy Directional Solidification," Met. Mat. Trans. A, 28A 1517-1531.

D. K. Banerjee, M. T. Samonds, U. R. Kattner and W. J. Boettinger,"Coupling of Phase Diagram Calculations for Multicomponent Alloys with Solidification Micromodels in Casting Simulation Software," Solidification Processing, 1997, edited by J. Beach and H. Jones, Department of Engineering Materials, University of Sheffield, UK 1997, p.354.

F. Zhang, S.L. Chen, Y.A. Chang and U.R. Kattner,"A Thermodynamic Description of the Ti-Al System," Intermetallics, submitted Nov. 1996.

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

Poster:

U.R. Kattner, "Phase Diagram Activities in the Metallurgy Division of NIST", CALPHAD XXVI, Palm Coast, FL, May 1997.

Presentations:

W. J. Boettinger, "Overview of Modeling the Solidification of Cast Alloys," at the Institute for Theoretical Physics Workshop, Quantitative Methods in Materials Research, University of California at Santa Barbara, Jan.27, 1997.

W. J. Boettinger, "Multicomponent Alloy Solidification," Annual Meeting, Consortium on Casting of Aerospace Alloys, NIST, April 21, 1997.

W. J. Boettinger, “Modeling of Superalloy Investment Castings: NIST - Industry Consortium”, April American Physical Society Meeting, Washington, DC, April 21, 1997.

W. J. Boettinger, “Coupling of Phase Diagram Calculations for Multicomponent Alloys with Solidification Micromodels in Casting Simulation Software”, CALPHAD ‘97, Palm Coast, FL, May 14, 1997.

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

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

Objectives:

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

Technical Description:

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

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

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

Planned Outcome:

This project will result in guidelines and models which can be used by the casting industry to predict when certain types of grain defects will form. The work will provide a method for predicting the thermal conditions at the solidification front which result from transient growth behavior as the dendrites propagate around corners and edges of the casting. The ability to predict defect formation by processes such as nucleation will depend in part on the outcome of other studies which are attempting to quantify the nucleation behavior of superalloys. The models developed in this project will provide predictive capability beyond that which is possible with models which are based solely on the local conditions within the casting.

External Collaborations:

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

Accomplishments:

A laboratory analysis of several superalloy single-crystal test castings was conducted. The castings were produced by Howmet Corp. to study the effects of mold geometry on the development of grain defects, such as spurious grains, low angle boundaries, and freckle grains. Optical metallography and x-ray topography revealed several defect forming tendencies associated with geometric features of the castings. Spurious grains were identified in some areas where the undercooling may have become relatively high before the arrival of the solidification front. Low-angle boundaries were observed in virtually all regions of the castings and may be attributed to a number of sources. A mold wall anomaly in the expansion zone is one such example. In the bulk, most of these boundaries resulted from extended growth of a freckle grain. The complex geometry of the platform region also caused the formation of low-angle boundaries as the nonplanar growth front advanced through a tortuous growth path. These analyses provided guidance for the development of models for defect prediction.

The Growth-Path method was developed to predict when conditions in the casting will be favorable for spurious grain nucleation. This method incorporates thermal simulation results and the anisotropic growth kinetics of a dendritic front to compute the time-minimized path to any given location in a 3-dimensional casting. Experimental nucleation data or an analytical nucleation rate expression can then be used to quantify the nucleation tendency along the path. The unique feature of the method is that the complete time-temperature history is accounted for. Additionally, the computation is time-efficient, since it need only be performed for a limited number of paths, eliminating the need for slower front-tracking methods.

A lattice model for single crystal dendritic growth was also developed, to predict the detailed features of a dendritic array as it progresses through a mold. The solid is modeled as an interconnected array of "needles" where the tips are tracked on a square lattice. The needles grow according to the local temperature and a specified relationship governing dendrite tip kinetics. New tips are generated according to a branch criterion, and each branching event results in four new tips which behave independently, according to their local conditions. The model provides a 3-dimensional map of local primary direction, the instantaneous shape of the growth front during solidification, a connectivity parameter for the dendritic network, a 3-D map of undercooling at the time of solidification, and a 3-D map of nucleation tendency, calculated in a fashion similar to that described for the Growth-Path method. Many features observed in the test casting have been reproduced using this model.

Outputs:

Publications:

Schaefer, R. J., Black, D. R., Vaudin, M. D., Mueller, B. A., and Giamei, A. F., "Geometry and Mechanisms of Dendrite Misalignments in Superalloy Single Crystals," pp. 37-40 in Solidification Processing 1997, ed. J. Beech and H. Jones, University of Sheffield (1997).

Presentations:

Schaefer, R. J., " Defect Formation Models," NIST Consortium on Casting of Aerospace Alloys Semi-Annual Meeting, Howmet Corp., Whitehall, MI, November, 1997.

Napolitano, R. E. and Schaefer, R. J., "Defect Formation near Corners and Edges," ICCA/NIST Annual Program Review, NIST, April 1997.

Project Title: **POROSITY IN CASTINGS**

Investigators: R. J. Schaefer, W. J. Boettinger, and R. D. Jiggetts

Objectives:

This project seeks to help the metal casting industry understand the origin and effects of porosity in aluminum die castings by characterizing the distribution and geometry of the porosity. It also seeks to develop a predictive model for microporosity formation during directional solidification through an analysis of the alloy solidification path and the flow of liquid metal through the mushy zone.

Technical Description:

Porosity is a common feature of metal castings, which may or may not be harmful depending on its location, size, and connectivity. In addition to mechanical weakening of a component, porosity may cause leakage in parts intended for hydraulic applications and may cause unacceptable roughness in machined surfaces. For some applications, small pores within the interior of a part may not interfere with the part's function, and there is then no need to eliminate them. Understanding the location and geometry of porosity may thus be critical.

The major sources of porosity in cast parts are the reduction in volume which occurs when a liquid metal solidifies, the presence of gas dissolved in the molten metal, and air trapped within the metal during filling of the mold. The importance of these sources varies greatly depending on the casting method, the part geometry, and the alloy composition. In many cases it is difficult to determine which of these sources is responsible for the porosity in a given set of castings. It is also difficult to understand the true geometry of porosity because a large interconnected network of interdendritic porosity will generally appear in a polished cross section as an array of small round pores. Better understanding of the nature and geometry of porosity and better models to predict porosity formation would both help the metal casting industry control the distribution and amount of porosity and thus reduce the number of rejected parts.

This project has used experimental and theoretical tools to study porosity: the former consists of the use of hot isostatic pressing (HIP) to analyze the connectivity of pores within castings, and the latter is the use of modeling to predict microporosity by an analysis of fluid flow through the alloy mushy zone to feed solidification shrinkage.

The porosity in castings can often be closed by the HIP process in which the casting is subjected to a high pressure gas at elevated temperature. However, this is effective only if the pores themselves are not pressurized via a connection to the surface of the casting. Examination of porosity in a HIPed casting can thus give an indication of how much of the porosity is not closed and therefore is presumably connected to the surface. This method is not effective, however, if the pores themselves contain gas which prevents their closure even if not connected to the surface. In this case, a heat treatment at the same temperature used in the HIP process but without the applied pressure can cause "blistering" of the casting, in which pores close to but not connected to the surface expand to form a visible lump on the casting surface. Thus heating of the casting with and without pressure can provide a variety of information on the connectivity and gas content of the pores.

Modeling of microporosity requires and accurate description of the pressure at each point in the liquid in the mushy zone of a casting. The pressure varies due to the fluid flow required to feed the solidification shrinkage. A fluid flow calculation is therefore necessary. Such a calculation requires a knowledge of the density of the liquid and solid as a function of temperature and liquid or solid composition, a description of the solidification path (temperature and composition of liquid and solid as a function of fraction solid) and a description of the permeability of the mushy zone. Since this model is being developed primarily for application to superalloys, the effects of dissolved gases are neglected. Porosity occurs when the pressure drops below a critical negative value.

Planned Outcome:

This project provides an evaluation of HIP as a diagnostic tool in the analysis of porosity in castings, particularly as a tool for determining the connectivity of porosity to the surface, which is a critical question for castings intended for hydraulic applications. Successful application of such a tool could provide guidance to die casters in how to minimize the deleterious effects of porosity.

The project will provide a predictive tool for microporosity formation which will, for the first time, account for the detailed effects of alloy solidification behavior and not require the use of empirical parameters.

External Collaborations:

The experimental part of this project was carried out in collaboration with The Top Die Casting Company, recipients of an ATP award (joint venture with Allied Signal and Stahl Specialty Company) for reduction of defects in aluminum castings. Top Die provided the castings used in this study and radiographs showing where some of the major porosity was located.

The modeling of porosity is carried out in collaboration with the members of the Consortium on Casting of Aerospace Alloys.

Accomplishments:

Metallographic analysis of die castings heated at a range of temperatures and pressures showed that most of the porosity in these castings contains gas. This, and the size and location of the pores, confirmed the conclusion of Top Die that the major source of porosity in these castings was gas trapped during filling of the die. When Top Die used an evacuated die, this source of porosity was greatly reduced, but the remaining pores still contained significant gas pressure. Nonetheless, it was still possible to conclude from the HIP experiments that clusters of micropores in the castings had typical dimensions of 250 to 500 µm.

A model for microporosity formation was developed, based on flow of liquid through the mushy zone to feed solidification shrinkage. The model calculates the mass fraction of liquid and solid, the composition of the liquid and the average composition of the solid as functions of the temperature. It then calculates the fluid flow and pressure drop in the mushy zone and the fraction of porosity based on the assumption that pores form when the pressure drops to zero. Calculations of fraction porosity as a function of temperature were carried out for a typical superalloy composition. Using the Scheil model of solidification (complete mixing in the liquid, no diffusion in the solid), the model predicts porosity to form more than 50°C above the temperature at which the last liquid remains. In contrast, the simpler but unrealistic lever law of solidification predicts no porosity.

Impact:

The experiments at NIST supported Top Die Company's interpretation of the origin of porosity in their castings, on the basis of which they modified their casting practice in such a way that they greatly reduced the number of rejects.

The model for microporosity formation provides a means of predicting porosity distribution without the need for empirical criteria containing numerical parameters which must be evaluated for each alloy. It has predictive capability to account for the variable tendency for porosity formation between different alloy compositions. UES, Inc. is now working to use this model in conjunction with their commercial ProCAST™ software for modeling investment castings.

Outputs:

Presentations:

Boettinger, W. J., "Microporosity Modeling," Annual Meeting, Consortium on Casting of Aerospace Alloys, NIST, April, 1997.

Project Title: **THERMOPYSICAL DATA FOR CASTINGS**

Investigators: A. Cezairliyan, J. McClure, and D. Basak

Objectives:

The objective of this project is to obtain accurate thermophysical properties data on selected multicomponent nickel and titanium based alloys of technological interest, primarily those used in the aerospace industry, in support of modeling of casting processes.

Technical Description:

This project is focused on the accurate determination of selected thermophysical properties of high temperature alloys of technological interest, particularly nickel and titanium based superalloys, important to the NIST Consortium on Casting of Aerospace Alloys. Millisecond- and microsecond-resolution pulse-heating techniques are used to make measurements in both solid and liquid phases up to about 300 K above their melting region. Work focuses primarily on measurements of selected key properties, such as enthalpy, specific heat capacity, heat of fusion, electrical resistivity, hemispherical total emissivity, and normal spectral emissivity.

Planned Outcome:

A database will be generated for selected thermophysical properties of nickel and titanium based alloys in both solid and liquid phases near the melting region.

Demonstration, for the first time utilizing optical techniques (radiometric and polarimetric), of the heating rate dependence of the melting behavior of an alloy will expand our understanding of the fundamental processes involved in melting of alloys.

External Collaborations:

A titanium alloy, Ti-6242, of interest to the aerospace industry was provided by Howmet, a leading company in casting of aerospace alloys. Discussions were held with the manufacturers of aircraft engines, such as General Electric and Pratt and Whitney, in relation to the properties of alloys used in aircraft engines. Measurement problems were discussed with the members of the Space Power Institute at Auburn University in relation to thermophysical properties of aircraft engine materials.

Accomplishments:

Definitive measurements of the properties (enthalpy, specific heat capacity, electrical resistivity, hemispherical total emissivity, and normal spectral emissivity) of a titanium alloy, Ti-6242, were made in the solid phase near the melting region. Accurate data on this alloy will be used by producers of aerospace alloy castings in modeling of casting processes.

For the first time, optics-based (radiometric and polarimetric) experiments were conducted to study the effect of heating rate on the melting behavior of the binary alloy 53Nb-47Ti (mass %). The heating rate ranged from 100 to 12,000 K/s. The results show that the onset of melting of the alloy, in contrast to pure metals, depends significantly on heating rate. Measurements designed to determine the source of the heating rate effect will continue to include both lower and higher heating rates than those used so far in order to clarify the source of the heating rate effect.

Impacts:

Thermophysical properties of alloys such as IN718, measured earlier in this project, are now available to the industrial members of the Casting Consortium and have been used by them in their simulations.

Outputs:

Publication:

Cezairliyan, A., Boettinger, W. J., Basak, D., Josell, D., and McClure, J. L., "Effect of Heating Rate on the Melting Behavior of the Alloy 53Nb-47Ti (Mass %) in Rapid Pulse-Heating Experiments," Int. J. Thermophys., in press.

Presentation:

Cezairliyan, A., "Thermophysical Properties of Aerospace Alloys," Annual Meeting of the Consortium on Casting of Aerospace Alloys, Gaithersburg, Maryland, April, 1997.

Project Title: **MAGNETICS FOR STEEL PROCESSING**

Investigators: F. Biancaniello, G. E. Hicho, L. J. Swartzendruber, and F. Bendec (Guest Researcher, Nuclear Research Centre, Negev, Israel)

Objectives:

The project seeks to provide U.S. industry with a scientific basis for the development of magnetic sensors to monitor the uniformity of mechanical properties of sheet steels as they are processed and to serve as a quality control device for the user.

Technical Description:

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

Planned Outcome:

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

External Collaborations:

Professor Harsh D. Chopra of Dartmouth College is a co-investigator on this project. He has performed the domain size/dislocation determination on the strained low carbon steel. NIST has provided strained samples and Professor Chopra has used a high resolution interference colloidal contrast technique to reveal the fine intra-grain magnetic domain structure.

Accomplishments:

The effect of plastic strains on the magnetic and mechanical properties were determined for a commercial ultra low carbon sheet steel. It was shown that, for plastic strains up to 10%, a linear relationship can be established between magnetic and mechanical properties.

Impact:

Our results on the effect of strain on magnetic properties of steel are being used by Materials Innovation (a U.S. company) to help develop new materials for use in electric motors.

Outputs:

Publications:

Swartzendruber, L. J., Hicho, G. E., Chopra, H. D., Leigh, S. D., Adam, G., and Tsory, E., "Effect of Plastic Strain on Magnetic and Mechanical Properties of Ultralow Carbon Sheet Steel," J. Appl. Phys. **81**, 4263 (1997).

Presentations:

Swartzendruber, L. J., Hicho, G. E., and Chopra, H. D., "Relationship Between Yield Stress and Magnetic Properties in Plastically Deformed Low Carbon Sheet Steel," Bulletin of the American Physical Society, vol. 42, p. 563, March 1997.

Patents Granted:

Steel Hardness Measurement System and Method of Using Same
Gabe Kohn, George Hicho, and Lydon Swartzendruber
U.S. Patent No. 5,619,135 issued 4/8/97

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, analysis of the durability and performance of magnetic devices and development of standard reference materials are key elements of this program. Some information is only obtainable by the use of unique measurement tools at NIST like the Center for Neutron Reseach facility, 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 requires new physical models or a logical extension of large-size behavior to small dimensions. Consequently, implementation of this new type of material into marketable products is significantly delayed. NIST is providing the measurement science to address this critical unknown.

Areas of present study include the following:

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

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

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

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

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

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

Project Title: **GIANT MAGNETORESISTANCE MATERIALS**

Investigators: W. F. Egelhoff, Jr., P. J. Chen (guest researcher),

Objectives:

The objective of this program is to provide assistance to U.S. companies in the magnetic data-storage industry so that they can operate successfully in the increasingly competitive world market. We have constructed an elaborate new fabrication and measurement facility to allow us to reach this objective. No facility of such complexity exists anywhere else in the world. Our work provides U.S. companies with a significant competitive edge by investigating the science underlying the manufacturing process, something these companies cannot do on their own.

Technical Description:

The magnetic data-storage industry is a major force in today's economy representing over $80 billion in annual sales, worldwide. The U.S. has a strong position in that industry, but intense competition from overseas industries, especially Japan, has put the U.S. position at risk. In our work we have focused on one material of key importance to this industry, a new class of magnetic materials which have a property known as the Giant Magnetoresistance (GMR) Effect.

These materials will be used in the next generation of hard-disk drives and possibly in computer memory chips. These materials are the focus of intense research and development efforts at companies as wide-ranging as IBM, Kodak, Sony, Toyota, and Honeywell (to name only a few). However, NIST's measurement and characterization capabilities greatly enhance the understanding of the science underlying the manufacturing process.

To address this need NIST set up a major new research program specifically aimed at providing the scientific understanding and measurement capability needed to allow U.S. industry to make the best GMR materials in the world. This program was centered on a new facility, known as the Magnetic Engineering Research Facility (MERF), which is the most completely 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 research is anticipated to help make U.S. companies the world leaders in this field of GMR materials. These companies are eagerly looking forward to working with us to transfer the improved manufacturing processes that we have developed into their production facilities. In fact, the process has already begun in the form of visits by NIST staff to the affected companies to discuss implementation of the NIST ideas. Unfortunately, this implementation has turned out not to be a trivial matter because the companies are locked into their first-generation production facilities. However, we are already working with these companies and with the manufacturers of production equipment to get the NIST ideas incorporated in second-generation production facilities.

External Collaborations:

We have collaborated with a number of companies in the area of GMR materials, including Hewlett-Packard, Motorola, IBM, Nonvolatile Electronics, Read-Rite, Quantum, Honeywell, Integrated Microtransducer Electronics, and Advanced Research Corporation and with a number of university groups, including those of Prof. Falco, U. of Arizona, Prof. Gomez, U. of Maryland, Prof. Berkowitz, U. C., San Diego, Prof. Kryder, Carnegie Mellon, and Prof. Judy, U. of Minnesota. We have also collaborated in this effort with W. H. Butler at the Oak Ridge National Laboratory. In all cases, either we have been making samples for these collaborators to analyse in their facilities or we have been examining their samples in our facilities.

Accomplishments for FY 1997:

- The Magnetic Engineering Research Facility (MERF) at NIST, the most completely instrumented thin-film deposition facility in the world, was maintained at an operational status of approximately 90% of available time, meaning the facility was down only 10% of the time.

- Once again this year, research at MERF set a new record for the largest value ever recorded in the type of material (a spin valve with one Cu layer) best suited to commercial products.
- It was discovered that specular electron scattering at the top and bottom surfaces of a spin valve plays a key role in achieving the largest possible GMR values.
- Two methods for increasing specular electron scattering were found. One is to deposit a film of Cu, Ag, or Au two atomic layers thick on top of the spin valve. The other involves depositing the spin valve in a partial atmosphere of oxygen. The oxygen atoms on the surface of the growing films act as a surfactant to produce a smoother surface.
- 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 through numerous publications in industry-focussed periodicals.

Impact:

The information on our record-setting results has been transferred to our collaborators at Motorola, IBM, Seagate, Hewlett-Packard, Nonvolatile Electronics, and Read-Rite. These collaborators are attempting to implement our findings in their production equipment. As far as we can determine, our latest results are not widely known. This advance knowledge together with our supporting consultations, is giving U.S. companies a head start in developing the next generation of production facilities.

Outputs:

Publications:

Egelhoff, W. F., Jr., Chen, P. J., Powell, C. J., Stiles, M. D., McMichael, R. D., Lin, C. L., Sivertsen, J. M., Judy, J. H., Takano, K., and Berkowitz, A. E., "The Growth of GMR Spin Valves using Pb and Au as Surfactants," J. Appl. Phys. 80, 5183 (1996).

McMichael, R. D., Watanabe, T., Dura, J. A., Borchers, J. A., Egelhoff, W. F., Jr., Chen, P. J.,and H. J. Brown, "Origins of the Coercivity Increase in Annealed Symmetric Spin Valves", IEEE Trans. Mag. 32, 4636 (1996).

Chopra, H. D., Hockey, B. J., Chen, P. J., McMichael, R. D., and Egelhoff, W. F., Jr., "Nanostructure, Interfaces, and Magnetic Properties in Giant Magnetoresistance NiO-Co-Cu-based Spin Valves," J. Appl. Phys. 81, 4017 (1997).

V. I. Nikitenko, V. S. Gornakov, L. M. Dedukh, Yu. P. Kabanov, L. H. Bennett, W. F. Egelhoff, Jr. P. J. Chen, R. D. McMichael, M. J. Donahue, L. J. Swartzendruber, A. J. Shapiro, and H. J. Brown ,"Magneto-optical Indicator Film Study of the Magnetization of a Symmetric Spin Valve," IEEE Trans. Mag. 32, 4639 (1996).

Hua, S. Z., Lashmore, D. S., Swartzendruber, L. J., Egelhoff, W. F., Jr., Raj, K. and Chopra H. D., "Observation of Domain Dynamics in GMR Co/Cu-based Polycrystalline Multilayers,

"J. Appl. Phys. 81, 1 (1996).

V. S. Gornakov, V. I. Nikitenko, L. H. Bennett, H. J. Brown, M. J. Donahue, W. F. Egelhoff, Jr., R. D. McMichael, and A. J. Shapiro, "Experimental Study of Magnetization Reversal Process in a Non-symmetric Spin Valve," J. Appl. Phys. 81, 5215 (1996).

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

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

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

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

McMichael, R. D., Chen, P. J. and Egelhoff, Jr., W. F., "Magnetization Ripple in Exchange-Biased Thin Magnetic Films," IEEE Trans. Mag. submitted 1997.

Chopra, H. D., Hockey, B. J., Chen, P. J., Salamanca-Riba, L., Hua, S. Z., Wuttig, M. and Egelhoff, Jr., W. F., "Detailed Structural Characterization of Symmetric Spin Valves using High-Resolution Transmission Electron Microscopy," Phys. Rev. B. submitted 1997.

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

Egelhoff, Jr., W. F., "Fluorine as a Surfactant for a Monolayer of Iron on Cu(100)," submitted to Proceedings of the 17th European Conference on Surface Science.

Presentations

*Egelhoff, Jr., W. F., "Recent Studies of GMR Multilayers at NIST," National Storage Industry Consortium Quarterly Workshop, Pittsburgh, October 3, 1996.

*Egelhoff, Jr., W. F., "Optimizing the Performance of GMR Spin Valves," 43rd National Symposium of the American Vacuum Society, Philadelphia, October 16, 1996.

*Egelhoff, Jr., W. F., "Recent Progress in GMR Spin Valves at NIST," DARPA/Motorola

Quarterly Workshop, Atlanta, November 11, 1996.

*Egelhoff, Jr., W. F., "Strategies for Achieving Large GMR at Low Switching Fields," DARPA GMR Modeling Workshop, Charlottesville, December 1, 1996.

*Egelhoff, Jr., W. F., "The Role of Specular Electron Scattering in GMR Spin Valves," Surface Science Lunch Lecture Series, NIST, January 6, 1997.

*Egelhoff, Jr., W. F., "The Role of Specular Electron Scattering in GMR Spin Valves, Part II," National Storage Industry Consortium Quarterly Workshop, San Diego, January 16, 1997.

*Egelhoff, Jr., W. F., "Optimizing the Growth of GMR Spin Valves," IBM Research Labs, Yorktown Heights, January 24, 1997.

*Egelhoff, Jr., W. F., "The Role of Specular Electron Scattering in GMR Spin Valves," DARPA/Motorola Quarterly Workshop, Phoenix, February 7, 1996.

*Egelhoff, Jr., W. F., "Optimizing the Growth of GMR Spin Valves," Physics Department, Univ. of Alabama, Tuscaloosa, March 5, 1997.

*Egelhoff, Jr., W. F., "Surface Effects in the Growth of GMR Spin Valves," Physics Dept., Louisiana State University, Baton Rouge, March 31, 1997.

Egelhoff, Jr., W. F., "The Role of Specular Electron Scattering in GMR Spin Valves," International Conference on Magnetics, New Orleans, April 2, 1997.

*Egelhoff, Jr., W. F., "The Role of Specular Electron Scattering in GMR Spin Valves, Part III," National Storage Industry Consortium Quarterly Workshop, Boulder, April 16, 1997.

*Egelhoff, Jr., W. F., "The Role of Specular Electron Scattering in GMR Spin Valves," IBM Almaden Labs, San Jose, April 18, 1997.

*Egelhoff, Jr., W. F., "The Role of Specular Electron Scattering in GMR Spin Valves," Physics Dept., Univ. of Md., College Park, May 2, 1997.

*Egelhoff, Jr., W. F., "Surface Effects in the Growth of GMR Spin Valves," American Vacuum Society Meeting, Albuquerque, May 21, 1997.

*Egelhoff, Jr., W. F., "The Effect of Impurities on the Properties of GMR Spin Valves," CEA-Saclay, Orsay Cedex, France, May 29, 1997.

*Egelhoff, Jr., W. F., "Optimizing the Growth of GMR Spin Valves," Cavendish Laboratory, Cambridge University, England, June 5, 1997.

*Egelhoff, Jr., W. F., "Recent Progress in GMR Spin Valves at NIST," Motorola Corporate Research Labs, Phoenix, June 17, 1997.

*Egelhoff, Jr., W. F., "Optimizing the Growth of GMR Spin Valves," National Storage Industry Consortium Annual Review, Monterey, June 18, 1997.

*Egelhoff, Jr., W. F., "Recent Progress in GMR Spin Valves at NIST," DARPA/Motorola Quarterly Workshop, August 1997.

*Egelhoff, Jr., W. F., "Surfactants in Metal-on-Metal Epitaxy," FOM Institute, Amsterdam, The Netherlands, September 15, 1997.

*Egelhoff, Jr., W. F., "Surfactants in Metal-on-Metal Epitaxy," 18th European Conference on Surface Science, Twente, The Netherlands, September 16, 1997.

____

* Invited talks

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

Investigators: R. D. McMichael, H. J. Brown, D. E. Mathews

Technical 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 control of the processing and micromagnetics of thin magnetic films. Specifically, this project is concerned with the thermal stability of "spin valve" multilayer films during elevated temperature processing steps, the micromagnetics of the ferromagnet/antiferromagnet interface in exchange biased layers, and the control of magnetic domain structure through lithographic patterning.

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

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

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

Planned Outcome:

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

External Collaboration:

This project was done in collaboration with the companies and universities of the National Storage Industry Consortium, NSIC/ATP Heads Project, and was supported through an intramural grant from the ATP Office. The NSIC members involved in this project were Applied Magnetics Corporation, U. Cal. San Diego, U. of Alabama, U. of Minnesota, Carnegie Mellon U., George Washington U., Headway Technologies, Hewlett-Packard, IBM, Kodak, Nonvolatile Electronics, Quantum, Read-Rite Corp., Seagate, Stanford U., Washington U., and New York U. The ATP funding for NSIC work ended in July 1997.

Accomplishments:

- We developed a method for characterizing the reversible and irreversible temperature dependence of spin valve magnetoresistance that involves measurement of magnetoresistance (R vs. applied field) at increasingly elevated temperatures and at room temperature following each heating. The measurements at high T reflect both reversible and irreversible changes, while the room T measurements reflect only irreversible changes as a function of annealing temperature. This method, and data for Co/Cu/Co spin valves with different protective cap layers was presented at the INTERMAG conference, and at NSIC quarterly meetings.
- We also developed a method for characterizing the rate at which irreversible changes take place at the elevated temperatures. This method involves monitoring the sample resistance as a function of time. In some samples, the resistance changes were found to fit an Arrhenius law model, and in these samples, the Arrhenius law parameters also predicted the temperature dependence of the magnetoresistance of the films, allowing predictions of sample lifetime at lower temperatures. This method, and results on several samples were presented at an NSIC quarterly meeting and a paper has been submitted for presentation at the Joint MMM/INTERMAG conference.
- Using ferromagnetic resonance measurements, we have shown that in addition to the

exchange bias field, there is an additional stabilization effect for small perturbations to the magnetization. This additional stabilization is isotropic and "follows" macroscopic motion of the magnetization. We have also shown that damping of the magnetization motion is greater when the magnetization lies in the plane of the film, in accord with the two-magnon theory of FMR damping.These results were presented at the INTERMAG meeting, and will be further reported at the MMM/INTERMAG meeting.

- We have proposed a standard problem for micromagnetics for use in comparing computational techniques. We have collected seven anonymous solutions with disturbingly different results.
- We have shown via micromagnetic computations that it is possible to use the shape of a thin film element to nucleate and trap a transverse wall and to move it from one end of the trap to the other. The transverse wall was discovered in this project in FY96, and was presented at the INTERMAG conference, and in a published paper. The trapping results are preliminary and have not yet been publicized.

Impact:

In an excerpt from the NSIC quarterly report, May 2, 1995, Jim Brug of Hewlett-Packard wrote: "Bob McMichael has been pushing on an area that is really important for industry in the understanding of the temperature stability of the thin films used in the multilayers. By now everyone is convinced of the advantages of the films for recording, but everyone is nervous about how well they will hold up running at elevated temperatures in devices. His work on annealing various types of GMR films to explore how the coercivity increases and the dR/R decreases is exactly what is needed to make these films useful." Representatives of other companies, including Sining Mao of Seagate, have indicated their belief that NIST's work on thermal stability was important to their research and development efforts, although it is difficult to quantify NIST's impact.

Outputs:

Publications:

M. J. Donahue and R. D. McMichael, ``Exchange energy representations in computational micromagnetics," Physica B, v. 233, p. 272, (1997).

R. D. McMichael and M. J. Donahue, ``Head to head domain wall structures in thin magnetic strips," IEEE Trans. MAG, v. 33, p. 4167 (1997).

R. D. McMichael, P. J. Chen, and W. F. Egelhoff, Jr., ``Anomalous properties of spin valves and elevated temperatures," IEEE Trans. MAG, v. 33, p. 3589 (1997).

R. D. McMichael, M. J. Donahue, ``Micromagnetic computational standard problem (abstract)," J. Appl. Phys., v. 81, p. 5242 (1997).

Presentations:

R. D. McMichael, ``Head-to-Head Domain Walls in Thin Magnetic Stripes," J19-5, APS March Meeting, March 19, 1997, Kansas City.

M. J. Donahue, ``Head-to-Head Domain Walls in Thin Magnetic Stripes," GC-07, INTERMAG '97, April 4, 1997, New Orleans.

R. D. McMichael, ``Ferromagnetic Resonance Studies of NiO-coupled Thin Films of Permalloy and Cobalt," BQ-15, INTERMAG '97, April 1, 1997, New Orleans.

R. D. McMichael, ``Anomalous Properties of Spin Valves at Elevated Temperatures," EA-05, INTERMAG '97, April 1, 1997, New Orleans.

*R. D. McMichael, ``Nanoscale Micromagnetics," Joint NSF-NIST Conference on Nanoparticles, National Science Foundation, 12-13 May, 1997, Arlington, VA

R. D. McMichael, ``Reversible/irreversible temperature dependence in spin valves and Ripple in NiO-pinned films" NSIC/HEADS quarterly meeting, Oct 2, 1996, Carnegie Mellon U., Pittsburgh, PA.

R. D. McMichael, ``Update on Thermal Stability in Spin Valves, "NSIC/HEADS quarterly meeting, April 15, 1997, NIST, Boulder, CO.

R. D. McMichael, ``Breakthrough in Thermal Stability: Spin-valves that beat the heat," NSIC Heads meeting, Jan 17, 1997, UCSD, La Jolla, CA.

R. D. McMichael, ``Time dependence of resistivity and GMR lifetime in spin valves" NSIC Annual meeting, 19 June, 1997, Monterey, CA.

---

* Invited presentation

Project Title: **MAGNETIC PROPERTIES OF NANOMATERIALS**

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

Objectives:

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

Technical Description:

Since the magnetic behavior of nanomaterials is largely unknown, much of the focus in this effort is directed toward measuring the magnetic characteristics of this new class of materials and checking if they are consistent with present theories explaining the behavior in conventional materials. For instance, it is not known whether magnetic domains, a characteristic feature of conventional ferromagnets, even exist in nanocrystalline or nanocomposite ferromagnets. 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 these materials. Consequently, efforts are ongoing to image the domain structure in these materials and their dynamics if they exist. Imaging by means of a ferrofluid decoration technique at domain walls as well as by means of a magneto-optic indicator film (the MOIF technique developed in our laboratory in collaboration with a group from Chernogolovka, Russia) on co-sputtered Ag-Co nanocomposites and electrodeposited nanocrystalline Ni is being pursued.

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 at NIST 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.

Flame processes have been shown to be a viable method for producing nanoscale magnetic oxide particles in a nonmagnetic matrix in the large quantities required by industry. However, the magnetic strength of such nanocomposites is inadequate, but could be increased sufficiently if the magnetic oxides were replaced by magnetic metals. Unfortunately, conventional flame processes use oxygen for burning, and fine metal particles quickly oxidize. Consequently, a special sodium flame process was developed in the Process Measurements Division of CSTL, and in collaboration with that division an attempt was made to prepare Fe/salt nanocomposites. It was anticipated that encapsulation of the Fe by salt would protect the metal from subsequent reaction with air.

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

Planned Outcome:

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

External Collaborations:

In collaboration with the University of Toronto (U. Erb) and the University of Saarlandes (J. Weissmueller), SANS measurements were performed on electrodeposited nanocrystalline Ni. In this collaboration U. Erb provided the samples and J. Weissmueller analyzed the SANS measurements. In a collaboration with the Russian Academy of Sciences at Chernogolovka, Russia (V. Nikitenko), a special magnetic domain imaging technique called MOIF has been developed. This technique has been used jointly to image several nanocrystalline and nanocomposite materials. R. Shull was elected as the Vice Chairman of the International Committee on Nanostructured Materials. An interagency group comprised of NIST, NSF, ONR, DOC/TA, AFOSR, NIH, and NASA was organized this year for assessing the status and trends in nanoparticles, nanostructured materials, and nanodevices; R. Shull was one of the organizing members.

Accomplishments in FY1997:

- The first SANS (small angle neutron scattering) data were measured on a magnetic nanocrystalline material, 20 nm grain-size Ni, containing a very small number of pores and thereby possessing a majority scattering which is of magnetic origin. The scattering was described well by a random magnetic anisotropy model which was independently developed to explain magnetic domain motion. Surprisingly the SANS analysis showed no correlation length comparable to the grain diameter, indicating magnetic direction fluctuations which do not scale with changes in magnetocrystalline anisotropy axes. Instead the correlation length scaled with the magnitude of the magnetic field.
- Magnetic domains were for the first time observed in a pure nanocrystalline material, 20 nm grain size Ni, using a ferrofluid decoration technique. Their walls were observed to be microns in length and unusually smooth in contrast to the very angular appearing domain walls in large-grained materials.
- In collaboration with the Process Measurements Division of CSTL, for the first time nanometer-sized Fe-containing particles encapsulated in salt were produced in a special flame process using a sodium flame. Mössbauer effect measurements unequivocally identified these metal-containing particles as pure Fe. Both large ferromagnetic particles and very small

superparamagnetic Fe particles were observed, with the superparamagnetic material comprising approximately 12% (by volume) of the Fe and being located in the NaCl coating of the large particles. This is one of the first results showing that the flame processing method can be used to produce unoxidized metals in nanometer sizes.

- A SBIR grant was awarded for the construction of a magnetic refrigerator using the results of NIST research on magnetic nanocomposite refrigerants the last few years.
- NIST was joined by NSF, ONR, DOC/TA, AFOSR, NIH, and NASA in sponsoring a world review of the status and trends in nanoparticles, nanostructured materials, and nanodevices. Key lead individuals were selected, a U.S. workshop was conducted, and foreign site visits were made in FY97. A report will be written in FY98.

Impacts and Technical Highlights:

NIST is now considered a leader in the fabrication and measurement of magnetic nanocomposite materials. 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.

Outputs:

Publications:

Shull, R.D., McMichael, R.D., Brown, H.J., Barker, J., Weissmueller, J., Erb, U., "Magnetic Microstructure of a Nanocrystalline Ferromagnet-Micromagnetic Model and Small-Angle Neutron Scattering," Nanophase and Nanocomposite Materials II, edited by S. Komarneni, J.C. Parker, and H. Wollenberger, MRS Symp. Proc. 457 (North Holland Publ. Co., N.Y., 1997) p. 231.

Shull, R.D., Yamamoto, T., Hahn, H.W.,"Magnetization of Iron-oxide/Silver Nanocomposites by Inert Gas Condensation," J. of Nanostructured Materials **9**, 539 (1997).

Presentations:

*Shull, R.D., "Applications of Magnetic Nanocomposites," Materials Research Society Fall Meeting, Boston, Massachusetts, December, 1996.

*Shull, R.D., "Magnetic Nanocomposite Refrigerants," IBM Almaden Laboratory Colloquium, San Jose, California, March, 1997.

*Shull, R.D., "Overview of NIST Activities," Joint NSF-NIST Conference on Nanoparticles: Synthesis, Processing into Functional Nanostructures, and Characterization, Arlington, Virginia, May, 1997.

*Shull, R.D., "Review of NIST Activities in Nanostructured Materials," WTEC Workshop on the Review of U.S. R&D Status and Trends in Nanoparticles, Nanostructured Materials, and Devices, NSF, Arlington, Virginia, May, 1997.

*Shull, R.D., "Properties of Nanostructured Magnetic Materials," Taipei International Symposium on Recent Trends in Technological Developments, Academia Sinica, Taipei, Taiwan, June, 1997.

*Shull, R.D., "Magnetic Properties of Nanocomposites," Fourth International Conference on Composites Engineering, Kona, Hawaii, July, 1997.

*Shull, R.D., "Properties and Applications of Magnetic Nanocomposites," NATO Advanced Study Institute on Nanostructured Materials: Science and Technology, St. Petersburg, Russia, August, 1997.

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

Shapiro, A.J., “Mössbauer Study of NaCl-coated Fe Nanoparticles,” International Conference on the Applications of the Moessbauer Effect ‘97, Rio de Janeiro, Brazil, September, 1997.

____
* Invited Presentations

METALS DATA AND CHARACTERIZATION

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

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

The measurements of microstructural, mechanical, chemical, and optical properties carried out under this program have an impact in a number of different technology sectors:

- Standard test methods are being developed to support the automotive industry in its effort to improve fuel efficiency by shifting to lighter materials, a shift which has highlighted the critical need for improved understanding and control of sheet metal formability. The Metallurgy Division's effort is being carried out in collaboration with the Manufacturing Engineering Laboratory's National Advanced Manufacturing Testbed (NAMT) program and with ATP-supported consortia of U.S. automakers and several universities.

- The accuracy of a high speed laser polarimeter technique for measuring the normal spectral emissivity of metals and alloys at high temperature has been demonstrated by measurements on a standard reference material (molybdenum). The millisecond resolution of the existing system is currently being upgraded to microsecond resolution, which should enable measurements extending to temperatures well above the melting point of refractory metals. These techniques provide industry with benchmark high temperature thermophysical properties measurements.

- 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, together with national standards for measurement and calibration procedures, will facilitate the acceptance of a wide range of U.S. products in international markets, as well as minimize product-acceptance disputes in domestic trade.

- Computational micromagnetic techniques are producing results which are important for understanding magnetization reversal in devices incorporating thin magnetic elements. Micromagnetic head-to-head domain wall structures and energies in thin magnetic strips have been calculated, resulting in a "phase diagram" for transverse and vortex type walls.

Project Title: **THERMOPHYSICAL PROPERTIES**

Investigators: A. Cezairliyan, J. L. McClure, D. Basak, K. Boboridis, and D. Josell

Objectives:

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

Technical Description:

This project focuses on the development and use of new techniques for the accurate measurement, at high temperatures, of selected thermophysical properties of materials, in both solid and liquid phases, utilizing rapid (millisecond- and microsecond-resolution) pulse-heating (volume and surface) techniques. The properties of interest are: enthalpy, specific heat capacity, thermal expansion, electrical resistivity, hemispherical total emissivity, normal spectral emissivity, melting temperature, heat of fusion, and thermal diffusivity.

Planned Outcome:

State-of-the-art of thermophysical measurements at high temperatures will be advanced. Accurate bench-mark thermophysical data on selected key materials will be generated. High-temperature thermophysical standards will be developed.

External Collaborations:

The laser polarimeter used for the measurement of normal spectral emissivity of the specimen during pulse heating was developed in collaboration with Containerless Research, Inc. The new accurate subsecond technique for the measurement of hemispherical total emissivity was developed in collaboration with a scientist from the National Research Laboratory of Metrology (Japan).

Accomplishments:

- Operation of the novel millisecond-resolution laser polarimeter for normal spectral emissivity measurements (which permits determination of true temperature from measured surface radiance temperature) on solids was further validated by performing measurements of specific heat capacity of molybdenum standard reference material in the temperature range 2000 to 2800 K. The present results are in agreement, within 1%, with the certificate values.
- Definitive experiments were conducted for the first time to demonstrate applicability of the millisecond-resolution laser polarimetry technique to the non-contact detection of phase transformations in metals and alloys at high temperatures. The measurements included detection of structural phase transformations (cobalt, hafnium, iron, titanium, and zirconium) and melting (molybdenum, nickel, niobium, zirconium, and the alloy 53Nb-47Ti).
- Applicability of the laser polarimetry technique to measurements of normal spectral emissivity of liquid metals was studied. A new system for operation at microsecond speeds was designed and partially constructed in collaboration with the Containerless Research Incorporated.
- The new accurate subsecond technique for the measurement of hemispherical total emissivity, developed during the previous year, was used to measure emissivity of niobium, molybdenum, and tungsten at temperatures above 2000 K.
- Radiance temperatures (in the wavelength range 530 to 1500 nm) of nickel at its melting point were measured. This work is needed for the establishment of high temperature reference points.
- The laser pulse system was used to measure thermal diffusivity of homogeneous as well as multilayered materials. Extensive measurements were performed on specimens consisting of molybdenum and alumina layers and several industrially important multilayered materials. Additional measurements were conducted on pure molybdenum specimens to further assess the operation of the system. Modifications to the system and refinements to the computer programs were made. An accurate knowledge of thermal diffusivity will play an important role in the selection, use, and assessment of thin films and specifically thermal barrier coatings in high temperature applications, such as in jet engine blades.

Impacts:

The high-speed (millisecond resolution) laser polarimeter, developed jointly by NIST and Containerless Research Incorporated (CRI), was commercialized by CRI and was successfully marketed internationally. This novel and unique instrument, which is capable of measuring accurately the normal spectral emissivity of a specimen surface without the requirement of a blackbody configuration, significantly simplifies accurate measurements of high temperatures.

NIST developed and successfully used a new technique for the measurement of hemispherical total emissivity of metals and alloys in subsecond-duration experiments. This technique will provide, with unprecedented accuracy, hemispherical total emissivity of electrically-conductive materials at temperatures above 1500 K.

Outputs:

Publications:

McClure, J.L. and Cezairliyan, A., "Radiance Temperatures (in the Wavelength Range 525 to 906 nm) of Vanadium at Its Melting Point by a Pulse-Heating Technique," Int. J. Thermophys., **18**, 291 (1997).

Josell, D., Cezairliyan, A., van Heerden, D., and Murray, B.T., "Thermal Diffusion Through Multilayer Coatings: Theory and Experiment," Nanostructured Materials, **9**, 727 (1997).

Josell, D., Cezairliyan, A., van Heerden, D., and Murray, B.T., "An Integral Solution for Thermal Diffusion in Periodic Multilayer Materials; Application to Iron/Copper Multilayers," Int. J. Thermophys., **18**, 865 (1997).

Kaschnitz, E., McClure, J.L., and Cezairliyan, A., "Radiance Temperatures (in the Wavelength Range 530 to 1500 nm) of Iron and Cobalt at Their Melting Points by a Pulse-Heating Technique," High Temp.-High Press., in press.

Cezairliyan, A., Krishnan, S., Basak, D., and McClure, J. L., "Application of Laser Polarimetry to the Measurement of Specific Heat Capacity of Molybdenum in the Range 2000 to 2800 K by a Pulse-Heating Technique," Int. J. Thermophys., in press.

Matsumoto, T. and Cezairliyan, A., "A Combined Transient and Brief Steady-State Technique for Measuring Hemispherical Total Emissivity of Electrical Conductors at High Temperatures: Application to Tantalum," Int. J. Thermophys., in press.

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., 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., in press.

Josell, D. and Cezairliyan, A., "Thermal Diffusion Through Multilayer Coatings: Theory and Experiment," Int. J. Thermophysics., in press.

Presentations:

Cezairliyan, A., "Measurements of Thermophysical Properties of Metals and Alloys at High Temperatures by Subsecond Pulse-Heating Techniques," Thermophysical Properties - Metallurgical Industry Needs and Resources Symposium, Johnstown, Pennsylvania, October,

1996. *(Invited).*

McClure, J. L., "Application of Laser Polarimetry to the Measurement of Specific Heat Capacity of Molybdenum in the Range 2000 to 2800 K by a Pulse-Heating Technique," 13th Symposium on Thermophysical Properties, Boulder, Colorado, June, 1997.

Cezairliyan, A., "Effect of Heating Rate on the Melting Behavior of the Alloy 53Nb-47Ti (Mass %) in Rapid Pulse Heating Experiments," 13th Symposium on Thermophysical Properties, Boulder, Colorado, June, 1997.

Basak, D., "Measurements of Selected Thermophysical Properties of the Alloy 53Nb-47Ti (Mass %) in the Range 1500 to 2100 K by a Millisecond-Resolution Pulse-Heating Technique," 13th Symposium on Thermophysical Properties, Boulder, Colorado, June, 1997.

Josell, D., "Thermal Diffusion Through Multilayer Coatings: Theory and Experiment," 13th Symposium on Thermophysical Properties, Boulder, Colorado, June, 1997.

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

Investigator: L. A. Bendersky

Objectives:

The goal of this project is the determination of very complex crystallographic structures and defects in new stable and metastable compounds, especially in systems of importance for microwave wireless applications. Mesoscopic microstructures are being studied to correlate the atomic structure with properties and appear to provide potential for novel magnetic and electrical properties.

Technical Description:

Improved new functional ceramics with better electric and magnetic properties are being sought in different ternary oxide systems. Such materials can be potentially used in a wide variety of electronic devices for microwave wireless communication. Wireless communication technologies are expected to comprise one of the most important growth businesses in the world electronic industry, with the projected market growth of the order of 50% per year.

This work is a close collaboration with Ceramics Division (T. A. Vanderah, R. S. Roth and I. Levin) studying phase equilibria and synthesis of complex oxides, particularly in the $BaO:Fe_2O_3:TiO_2$ and $SrO\text{-}Nb_2O_5\text{-}TiO_2$ systems. Most of the oxides apparently have a new structure type and require complete structural determination. Structural studies by x-ray diffraction often are not successful; therefore, high-resolution transmission electron microscopy (HRTEM) and computer simulation modeling are employed to study these compounds. The work will establish the correlations between structural and physical properties of the studied compounds, and will develop an understanding of the physics behind these correlations. This research is a natural extension of our previous work and our expertise in determining complex metal structures, including quasicrystlline and nanocrystalline alloys.

Planned Outcome:

Identification of a group of $BaO:Fe_2O_3:TiO_2$ compounds as a new class of materials with a "self-assembled" magnetic multilayer structure having crystallographically flat interfaces. The material may have unusual properties related to the magnetic interactions between layers, similar to the properties of artificial magnetic multilayers, and may therefore be of interest for data storage research.

Understanding of the relationship between structure and dielectric properties of a series of $SrO\text{-}Nb_2O_5\text{-}TiO_2$ compounds. The results of this study can be used by laboratories and industries working on devices for microwave applications.

External Collaborations:

Cooperative research program with NKK, Japan (Dr. S. Mitao) to study microstructural stability of gamma titanium-aluminides.

Collaboration with Dr. S. Banerjee, Bhabha Atomic Research Center, Bombay, on microstructural evolution and ordering in Zr-Al-Nb and Ni-Al alloys.

Collaboration with Dr. T. Sigrist, AT&T Bell Labs on structural determination of compounds in the $BaO:Fe_2O_3:TiO_2$ system.

Collaboration with O.M. Stafsudd, UCLA, on the relationship between structure and dielectric properties of a series of $SrO\text{-}Nb_2O_5\text{-}TiO_2$ compounds.

Accomplishments:

The structural characterization of six newly discovered compounds from the $BaO\text{-}Fe_2O_3\text{-}TiO_2$ system has been completed. The following results were achieved:

1. All six structures, the E, M, K, N, L and J phases, were shown to belong to the previously unknown class of ordered intergrowth structures built out of two types of alternating slabs, P and H-type. The basic framework of the structures consists of a sequence of close-packed Ba/O layers. The P slab has a perovskite-like structure where Ti cations are accommodated predominantly in the octahedral positions. The H-type slabs have a periodicity triple in its basal plane with respect to the P slab. The structure of the H-type slab is shown to be closely related to the 12:14:15 phase and magnetite-type. The H-type slabs are expected to be rich in Fe (which is accommodated in both octahedral and tetrahedral coordinations) and dilute in Ba.
2. The presence of a one-dimensional structural disorder was observed and explained for the new phases. This unusual disorder phenomena was shown to be related to the lower symmetry of the H-type slabs and reflects the poor spatial correlation between these slabs.
3. A strongly heterogeneous distribution of Fe suggests that all six phases can be considered as natural "self-assembled" magnetic multilayer structures with crystallographically flat interfaces and potentially interesting properties.

Two representative phases of the $BaO\text{-}Fe_2O_3\text{-}TiO_2$ compounds, L and M, have been studied (with J. Bonevich) by energy-filtered TEM/EELS imaging to analyze compositional distribution of Fe, Ti and Ba. The imaging shows that H-type slabs have an enhanced Fe concentration and the perovskite slabs are Ba-rich. The distribution of Ti is relatively uniform. This chemical inhomogeneity is consistent with the proposed structural models of the phases.

Experimental work on unknown compounds from the $SrO-Nb_2O_5-TiO_2$ system has been conducted (with I. Levin and T. Vanderah). A series of structurally related phases $A_nB_nO_{3n+2}$ with $A=Sr^{2+}$ and $B=(Ti^{4+}, Nb^{5+})$ have been prepared. Members of the homologous series with $n = 4, 5, 6, 7$, and non-integer values between 4 and 5 were characterized by HREM/TEM, bulk X-ray powder diffraction, and capacitive measurements of relative permittivities and temperature coefficients. Preliminary capacitive measurements from 100 Hz to 5 MHZ of relative permittivities and temperature coefficients indicate some unusual differences for successive members of the series, despite their crystallographic and chemical similarities.

Experimental and modeling work on unknown compounds with $Ca_2Ta_2O_7$ stoichiometry has been conducted. Four different, previously unknown polymorphic modifications (3, 6, 7 and 12 layers) were discovered and characterized. Structural models of these compounds were proposed based on the different stacking sequences and shears of complex layers of pyrochlore structure. The modeling work is in progress.

Impact:

The $BaO:Fe_2O_3:TiO_2$ and $SrO-Nb_2O_5-TiO_2$ phase diagrams determined by NIST are of immediate interest to U. S. industry involved in the production of ceramics for wireless communications systems, e.g. for microwave circulators and isolators. An understanding of structures and defects of the studied compounds, as well as the structure/properties correlations, will lead to an intelligent approach to tailoring microstructure and properties of such materials.

Outputs:

Publications:

Levin, I., Bendersky, L. A., Brandon, D. G., and Ruhle, M., "Cubic to Monoclinic Phase Transformations in Alumina," *Acta Materialia* (1997), (in press).

Mitao, S. and Bendersky, L. A., "Morphology and Growth Kinetics of Discontinuous Coarsening in Fully Lamellar Ti - 44 Al (at%) Alloy," *Acta Materialia* (1997), (in press).

Bendersky, L. A. and Waterstrat, R. M., "Incommensurate Structure of the Phase Zr_3Rh_4," *J. Alloys and Compounds*, **252**, L5, (1997).

Bendersky, L. A., Vanderah, T. A., and Roth, R. S., "Structural Features of "$Ba_4Fe_4Ti_3O_{16}$" and "$Ba_{26}Fe_{20}Ti_{21}O_{98}$" as Revealed by High Resolution Electron Microscopy," *J. Solid State Chemistry,* **125**, 281, (1996).

Bendersky, L. A., Vanderah, T. A., and Roth, R. S., "High-resolution electron microscopy of magnetic dielectric oxides in the $BaO:Fe_2O_3:TiO_2$ system," published in *Solid-State Chemistry of Inorganic Materials,* Eds. Davis, P. K., Jacobson, A. J., Torardi, C. C., and Vanderah, T. A., MRS, **453,** (1997), p. 489.

Mitao, S. and Bendersky, L. A., "Morphology of Discontinuous Coarsening in Fully Lamellar Ti - 44 Al (at%) Alloy," Proceeding of the Second Int. Symposium on Structural Intermetallics, September (1997), (in press).

Presentations:

Bendersky, L. A., Vanderah, T. A., and Roth, R. S., "High-resolution electron microscopy of magnetic dielectric oxides in the $BaO:Fe_2O_3:TiO_2$ system," MRS 1996, Symposium: *Solid-State Chemistry of Inorganic Materials.*

Mitao, S. and Bendersky, L. A., "Morphology of Discontinuous Coarsening in Fully Lamellar Ti - 44 (at%) Al Alloy," International Symposium on Structural Intermetallics, Seven Springs, PA., 1997.

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

Investigators: D. Josell and T. Foecke

Objectives:

This project will determine the thermal resistance associated with interfaces in multilayer materials. This quantity is tied directly to the effectiveness of these materials as thermal barrier coatings for engine applications being considered by our industrial power generating partners.

This project will also ascertain the relationship between the yield stress and layer thickness of model multilayer materials. Efforts will also be made to determine the operating deformation and fracture mechanisms. In addition, creep properties of model multilayer systems will provide thermodynamic free energies associated with interfaces. The mechanical and thermodynamic properties are required to predict the lifetime and stability of multilayer thin film materials of interest to the United States Air Force.

Technical Description:

Thermal barrier coatings protect engine parts from the elevated temperatures of the combustion process. It has been proposed that the presence of the numerous interfaces in multilayer thermal barrier coatings will decrease their thermal conductivity, making multilayer coatings more effective thermal barriers than the materials from which they are manufactured. Measurements of thermal transport properties of multilayer thermal barrier coatings are therefore being made at elevated temperatures, to simulate operating conditions, using a pulsed laser

(<100 ns) heating technique.

Mechanical properties are being determined through analysis of stress-strain curves obtained during room temperature tensile tests and elevated temperature creep tests of multilayer films. A novel sample geometry that allows straining of cross-sectional samples in-situ in the transmission electron microscope is also being used to study deformation and fracture at magnifications of 500,000, permitting direct observation of dislocation motion and crack advance during straining.

Planned Outcome:

The industrial consortium providing the thermal barrier coatings for measurement at NIST will decide whether or not it will further pursue study of these materials, and eventually use them in thermal barrier coatings, based, in part, on the materials properties determined at NIST.

Mechanical and creep properties will be furnished to the Air Force through joint projects with scientists at The Johns Hopkins University and Ohio State University.

External Collaborations:

Daniel Josell's collaboration with the industrial consortium composed of Battelle, Howmet, EPRI, and Solar Turbine continues. The industrial group continues to supply thermal barrier coatings and NIST continues to determine the thermal transport properties of those coatings at potential operating temperatures using the Metallurgy Division's pulsed laser heating system.

A formal collaboration between Daniel Josell and Professor D. Shechtman of the Technion, now up for renewal by the US-Israel Binational Science Foundation for a third year, with Dr. D. van Heerden of Johns Hopkins University, continues to study structural transformations in multilayer materials.

A new collaboration has been formed between Daniel Josell and Professor T. Weihs of the Johns Hopkins University through a joint project funded for four years as of September, 1997 by the Air Force. This work will focus on the effects of interfaces on creep of multilayer materials at high temperatures.

A joint effort between Timothy Foecke and Professor Weihs, funded by AFOSR, to study the mechanical properties and thermal stability of Nb/Nb_5Si_3 microlayered materials, continues.

An ongoing collaboration between Timothy Foecke and Professor P. Anderson of Ohio State University studying dislocations in single crystal metallic nanolaminates has been expanded through the funding of a student by the AFOSR through an AASERT grant. Daniel Josell will participate in this new study of the creep and stability of multilayer coatings in the design and analysis of experiments based upon theory and experiments that he previously published.

Timothy Foecke has initiated a collaboration with Professor S. Barnett of Northwestern University to image the defect structures produced by a microhardness indent in superhard NbN/W single crystal superlattices.

Accomplishments:

- The electron beam deposition system for fabrication of multilayer materials has been improved through the inclusion of a new deposition chamber and new process control. Low and high angle x-ray superlattice diffraction peaks from fabricated multilayer coatings indicate excellent system operation.

- The effect of annealing on thermal transport through molybdenum/alumina multilayers was studied. The results permit the upper bound for the interface resistance at each interface in the coatings to be placed at a value in agreement with work on metal/metal interfaces, orders of magnitude below the value motivating industrial multilayer thermal barrier coatings research.
- The dislocation generation and motion observed during in situ TEM straining experiments were analyzed to determine dislocation pileup and bowing stresses. It was found that stresses in excess of 2.6 GPa were maintained at the head of a pileup containing more than 30 dislocations in a 30 nm Cu /60 nm Ni single crystal multilayer. This value is more than one half the theoretical strength of either constituent material.

Impact:

Observations of dislocation pileups and the effect of interfacial dislocations on glissile dislocations has forced the revision of theoretical treatments of nanolaminate mechanical behavior by most modeling groups. Previously, it was doubted that dislocations could be energetically stable in a nanoscale microstructure, and it was believed that a pileup was impossible.

Thermal transport properties of coatings provided by an industrial consortium (EPRI, Howmet, Battelle, and Solar Turbine) were determined at elevated temperatures using NIST's pulsed laser heating system. The consortium will decide by the end of 1997, based, in part, on these measurements, whether to continue their program on multilayer thermal barrier coatings for engine applications.

Outputs:

Publications:

Foecke, T., "Novel Sample Geometry for In Situ TEM Deformation Experiments," Scripta Materialia (in press).

Foecke, T., "Observation of Generation and Motion of 'Orowan' Bows in a Single Crystal Metallic Nanolaminate," Journal of Materials Research (in press).

Foecke, T., and van Heerden, D., "Deformation Mechanisms in Metallic Nanolaminates," in Proceedings of the Symposium on Chemistry and Physics of Nanostructures and Related Non-Equilibrium Materials, Eds. E. Ma, et al., **193,** TMS, Pittsburgh, PA. (1997).

Josell, D., Cezairliyan, A., van Heerden, D., and Murray, B. T., "An Integral Solution for Thermal Diffusion in Periodic Multilayer Materials: Application to Iron/Copper Films," International Journal of Thermophysics **18**, 865 (1997).

Josell, D., Cezairliyan, A., van Heerden, D., and Murray, B.T., "Thermal Diffusion Through Multilayer Coatings: Theory and Experiment," Nanostructured Materials **9**, 727 (1997).

Josell, D., Cezairliyan, A., and Bonevich, J. E., "Thermal Diffusion Through Multilayer Coatings: Theory and Experiment," International Journal of Thermophysics (in press).

Wang, Z. L., van Heerden, D., Josell, D., and Shapiro, A. J., "Energy Filtered High-Resolution Electron Microscopy for Quantitative Solid State Structure Determination," Journal of Research of the National Institute of Standards and Technology **102**, 1 (1997).

Josell, D., and Carter, W. C., “Implications and Applications of Zero Creep Experiments for Multilayer Stability,” in Creep and Stress Relaxation in Miniature Structures and Components, Ed. H. D. Merchant, **271** TMS, Warrendale, PA. (1996).

Tepper, T., Shechtman, D., van Heerden, D., and Josell, D., "Fcc Titanium in Titanium/Silver Multilayers," Materials Letters (in press).

Tepper, T., Shechtman, D., van Heerden, D., and Josell, D., "Allotropic Phase Formation in Ti/Zr Multilayers," Materials Letters (in press).

Presentations:

Josell, D., "Elastic, Plastic, and Creep Properties of Multilayered Materials," invited talk at Yale University, September, 1997.

Josell, D., "Interfacial Materials: Microstructural Stability and Thermal Transport Properties of Multilayers," invited talk at Johns Hopkins University, September, 1997.

Josell, D., "Layer Stability and Interfacial Free Energies from the Creep of Multilayers," invited talk at 4th Annual International Conference on Composites Engineering, Kona, Hawaii, July, 1997.

Josell, D., "Thermal Diffusion Through Multilayer Coatings: Theory and Experiment," 13th Symposium on Thermophysical Properties, Boulder, Colorado, June, 1997.

Josell, D., "Implications and Applications of Zero Creep Experiments for Multilayer Stability," invited talk at TMS Fall Meeting, Symposium on Creep and Stress Relaxation in Microstructures, Cincinnati, October, 1996.

Josell, D., "Multilayer Materials: Theory and Experiment for Thermal Transport, Zero Creep and Structural Stability," invited talk at the Technion, Israel, October, 1996.

Josell, D., "Thermal Transport Through Multilayer Materials: Theory and Experiment," invited talk at Joint NSF-NIST Program Review Conference on Nanoparticles, NSF, Arlington, VA. May, 1997.

Foecke, T., "Mechanical Properties of Nanolayered Materials," invited talk at Johns Hopkins University, November, 1996.

Foecke, T., "Deformation Mechanisms Particular to Nanolaminates," invited talk at TMS, Symposium on Chemistry and Physics of Nanostructures and Related Non-Equilibrium Materials, Orlando, February, 1997.

Foecke, T., "Deformation Mechanisms Particular to Nanolaminated Materials," invited talk at Society for Experimental Mechanics Spring Meeting, Bellevue, WA, June, 1997.

Foecke, T., "Fracture Mechanisms in Nanomaterials," invited talk at Joint NSF-NIST Program Review Conference on Nanoparticles, NSF, Arlington, VA. May, 1997.

Foecke, T., "Deformation and Fracture in Metallic Nanolaminates," at Symposium on Fundamentals of Deformation and Fracture, TMS Fall Meeting, Cincinnati, OH, October, 1997.

Project Title: **HARDNESS STANDARDS**

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

Objectives:

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

Technical Description:

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

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

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

Standardization of the national Rockwell C hardness scale (HRC), identified as being in greatest demand by U.S. companies, has been accomplished, and HRC transfer standards have been calibrated with the assistance of the statistical expertise of ITL. The test cycle used to standardize the HRC scale was chosen to ensure compatibility with U.S. industrial practice, and to provide an acceptable level of precision and repeatability in the hardness measurements. International HRC scale intercomparisons with countries in Europe and Asia have been made to ensure compatibility with the Rockwell C hardness scales of other countries. Certification of Rockwell hardness indenters as NIST Standard Reference Materials is also currently under development with the assistance of MEL.

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

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

Planned Outcome

The short term goals of this project are to standardize each of the Rockwell hardness scales, and provide a means to transfer the national hardness scales to industry through the production and sale of calibrated SRM hardness test blocks and certified indenters. An accreditation program for hardness calibration laboratories will be developed, to be managed by NVLAP. ASTM hardness test method standards will be revised to reflect the use of the NIST SRMs and NVLAP programs. It is anticipated that this program will not end, but will continue to evolve with the changing needs of U.S. industry and with advances in technology.

External Collaborations

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

Accomplishments:

Approximately 100 test blocks at each of three levels of the Rockwell C scale have been calibrated and delivered to the Standard Reference Materials Program.

An intercomparison using the NIST Rockwell C scale SRM test blocks was conducted between NIST and the National Research Laboratory of Metrology in Japan and found agreement within ±0.1 HRC for all three levels. An intercomparison of the HRB scale was also conducted with Japan and found agreement within ±0.15 HRB for four hardness levels.

A study was conducted to benchmark the expected shift in the U.S. HRC scale resulting from the release of NIST SRMs.

Impact:

NIST's involvement in the standardization of the U.S. hardness scales can be evidenced by the many industry requests for information concerning the SRM test blocks, the movement of ASTM towards revising the Rockwell hardness test method standard, industry requests to have a hardness calibration laboratory accreditation program developed, and the introduction and expanding use of uncertainty in hardness measurements.

The NIST program has also provided strong support for the ISO decision to adopt test cycles for the standard test method for the Rockwell C Scale which are consistent with industrial practice rather than the longer cycles typically used in hardness research.

Outputs:

Publications:

Song, J.-F., Low, S., Pitchure, D., Germak, A., DeSogus, S., Polzin, T., Yang, H.-Q., Ishida, H., "Establishing a Common Rockwell Hardness Scale Using Geometrically Calibrated Standard Diamond Indenters," Proceedings of XIV IMEKO World Congress, June (1997).

Song, J.-F., Low, S., Pitchure, D., Germak, A., DeSogus, S., Polzin, T., Yang, H.-Q., Ishida, H., "Establishing a Worldwide Rockwell Hardness Scale With Metrology Traceability," *Metrologia* **34,** 4 (1997).

Presentations:

Low, S., "The HRC Test Cycle and Recommendations For Revising ASTM E18," ASTM Committee Week, New Orleans, Louisiana, November 1996.

Low, S., "NIST Hardness Standards," Materials Solutions Conference, ASM International Indianapolis, Indiana, September 1997.

Low, S., "Standardization of Hardness at NIST," Japanese Industrial and Student Visitors at NIST, Gaithersburg, Maryland, September 1997.

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

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

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

Objectives:

In cooperation with universities and industry, we are helping to determine methods for characterizing magnetic materials of importance to science and industry and to provide methods and standard reference materials for accurate and traceable magnetic measurements.

Technical Description:

Using the facilities and expertise available at NIST, we determine the magnetic properties of materials important to the scientific and industrial community and develop methods for improved measurements of these properties. We also develop and produce standard reference materials to provide for accurate and traceable calibration of instruments used in the measurement of magnetic properties important to science and industry. In the past NIST has issued SRM772, a nickel sphere, as a magnetic moment standard, and Pt, Pd and aluminum wires and manganese fluoide as magnetic susceptibility standards. The supply of these SRMs has been exhausted for several years and needs to be replenished.
This project determines the parameters necessary to fully characterize magnetic materials; these parameters can then be used in models which correctly predict the behavior of the magnetic material under actual operating conditions.

Planned Outcome:

Companies producing vibrating sample magnetometers and other types of magnetometers rely on NIST to provide standard reference materials for the calibration of these instruments. There is an urgent need to restock the nickel ball standard, SRM 722 and for the provision of new standards more appropriate for newer instruments such as SQUID magnetometers and alternating gradient magnetometers. One planned outcome is a series of SRMs for use in calibrating magnetometers. The first will be a re-issue of SRM772, a nickel sphere with a diameter of 2.5mm and with its absolute magnetic moment certified to ±0.3%. A smaller sphere fabricated from single crystal YIG and a thin nickel disk are also planned. In addition to SRMs, improved characterization methods for describing the time decay and accommodation properties of magneitc recording media will be provided to aid the magnetic recording industry in their development of improved materials.

External Collaborations:

External collaborators include Materials Innovation, Inc., Fluxtrol, Inc., Digital Measurement System, and the Institute for Magnetics Research at George Washington University.

Accomplishments:

The equipment for performing the absolute measurements required to certify magnetic moment standard reference materials has been assembled. Final testing and adjustment of this equipment is now underway. Materials suitable for the Ni ball SRM were obtained and sent to a vendor for fabrication into spheres of the required diameter. Improved methods for measurement of the stability of recording materials were devised. These methods were used to characterize accommodation and time decay in some high-density recording materials.

Impact:
A commercial instrument maker, Digital Measurements Systems, Inc., is developing software for the measurement of accommodation in recording materials which is based on cooperative work between NIST and George Washington University.

Output:

Publications:

L.H. Bennett, L.J. Swartzendruber, P. Rugkwamsook, E. Della Torre, and F. Vajda, Experimental Validation of the Preisach Accommodation Properties of Recording Media, J. Appl. Phys. 81, 5227 (1997).

L. J. Swartzendruber, L.H. Bennett, F. Vajda, and E. Della Torre, Relationship Between the Measurement of Accommodation and After-effect, Physica B223, 324 (1997).

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

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

Investigators: R. B. Clough, R. deWit, R. J. Fields, T. J. Foecke, D. E. Harne, G. E. Hicho, L. E. Levine, E. N. Pugh, F. Bendec and A. Stern (Guest Researchers, Nuclear Research Centre, Negev, Israel) and R. Thomson (Contractor)

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

obtaining the data required for implementing the models to the auto companies and their suppliers.

Technical Description:

Major research efforts within the U.S. auto industry are driven by the need to reduce the weight of future vehicles to meet USCAR and PNGV goals. This can most readily be accomplished by the substitution of lightweight materials for the heavy materials currently used. This project consists of two parts: (1) development of a low cost powder processing technology for aluminum alloy and particle reinforced aluminum (PRA) parts, and (2) advancement of formability technology for lightweight sheet metals. In the first part, aluminum alloy and aluminum composite powder metallurgy (PM) materials would be substituted for iron-based PM products. In the second, 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 focussed on modeling each step in these consolidation processes from powder to fully dense part. Modeling provides the basis for knowing what to measure about a powder or a process to monitor consistency and to more rapidly design successful processes. 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.

The 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 an advanced computer program 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 describes the densification of reinforced (or unreinforced) metal powder in terms of the processing conditions. This will result in a commercial software package that accurately models potential processes and that saves U.S. industry time and money which would otherwise have to be spent on trial-and-error investigations.

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

External Collaborations:

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

Formability research has largely been carried out in conjunction with the ATP and NAMT project participants: Chrysler, Ford, General Motors, Budd, Alcoa, US Steel, Livermore Software Technology Corporation and the Autobody Consortium, consisting of 20 OEM's and suppliers to the industry, as well as the University of Ohio, the University of Michigan, and Northwestern University. Collaboration has mainly involved Prof. Ghosh at U. of MI, Prof. Wilson at Northwestern, Alcoa and General Motors. Material and advice on commercial forming processes were supplied by the industrial collaborators.

Accomplishments:

A shape insensitive, *in situ* density sensor was developed and successfully operated to provide benchmark data for the powder consolidation modeling effort. The reinforcement hardening effect predicted by the Cambridge model was validated for mixtures of 2024 aluminum alloy and SiC powders.

A portion of the IMM workshop on Mechanics and Materials Issues in the Automobile Industry was devoted to exploring the role that NIST should play in improving metal forming technology. While the NIST focus on fundamental and standards related issues was basically supported at this workshop, our research on surface roughening and friction received significant industrial endorsement.

To gauge the state-of-the-science, a focussed session entitled "Dislocations in Deformed Metals and Semiconductor Thin Films and Multilayers" at the March American Physical Society meeting was organized by NIST. In this meeting, it became clear that new approaches to understanding, modeling, and predicting the role of dislocation structures were emerging and that NIST was in the forefront of this development.

A general theory for interpreting Bragg diffraction from dislocations was completed and applied to the specific case of screw dislocations. A set of ultra-small-angle X-ray scattering data was obtained from several single-crystal aluminum samples deformed *in situ.* High resolution diffraction imaging experiments were also performed on similar, deformed aluminum samples. The results of these measurements were found to be crucial for the correct interpretation of the small-angle scattering data.

A first generation, plane strain tensile test fixture was designed and built. A contract between NIST and University of Michigan was signed to develop a channel forming test to evaluate the utility of the data obtained from the plane strain tensile test under investigation at NIST.

Impacts:

Models of reinforced powder consolidation are now available and are being 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.

A new measurement method has been developed to quantify the dislocation content of deformed metals. When used to develop an improved prediction of metal deformation, coupled with our work on surface roughening and data from standard test methods, this research could save industry at least 50 to 100 million dollars per year.

Outputs:

Publications:

deWit, R., "Diffraction Elastic Constants of a Cubic Polycrystal," J. Appl. Cryst. **30**, 510 (1997).

deWit, R., Fields, R. J., Low, S. R., Harne, D. E., and Foecke, T. J., "Fracture Testing of Large-Scale Thin-Sheet Aluminum Alloy," in Fatigue and Fracture Mechanics: 27th Vol., ASTM SP 1296, R. S. Piascik, J. C. Newman, and N. E. Dowling, eds., American Society for Testing and Materials, pp. 451-468 (1997).

Levine, L. E. and Thomson, R., "X-ray Scattering by Dislocations in Crystals: General Theory and Application to Screw Dislocations," Acta Cryst. **A53**, 590 (1997).

Levine, L. E., Fields, R. J., Black, D. R., Burdette, H., and Long, G. G., "*In situ* Measurements of Dislocation Structure Evolution in Plastically Deformed Single Crystal Aluminum," Bull. Amer. Physical Soc. **41**, 40 (1996).

Levine, L. E., Long, G. G., Black, D. R., and Thomson, R. "*In situ* Measurements of Dislocation Structure Evolution in Al Single Crystals Deformed in Tension," National Synchrotron Light Source Activity Report (1996).

Levine, L. E., Thomson, R., Long, G. G., Black, and Fields, R. J., "NIST Research in Support of ATP's Springback Predictability and Agile Precision Sheet Metal Stamping Projects," in Proceedings of ATP's MVMT Public Meeting in Ann Arbor (through WERB).

Livne, Z., Munitz, A., Rawers, J. C., and Fields, R. J., "Consolidation of Nanoscale Iron Powders," NISTIR 5990.

Livne, Z., Fields, R. J., and Agulyansky, A., "Evaluation of Press-and-Sinter Parameters for Ta_2O_5 by the Diametral Compression Test," NISTIR 6024.

Munitz, A., Livne, Z., Rawers, J. C., and Fields, R. J., "Cold Compaction of Ball-milled Iron Powders," NISTIR 5991.

Presentations:

Foecke, T. J., "What Should Be the NIST Focus in Metal Forming Research?," Institute of Mechanics and Materials Workshop on Mechanics and Materials Issues in the Automotive Industry, Ann Arbor, Michigan, September, 1997.

Fields, R. J., "Sheet Metal Forming Activities at NIST," Institute of Mechanics and Materials Workshop on Mechanics and Materials Issues in the Automotive Industry, Ann Arbor, Michigan, September, 1997.

deWit, R., "NIST Research Program on Lightweight Materials for Automotive Applications," North American Deep Drawing Research Group Spring Meeting, Golden, Colorado, May, 1997.

Levine, L. E., "Deformation of Metals: The Inside Story," Washington State University, November, 1996; Lawrence Livermore National Lab., November, 1996; Catholic University, January, 1997; Washington University, February, 1997; and Univ. of Texas at Austin, March, 1997.

Fields, R. J., "NIST's Progress in Modeling PRA Consolidation," USCAR quarterly review meetings in Detroit, Michigan, March, 1997; at Stackpole, Ltd. in Mississauga, Canada, May, 1997; at NCMS in Ann Arbor, Michigan, August, 1997.

Fields, R. J., "*In Situ* Density Measurements during Isostatic Consolidation of Powders," Metal Powders Industries' International Conference on Powder Metallurgy and Particulate Materials, Chicago, Illinois, July, 1997.

Clough, R. B., "Fundamentals of Metal Powder Consolidation and Deformation," Workshop for ATP Project on Dynamic Magnetic Consolidation, IAP Corp., Dayton, Ohio, March, 1997.

Project Title: **PERFORMANCE OF STRUCTURAL MATERIALS**

Investigators: R. B. Clough, R. J. Fields, T .Foecke, D. E.Harne, E. N. Pugh, R. E. Ricker, D. A. Shepherd, J. H. Smith, M. R. Stoudt, C. R. Hagwood (Statistical Engineering Division, ITL), and R. C. Cammarata (Guest Researcher, The Johns Hopkins University)

Objectives:

In this project, the expertise and facilities of the Materials Performance Group is used to provide assistance to US industry and other Federal agencies in the broad area related to the service performance of structural metals and alloys. Outputs include test methods and data.

Technical Description:

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

In FY 97, work was conducted on six sub-projects:

- **Stress Rupture of Lead-Free Plumbing Solders**

This on-going work is being carried out in collaboration with the Copper Development Association (CDA) and with the B16 Committee of ASME, and is designed to establish permissible pressures for copper tubes joined by lead-free solders. This is driven by the 1986 amendments to the Safe Drinking Water Act which prohibited the use of lead-containing solders in potable water systems. Despite the fact that thirteen lead-free solder alloys are contained in ASTM's Standard Specification for Solder Metal (B32), the current ASME Codes specify joint strengths for only one lead-free solder, Alloy Sb5 (95Sn-5Sb), and these are based on limited data reported by NIST in the early 1940s, so that unusually large safety factors are imposed.

In the NIST studies, stress rupture tests are being conducted on soldered sleeve joints in copper tube for times up to one year at temperatures in the range 100-250 °F. In addition to Alloy Sb5, two other lead-free solders are being tested, namely Alloy E (4Cu-0.5Ag-bal.Sn) and Alloy HB (5Sb-0.3Ag-3.5Cu-1Ni-bal.Sn). The testing program is being supported by studies of the mechanism(s) of failure to assist in statistical analysis of the data and in life prediction modeling.

- **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. Our focus in this activity is the development of design standards and testing procedures for new cylinders, which currently are constructed of steel, aluminum alloys or composites.

- **Eta-phase Precipitation and Low Cycle Fatigue in Alloy 706**

A major thrust of U.S. heavy manufacturing industry is the development of large land based gas turbine engines for power generation. In support of this, U.S. industry intends to produce large near-net-shape forgings of nickel-based alloy 706 using a novel incremental forging process. Limitations on the cooling rates possible in such large forgings are thought to reduce low cycle fatigue resistance by promoting intergranular precipitation of eta-phase which, in turn, causes the grain boundary regions to be denuded with respect to strengthening niobium-containing precipitates. Controlling the occurrence of this phase has been identified as a primary metallurgical challenge in the near-net-shape forging of Alloy 706.

In FY97, NIST collaborated with ATP recipient Wyman-Gordon Inc. on this problem. Using our electron microscope capabilities, grain boundary microstructures have been characterized in samples of Alloy 706 provided by Wyman-Gordon Inc, and the findings have been correlated with the results of fatigue tests conducted at NIST in air and vacuum at 750 and 900 °F. These studies assisted Wyman-Gordon Inc in the identification of heat treatments which minimize the deleterious effects of eta-phase precipitation on fatigue resistance.

- **Mechanical Properties of Orthorhombic Titanium Aluminides**

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

- **Influence of Nanolayered Surface Films on Fatigue Initiation**

Previous studies at NIST and elsewhere have established that the high density of interfaces in metallic nanolaminates result in significantly greater yield stresses and hardness than those of the component materials. The NIST studies, conducted on monocrystal electrodeposited nanolaminates of Cu-Ni, demonstrated that this effect is due to the interaction of dislocations with the interfaces. This project extends this work to study the effect of thin nanolaminate films on the mechanical properties of the substrate material, specifically on the initiation of fatigue cracks in polycrystal Cu-Ni and other FCC copper alloys. The objective is to evaluate the possibility that such films can significantly increase the service life of critical components.

- **Metallurgy of the R.M.S. Titanic**

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

Planned Outcomes:

- The work on lead-free solders will generate permissible pressure ratings for the applicable ASME Codes for solder joints in copper plumbing tube for use in potable plumbing systems. Initially, ratings will be generated for three solder alloys, but it is probable that industry will request tests on additional alloys.
- New technical standards will be developed for the design, manufacture and testing of high strength steel, aluminum alloy, and composite cylinders used in the transportation of high pressure gases.
- 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 work on nanolayered surface films will examine the possibility that such films can significantly improve the fatigue resistance of critical structural components.
- A determination of whether any metallurgical mistakes were made during the construction of the RMS Titanic will be attempted. Mechanical property data will be available for use in finite element simulations to attempt to explain the sequence of events during the sinking, most importantly the breakup of the ship on the surface.

External Collaborations:

- The work on lead-free plumbing solders is being conducted cooperatively with the CDA and with 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 research on Alloy 706 was carried out in close collaboration with engineers at Wyman-Gordon, Inc., who had ATP support for a project entitled "Cost-Effective, Near-Net-Shape, Superalloy Forgings for Power Generation Gas Turbines." A Wyman-Gordon staff member was appointed an Industrial Research Associate at NIST and participated in some of the experimental work.
- The studies of orthorhombic Ti-Al-Nb alloys are being conducted in collaboration with the U.S. Air Force Wright Laboratory which is also providing financial and material support, and with the aerospace companies and universities participating in the IHPTET Program.
- The research on nanolayered surface films is being performed in cooperation with the Nanoscale Materials Group at The Johns Hopkins University.
- The project on the metallurgy of the RMS Titanic is being performed under the auspices of the Discovery Channel and the Society for Naval Architects and Marine Engineers. Collaborators on this project include Prof. Phil Leighly (Univ. of Missouri, Rolla, MO), Dr. Harold Reemsnyder (Homer Labs, Bethlehem Steel, Bethlehem, PA), George Tulloch (RMS Titanic, Inc., New York, NY), Bill Garzke (Gibbs and Cox and SNAME, Arlington, VA), Dr. Jim Matthews (Defense Research Establishment - Atlantic, Halifax, NS), Bob Brigham (CANMET, Ottawa, Quebec), Ed McCutcheon (Cmdr., USCG (Retired), Bethesda, MD), and Prof. Bill Gerberich (Univ. of Minnesota, Minneapolis, MN).

Accomplishments:

- In the work on stress rupture of lead-free solders, testing was completed on alloy Sb5. The data were presented to ASME Committee and calculated permissible pressure ratings for plumbing joints are being circulated for letter ballot. Tests on Alloys E and HB are nearing completion. Significant progress was made in both the statistical analysis of the data and the basic studies of the failure mechanisms.
- In collaboration with DOT personnel, final specifications were developed for the use of ultrasonic methods for retesting high pressure steel cylinders in place of hydrostatic methods. Also, five ISO draft standards for steel and aluminum cylinders were completed and will be published in FY98.
- The NIST studies of Alloy 706 forgings successfully correlated grain boundary precipitation of eta-phase with elevated temperature fatigue resistance, and thus assisted ATP recipient Wyman-Gordon Inc. in the identification of heat treatments which minimized the deleterious effects of eta-phase precipitation on the fatigue resistance of the material.
- The deleterious components of the microstructure of both the hull steel and rivets of the RMS Titanic have been identified. For the hull steel, these include large MnS inclusions, large ferrite and pearlite grain size, coarse pearlite lamella, low Mn content, and low Mn/C ratio. In the rivets, which were composed of wrought iron, the slag content was found to be 3 to 4 times that normally found in contemporary material (9.2% versus 2.5%). Also, the direction of the stringers within the rivets was found to change from longitudinal within the shaft to transverse at the intersection of the shaft and the head formed during installation. Given that wrought iron has little transverse ductility, this is postulated as a failure mechanism for lost rivets

during the collision. Lost rivets and parted seams were found, in other parts of the overall study, to have been a major component of the flooding of the ship, and thus the sinking.

Impacts:

- Significant progress has been made in the process for introducing expanded permissible pressure data for lead-free solders into the ASME Codes. When completed, these data will provide the U.S. building construction industry with far greater choice 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 and other commercial 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 NIST research on Alloy 706 helped ATP recipient Wyman-Gordon Inc. to develop a heat treatment for a large forging which met the fatigue specification of its customer. This was the first large scale forging sold in the US by a domestic company, such forgings being bought previously from overseas suppliers. This advance opens a large market to Wyman-Gordon Inc.
- 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.

Outputs:

Publications:

Fields, R. J., "Characterization of Intergranular Eta Phase and Its Effect on the Low Cycle Fatigue Properties of Near-net Shape Alloy 706 Forgings," in the Proceedings of the Public Meeting on Materials Processing for Heavy Manufacturing, Rockville Maryland (September 24, 1996).

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

Presentations:

Clough, R. B., "Stress-Rupture Data for Lead-Free Solder Joints for Use in Potable Water Systems," Meeting with CDA and ASME staff, New York, NY, August, 1997.

Fields, R. J., "Characterization of Intergranular Eta Phase and its Effect on the Low Cycle Fatigue Properties of Near-net Shape Alloy 706 Forgings," Public Meeting on Materials Processing for Heavy Manufacturing, Rockville, MD, September 24, 1996.

Fields, R. J., "NIST Internal Research in Support of Cost Effective Near-net Shape Superalloy Forgings for Power Generation Gas Turbines," Wyman-Gordon's Annual Project Review for ATP, Worcester, MA, 1996.

Foecke, T., "Metallurgy of the RMS Titanic," University of Minnesota Department Colloquium, July 9, 1997.

Foecke, T., "The History of Fracture Mechanics," Fifth IMM Summer School on the Mechanics-Materials Linkage (banquet keynote address), The Catholic University of America, August 14, 1997.

Foecke, T., Public Affairs presentation to gifted and talented high school students on *Titanic*, NIST, August 20, 1997.

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

Investigators: F. Biancaniello, J. L. Fink, E. N. Pugh, R. E. Ricker, M. R. Stoudt, S. D. Ridder, and D. A. Little (Guest Researcher, University of Texas at El Paso)

Objectives:

The primary objective of this project is to develop test methods that enable U.S. industry to produce, market and use materials that resist degradation in corrosive environments.

Technical Description:

An analysis by Battelle Columbus Laboratories (BCL) in 1995 determined that the annual cost of corrosion to the US economy exceeds $300B. Corrosion impacts virtually every industry, but in FY97 our work focussed on corrosion issues in three specific industrial sectors.

The first of these focus sectors is the aircraft industry for which the 1995 BCL study estimated corrosion costs at $13B annually. While corrosion rarely causes catastrophic failures in this industry, this cost of corrosion is due to the cost of the repairs and maintenance currently employed to avoid corrosion failures and from the premature retirement of aircraft due to excessive corrosion damage. These costs are expected to rise as the average age of commercial and military aircraft increases. To help reduce the cost of corrosion in aging aircraft, NIST is collaborating with the U.S. Air Force's Wright Laboratory to develop test methods that will enable the development of more corrosion resistant alloys, corrosion prevention technologies, and standards for evaluating the ability of NDE techniques to detect and quantify corrosion damage.

Much of the corrosion damage in aircraft occurs hidden in small crevices and joints where it is difficult to detect, much less measure, corrosion. Another complication arises from the intermittent nature of this hidden corrosion. This results from the fact that the electrolyte responsible for attack is generally condensed moisture contaminated by various salts; the presence of the moisture film depends on the relative humidity, which, in turn, varies with service conditions. NIST responded to this set of problems by developing a test method that utilizes electrochemical techniques, which usually require complete immersion of specimens in an electrolyte, to measure corrosion rates inside a crevice under normal atmospheric conditions. The feasibility of the technique was demonstrated in laboratory tests on simulated crevices in Al alloy 2024 contaminated with different salts; the results established that the corrosion rate varied over four orders of magnitude with changes in relative humidity.

Exfoliation corrosion, a form of intergranular attack, is also a serious problem in Al sheet in aging aircraft, and existing test methods such as the EXCO Test (ASTM G34) do not provide data which enable quantification of the effects of alloy chemistry and heat treatment on susceptibility to this form of attack and sometimes fails to even predict behavior in service. NIST is now evaluating the electrochemical behavior of the relevant Al alloys in the solution used in the EXCO tests and this is expected to lead to the development of a quantitative electrochemical method for measuring the susceptibility.

The second focus sector is the pulp and paper industry, where the processing environments place severe demands on the materials used for critical components. Our current focus is on suction roll shells which cost hundreds of thousands of dollars each and have a service life of only five to eight years because of the combined action of cyclic loading and corrosive attack. Attempts to develop more corrosion resistant alloys are hindered by the lack of standard test methods that accurately predict service performance of the candidate alloys, and consequently NIST is working with CRADA partner Sandusky International, the only U.S. manufacturer of these critical components, to develop such tests. To date, a thorough electrochemical evaluation has been made of two duplex stainless steels for which service data are available, and work is proceeding on the development of a suitable test method.

The chemical process industry represents the third focus sector. Austenitic stainless steels are used throughout this major US industry primarily due to their superior resistance to pitting corrosion. The alloys examined in this study contain high nitrogen contents, known to increase pitting resistance of stainless steels, and are being developed by Crucible Materials Corporation and NIST under a CRADA, using a powder metallurgy approach. The materials produced in this CRADA were so resistant to pitting corrosion that the existing test methods used by industry such as ASTM G61, G48, and critical pitting temperature tests fail to induce this form of attack. As a result, a test method was needed that would enable comparison of the different alloys produced and identification of the optimum composition and processing conditions. To overcome this obstacle, NIST modified an existing standard method by modifying the composition and increasing the temperature of the test solution. In addition, the composition and elevated temperatures of this environment required development of a reference electrode. This test method proved capable of quantifying the pitting resistance of the alloys and, through multiple regression analysis, proved capable of quantifying the relative influence of alloying elements. This test method has now been incorporated into Crucible's alloy development program.

Planned Outcomes:

The outputs of this ongoing project will be primarily test methods of the types described above, but, based on past experience, it is anticipated that future outputs will also include predictive models, data generation and materials characterization.

External Collaborations:

NIST collaborated with the U.S. Air Force and the University of Texas at El Paso on the development of test methods for aging aircraft, with Sandusky International through a CRADA on duplex stainless steels in the pulp and paper processing industry, and with Crucible Materials Corporation through a CRADA on evaluation of the pitting corrosion resistance of nitrogenated stainless steels.

Accomplishments:

This project has resulted in the creation of two new measurement methods during this FY: (1) a method for the measurement of crevice corrosion rates in Al alloys during atmospheric exposure that utilizes a unique sample geometry with electrochemical measurement techniques, and (2) a method for evaluation of the influence of alloying elements on the pitting resistance of nitrogenated stainless steels. The first of these could lead to the development of a new standard test method while an existing standard could be modified to incorporate the second (ASTM G61). In addition, the metallurgical and electrochemical knowledge gained during the development of these methods and during work on the other methods in progress should lead to similar developments and metallurgical advances in the future.

Impacts:

Sandusky International has reported that the results of NIST's research shared with them through the CRADA has already had a significant impact on their research and development planning. Crucible Materials Corp. is incorporating the test method developed for nitrogenated stainless steels into their alloy development program. Following presentation of the crevice corrosion test method at the Aging Aircraft Conference in July, a U.S. Air Force Contractor approached NIST and discussed using this method in their program to develop and evaluate corrosion prevention compounds (corrosion inhibitors) for preventing crevice corrosion in aircraft.

Outputs:

Publications:

Ricker, R. E. and Duquette, D. J., "Corrosion Fatigue of Aluminum Alloys," submitted for publication in the proceedings of the First Joint DoD, FAA, and NASA Conference on Aging Aircraft, Ogden UT (8-10 July 1997).

Ricker, R. E. and Fink, J. L., "Crevice Corrosion Metrology for Aging Aircraft," submitted for publication in the proceedings of the First Joint DoD, FAA, and NASA Conference on Aging Aircraft, Ogden UT (8-10 July 1997).

Biancaniello, F. S., Ricker, R. E., and Ridder, S. D., "Structure and Properties of Gas Atomized HIP-Consolidated High Nitrogen Stainless Steel," submitted for publication in the proceedings of 5th Intl. Conference on Advanced Particulate Materials and Processes," West Palm Beach, FL April 7-9, 1997, Metal Powder Industry Foundation.

Ricker, R. E., "Aqueous Corrosion Resistance of Nickel and Iron Aluminide," Proceedings of International Symposium on Nickel and Iron Aluminides: Processing, Properties and Applications" S. C. Deevi, V. K. Sikka, P. J. Maziasz, R. W. Cahn eds., ASM Intl., Materials Park, OH, pp. 253-263 (1997).

Bandyopadhyay, S., Miller, A. E., Chang, H. C., Banerjee, G., Yuzhakov, V., Yue, D.-F., Ricker, R. E., Jones, S., Eastman, J. A., Baugher, E., and Chandrasekhar, M., "Quasi-periodic Quantum Dot Arrays Produced by Electrochemical Synthesis," Nanotechnology, **7**, pp. 360-371 (1996).

Ricker, R. E., Miller, A. E., Yue, D.-F., Banerjee, G., and Bandyopadhyay, S., "Nanofabrication of a Quantum Dot Array: Atomic Force Microscopy of Electropolished Aluminum," J. of Electronic Materials, **25**, No. 10, pp. 1585-1592 (1996).

Presentations:

Ricker, R. E., "Corrosion Fatigue of Aluminum Alloys," presented at the First Joint DoD/FAA/NASA Conference on Aging Aircraft, Ogden UT 8-10 July 1997.

Ricker, R. E., "Crevice Corrosion Metrology for Aging Aircraft," presented at the First Joint DoD/FAA/NASA Conference on Aging Aircraft, Ogden UT 8-10 July 1997.

Meetings Arranged:

"Corrosion Deformation Interactions II" A NIST staff member served on the International Scientific Organizing Committee for this meeting and organized financial support for US participants in this meeting held in conjunction with EuroCorr/96, Nice, France.

“Environmental Effects on Ceramic, Intermetallics and Composites,” A NIST staff member is serving as co-chair for this symposium to be held during Materials Week 1998.

"Hydrogen Effect in Metals (HEM)/Corrosion Deformation Interactions (CDI)" A NIST staff member is serving as co-chair of the organizing committee for this meeting of these two series of International meetings to be held jointly in Jackson Hole, WY, in Sept. of 2001.

Project Title: **MAGNETO-OPTICAL IMAGING**

Investigators A.J. Shapiro, R.D. Shull, V.I. Nikitenko*, V.I. Gornakov*
*Guest Scientist, Institute for Solid State Physics, Russian Academy of Sciences.

Objectives:

The objective is to develop techniques for obtaining direct experimental images in real time of magnetization reversal processes for technologically important magnetic materials, such as nanostructured material including multilayers, spin valves, and granular structures. In order to do this a new, nondestructive method, the Magneto-Optical Indicator Film (MOIF) technique, was developed in cooperation between NIST and the Institute for Solid State Physics of the Russian Academy of Sciences. The obtained information, such as static and dynamic magnetization and remagnetization processes and their relationships to thin film characteristics and defects, provides nondestructive characterization of the quality of artifically constructed nanostructures, magnetic devices, and bulk ferromagnets.

Technical Description:

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

Planned Outcome:

The MOIF method is expected to become a standard nondestructive quality control imaging technique for next generation magnetic materials for sensors and storage devices, to contribute to the fundamental understanding of the remagnetization process in artificial magnetic materials, and to allow the investigation of domain wall nucleation and motion in magnetic materials as a function of their microstructure and processing variables.

Accomplishments:

- It was shown that epitaxial NiO/NiFe bilayers on single crystal MgO exhibit unidirectional magnetic anisotropy, as revealed by a shift of the hysteresis loop of the ferromagnet along the fields axis. We have studied experimentally the magnetization reversal of epitaxial NiO/NiFe bilayers and extended the model of magnetic exchange biasing to describe the measured enhanced coercivity and asymmetry observed in them. The relative activity of various domain nucleation centers was also observed. For the first time the influence of dislocations on these processes was determined.
- Direct experimental examination of the static and dynamic magnetization reversal processes in $[Co_{64}Ni_{31}Cu_5$ (2nm)/Cu(2nm)$]_{200}$ magnetic multilayers was conducted in real time, proving that the MOIF technique can be utilized as a non-destructive characterization method for quality control.
- By means of the MOIF technique the magnetic domain structure of a Si/NiO/Co/Cu/Co/Ta nonsymmetric bottom spin valve was imaged. It was demonstrated that the first stage of magnetization reversal is characterized by the nucleation of many microdomains. With increasing reversed field, the domain walls move over small distances (5-20 micrometers) until annihilation. The magnetic domain size depends on the thickness of the Co layer.

Outputs:

Publications:

V. S. Gornakov, V.I. Nikitenko, . L.H. Bennett, H.L. Brown, M.L. Donahue, W.F. Egelhoff, R.D. McMichael, and A.J. Shapiro. “Experimental study of magnetization reversal processes in nonsymmetric spin valve”. J. Appl. Phys. 81 (8), 15 April 1997.

L.H. Bennett, M.J. Donahue, A.J. Shapiro, H.L. Brown, R.D. McMichael, V.S. Gornakov, V.I. Nikitenko, “Investigations of domain-wall formation and motion in magnetic multilayers”, Physica B, 223 (1997) 356-364.

Presentations

V.I. Nikitenko, L.M. Dedukh, V.S. Gornakov, Yu. P. Kabanov, L.H. Bennett, M.J. Donahue, L.J. Swartzendruber, A.J. Shapiro, and H.J. Brown. “Spin Reorientation transition and domain structure in magnetic multilayers”, presented at INTERMAG 97, New Orleans, Louisiana, Apr 1997.

V.I. Nikitenko, L.M. Dedukh, V.S. Gornakov, Yu. P. Kabanov, L.H. Bennett, M.J. Donahue, L.J. Swartzendruber, A.J. Shapiro, and H.J. Brown.” Investigations of spin reorientation transition in antiferromagnetically coupled multilayers.”, March Meeting of The

Amer.Phys.Society. 1997.

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

Investigator: Eva Drescher-Krasicka

Objectives:

The objective of this project is to develop new, highly sensitivite methods of measuring stresses by scanning acoustic microscopy. This study is in contrast to the multiple descriptions of the dependence of acoustic wave velocity dependance on residual or applied stress. Our efforts are directed toward sensitive stress measurements by monitoring the change of the amplitudes of the polarized modes received from the stressed area. The goal is to show feasibility of the method, and to calibrate acoustic microscopic measurements of internal stresses by applying loads to specimens for which the stress distribution can easily be calculated.

Technical Description:

Many attempts have been made to measure internal stresses ultrasonically by exploiting the third order changes in elastic constants which accompany changes in internal stress. Until recently all of these approaches have employed measurements of the phase velocities of elastic waves. However, these velocities vary only weakly with changes in elastic constants, and attempts to use this approach to measure residual stresses have met with only limited success. A program has been underway at NIST to use other characteristics of ultrasonic waves, which are more sensitive to changes in elastic constants than phase velocity, and which can be detected using an acoustic microscope.

One of these methods makes use of the fact that isotropic materials have two shear wave modes which travel at the same velocity, but which are polarized (direction of particle vibration in the wave) in orthogonal directions. In the presence of an internal stress, the velocities of these waves are altered minutely, as is their polarization. While it is extremely difficult to detect these changes directly, interference effects lead to dramatic intensity variations which correspond to stress levels.

In addition to providing measurements of stresses, this new measurement method promises to provide through thickness information to help in the "tomographic" reconstruction of internal stress fields. To make accurate "tomographic" reconstructions of internal stress fields, inplane information on internal stresses is needed. Leaky-wave ultrasonic modes offer another, novel characteristic of ultrasonic waves which can provide this information, and are extremely sensitive to changes in elastic constants. Mathematically this is seen by expressing the waves in their plane wave or cylindrical form, and matching displacements and normal tractions across the interface by allowing a complex phase velocity for the mode along the interface.

In a wave propagation context these modes appear to 'leak' away from the interface, at an angle which is characteristic of their Poynting vector. The Poynting vector of a leaky mode describes the elastic power flowing out of an arbitrary volume through which the mode is traveling. The 'asymptotic' leakage angle (the macroscopic angle observed at some distance from the interface) and attenuation, as well as the phase velocity, of these waves can be extraordinarily sensitive to the frequency of the impinging beam.

Indeed, the theory of leaky waves has previously been extensively developed by the authors from the Metallurgy Division, and the existence and many properties of such waves have been experimentally confirmed. In this work we quantitatively explore the possibility that the leakage angle for such modes greatly amplifies changes in elastic constants in the materials on either side of the interface, and by measuring this angle using acoustic microscopy, one can measure the in-plane changes of internal stress as a function of depth which cannot easily be obtained by interference effects.

Planned Outcome:

The ultimate goal of this project is to establish a new method, based on acoustic microscope measurements, to evaluate the distribution of the residual stresses inside of a solid sample.

External Collaboration:

The 1997 work was done in close collaboration with Professor John Willis from the Department of Applied Mathematics and Theoretical Physics in Cambridge, U.K., with Dr. John A. Simmons, formerly of the Metallurgy Division and with Professor Ron Kline and his student, Linqiang Jiang, formerly from the University of Oklahoma.

Accomplishments:

FY 1997 work successfully proved the sensitivity of the shear, longitudinal and leaky modes to residual and applied stresses.

Impacts:

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

Outputs:

Publications:

Drescher-Krasicka, E. Willis, J. R., *Nature,* Vol. **384**, November (1996).

Simmons, J. A., Drescher-Krasicka, "Internal Stresses Effects on Leaky Waves at Composite Interfaces, an extended abstract at the 4th International Conference on Composites Engineering," Big Island of Hawaii, July (1997), Conference Proceedings, pp. 911-912.

Presentations:

Simmons, J. A., Drescher-Krasicka, E., paper at the 4th International Conference of Composite Engineering, Big Island of Hawaii, July, 1997.

Project Title: **ELECTRON MICROSCOPY**

Investigator: J. E. Bonevich

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 Microscopy Facility primarily serves the Metallurgy and Ceramics Divisions as well as other NIST staff and outside collaborative research efforts.

Technical Description:

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

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

Planned Outcome:

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

External Collaborations:

Prof. Searson (Johns Hopkins University) provided electroplated Cu/Ni/Co multilayer nanowires for characterization by holography and high-resolution composition mapping. Prof. Searson also supplied nanoscale ZnO particles for surface morphology and structure measurements. The Naval Research Laboratory supplied nanoscale Au and Pd catalytic particles for mean inner potential measurements. Prof. Pozzi (Bologna University, Italy) collaborated on interpretating holographic observations of superconducting materials.

Accomplishments:

- Atomic resolution compositional mapping was applied to a new class of materials with naturally-occurring magnetic multilayers. Phases in the BaFeTiO system were shown to possess an Fe-rich phase separated by a Ba-rich dielectric spacer material. These new materials are expected to find applications in microwave devices.
- Compositional mapping was applied to magnetic spin-valve TaO/Co/Cu/Co/NiO materials grown by sputter deposition. Annealing of these materials at standard semiconductor processing temperatures produce a degradation of magnetic properties. The mapping revealed the formation of large metallic Ni islands from the NiO substrate, resulting in the structural disruption of the Co magnetic layers.
- High-resolution imaging of $BaTiO_3$/MgO photonic materials has revealed the formation of amorphous zones in close proximity to the barium titanate/magnesia interface. The zones result from non-stoichiometries in the barium titanate thin films and cause degradation in the desired dielectric properties.
- Mean inner potentials and surface morphologies of nanoscale Au/Pd particles were measured by electron holography. The particles were shown to have alloyed compositions with non-equilibrium structures, such as multiple-twinning, and faceted surfaces. Mean inner potentials varied from 17-20 eV.
- The theoretical treatment of vortex image contrast in superconductors has been refined. The results show that the London model of a vortex is a useful computational tool for 1-D trace profiles of the electron phase. The extended analytical model correctly interprets the phase profiles resulting from the significant broadening of the magnetic field that occurs in thin film specimens. Good agreement with the experimental data has been achieved.
- A division-wide image processing and computation facility was created with workstations, image scanners, and processing software as well as a high resolution photographic quality printer. The facility provides image analysis and quantitative metallography capabilities.

Impact:

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

Outputs:

Publications:

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

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

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

Bonevich, J., Capacci, D., Harada, K., Kasai, H., Matsuda, T., Patti, R., Pozzi G., and Tonomura, A., "On the Influence of Specimen Thickness in TEM Images of Superconducting Vortices II," Microscopy and Microanalysis, Vol. 3, Suppl. 2, 505 (1997).

Bonevich, J., "Electron Holography of Electromagnetic Fields," Microscopy and Microanalysis, Vol. 3, Suppl. 2, 1059 (1997).

Turner, S., Bonevich, J., Maslar, J., Aquino, M., Zachariah, M., "TEM and Electron Holography of Nanophase TiO2 Generated in a Flame Burner System," MRS Symp. Proc., Vol. 457, 93 (1997).

Presentations:

Bonevich, J., "Electron Holography - Theory and Applications," Invited talk at Dept. of Materials Science, Johns Hopkins University, Baltimore, Maryland, April, 1997.

Bonevich, J., "Applications of Electron Holography and Phase Imaging," Invited talk at National Institutes of Health, Bethesda, Maryland, May, 1997.

Bonevich, J., "Electron Holography - The Phase Problem," Invited talk at the Meeting of the Microscopy Society of America, Cleveland, Ohio, August, 1997.

METALS PROCESSING

The properties of metals and their alloys depend strongly on their processing history. For example, the distributions of phases, grain structure, alloy compositional segregation, and defects in final commercial products depend on the conditions under which materials are processed and fabricated. These distributions in turn are crucial in determining the alloy strength, ductility, homogeneity, and other properties important for industrial applications. The Metals Processing Program focuses on measurements and predictive models needed by industry to design improved processing conditions, provide better process control, develop improved alloy and coating properties, tailor material properties for particular applications, and reduce costs.

Major successes in applying measurements and modeling to processing applications have been achieved in interactions with the aerospace, powder metallurgy, electroplating and electronics industries. Predictive models 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 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. Critical mechanistic, chemical and process variables controlling the structure/ property relationships of coatings and thin films produced by electrodeposition are being developed to take further advantage of this electrochemical process, which does not require high purity starting materials and is readily adaptable to large scale production.

Measurements and predictive models for processing being pursued in this program are of three kinds:

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

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

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

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

Project Title: **PROCESSING OF ADVANCED MATERIALS**

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

Objectives:

Objectives of this project are to provide industry with measurements, sensors, predictive models, methodologies and standards needed to apply intelligent processing techniques to 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.

Technical Description:

State of the art techniques are employed in the processing and synthesis of high performance materials. Predictive models and thermodynamic assessments are developed to aid in microstructure, composition, porosity and property control. This research is part of a long-term research effort on advanced processing, emphasizing rapid solidification and powder metallurgy. One outgrowth of the program was a highly successful NIST/Industry Consortium project on applying intelligent processing concepts to rapidly-solidified nickel-based superalloy powders produced by atomization techniques. Current research is focussed on three main areas. The first area is collaboration with powder metallurgy companies to apply NIST-developed techniques for nozzle optimization and control of industrial atomizers. 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 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 collaborations with industry and academia.

Planned Outcome:

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

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

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

External Collaborations:

Collaborations are being conducted with Crucible Materials Corporation on (1) thermodynamic predictions, (2) corrosion measurements and kinetic models through an ATP CRADA on enhanced corrosion properties of high nitrogen stainless steels produced by atomization and (3) hot isostatic pressing (HIP). A CRADA project with Carpenter Technology Corporation is underway to apply NIST nozzle design optimization techniques to the production of fine powder for the metal injection molding industry. Cooperative work is being done with Johns Hopkins University to investigate short range order in metallic glasses.

Accomplishments:

- A system has been installed to perform diagnostics on gas flows in industrial-sized powder atomization systems. Optical sensors applicable to analyses of advanced powder production systems have been developed through SBIR and NIST interactions.
- Two new standard reference materials, C1150b (white cast iron) and 1267a (446 ferritic stainless steel) have been produced by rapid solidification of gas atomized powders and HIP consolidation. These more homogeneous SRM’s, requested by ASTM Committee E1, will allow improved measurement of industrial materials.
- A predictive model has been developed for predicting nitrogen solubility, phase stability and enhanced properties in gas atomized high nitrogen stainless steels.

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.
- More homogeneous standard reference materials have been produced, allowing

improved measurement of industrial materials.

Outputs:

Publications:

Biancaniello, F. S., Ricker, R. E., and Ridder, S. D. "Structure and Properties of Gas Atomized, HIP-Consolidated High Nitrogen Stainless Steel," Advanced Particulate Materials & Processes, (Metal Powder Industries Federation, Princeton, NJ, 1997) pp. 309-316.

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

Presentations:

Biancaniello, F. S. "Gas Atomized High Nitrogen Steel for Armor Applications," Aberdeen Proving Grounds, Aberdeen, MD., June, 1997.

Biancaniello, F. S. "Recent Studies on Powder Processed Nitrogenated Stainless Steel," TMS Symposium on P/M Current Research and Industrial Practices, Indianapolis, Indiana, Sept., 1997.

Biancaniello, F. S. "New Process Control Agents for Mechanical Alloying and Ball Milling," TMS Symposium on P/M Current Research and Industrial Practices, Indianapolis, Indiana, Sept., 1997.

Biancaniello, F. S. "Structure and Properties of Gas Atomized, Hip-Consolidated High Nitrogen Stainless Steel," 5th International Conference on Advanced Particulate Materials and Processes, West Palm Beach, Florida, April, 1997.

SRM's in production:

SRM #C1150b	White Cast Iron
SRM #C1267a	Ferritic Stainless Steel (446 SS)

SRM's under development:

SRM #1245a	Inconel 625

Project Title: **SOLIDIFICATION MODELING**

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

Objectives:

Analytical and numerical models of solidification processes are developed by NIST with special emphasis on solute segregation during alloy solidification and crystal growth. Such models will allow the prediction of microstructure and segregation as a function of processing conditions, for example, solidification velocity, thermal conditions, 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. 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 help explain the role of fluid flow in terrestrial processes. Dendritic growth is always present in castings and determines the scale of microsegregation; phase field models are being implemented which allow the calculation of solute distribution for complex dendritic morphologies. These calculations allow studies of tip kinetics, solute redistribution, and coarsening.

Planned Outcome:

Models for alloy solidification and crystal growth processes will be tested and made available to industry and academia. These models will improve our ability to determine the optimum processing conditions for a given material. In addition, they will define critical experiments for determining thermophysical properties necessary for accurate modeling.

External Collaborations:

Modeling and interpretation of experiments on the directional solidification of lead bromide doped with silver bromide has continued in collaboration with scientists at Northrop Grumman Science and Technology Center. A model was developed for the growth of in-situ composites in the monotectic aluminum-indium system in collaboration with Prof. J. B. Andrews of the University of Alabama at Birmingham. NIST is participating in an experiment on the onset of cellular growth in bismuth-tin alloys with Prof. R. Abbaschian of the University of Florida. Collaboration with Marshall Space Flight Center on interface instabilities during melt and solution growth has continued.

Phase field calculations of solute trapping are being conducted with Prof. A. Wheeler, Southampton University, and of grain boundary formation with Prof. R. Kobayashi, Hokkaido University.

Accomplishments:

- The role of convection and interface instability in causing inhomogeneities in dopant distribution in the acousto-optical material lead bromide has been analyzed in collaboration with N. B. Singh. Measurements of the diffusion coefficient of silver bromide in lead bromide were carried out at Northrup-Grumman Science and Technology Center; the diffusion coefficient is an important parameter in modeling crystal growth in this system. An analysis of the effect of convection and container walls on the growth of dendrites into pure supercooled melts has been developed. The results indicate the processing conditions needed to avoid both convective and wall effects.
- A previous model of eutectic solidification has been extended to monotectic solidification in which aligned rods of a liquid phase are formed in a solid matrix. The new model accounts for diffusion in rod phase and has been applied to the aluminum-indium system.
- Analytic and numerical calculations have been performed in order to determine the fluid flow conditions required to avoid step bunching during crystals growth of KDP, large crystals of which are required for laser fusion applications. Realistic modeling of the growth process required extension of a previous theory to include nonlinear anisotropic interface kinetics. Bunching of the elementary steps during layerwise growth causes impurity segregation resulting in inhomogeneous optical properties that lead to decreased damage thresholds in the crystals.
- The phase field technique has been extended to treat directional solidification. Microstructure prediction with a specified growth velocity and temperature gradient is now possible and the formation of arrays of cells and dendrites is being studied. An understanding of the factors that determine the characteristic spacing of these arrays will lead to more robust models for segregation spacing in cast materials.

Impact:

Optimized commercial growth conditions identified in the NIST research can now be used to produce quality lead bromide-silver bromide crystals as a non-linear optical material.

Supercomputer calculations of a single dendrite will permit construction of improved models of microsegregation processes for castings that will lead to improved mechanical properties.

Outputs:

Publications:

Boettinger, W. J. and Warren, J. A., ``Prediction of Solidification Microstructure using the Phase-Field Method," Proceedings of the General COST512 Workshop on Modeling in Materials Science and Processing, Ed. by M. Rappaz and M. Kedro, European Commission, Brussels, 1996, p. 11-20.

Warren, J. A. and Boettinger, W. J., ``Numerical Simulation of Dendritic Alloy Solidification

Using a Phase Field Method," Solidification Processing, 1997, edited by J. Beach and H. Jones, Department of Engineering Materials, University of Sheffield, UK 1997, p. 442.

Singh, N. B., Mani, S. S., Adam, J. D., Coriell, S. R., Glicksman, M. E., Duval, W. M. B., Santoro, G. J., and DeWitt, R., ``Direct Observations of Interface Instabilities," J. Crystal Growth 166, 364 (1996).

Singh, N. B., Glicksman, M. E., Coriell, S. R., Duval, W. M. B., Santoro, G. J., and DeWitt, R. ``Measurement of Diffusion Coefficient Using a Diaphragm Cell: $PbBr_2$-AgBr System," J. Crystal Growth 167, 107 (1996).

Coriell, S. R., Murray, B. T., Chernov, A. A., and McFadden, G. B., ``Step Bunching on a Vicinal Face of a Crystal Growing in a Flowing Solution," J. Crystal Growth 169, 773 (1996).

Sekerka, R. F., Coriell, S. R., and McFadden, G. B., ``The Effect of Container Size on Dendritic Growth in Microgravity," J. Crystal Growth 171, 303 (1997).

Coriell, S. R., Mitchell, W. F., Murray, B. T., Andrews, J. B., and Arikawa, Y., ``Analysis of Monotectic Growth: Infinite Diffusion in the L_2 Phase," J. Crystal Growth 179, 647 (1997).

Coriell, S. R., Chernov, A. A., Murray, B. T., and McFadden, G. B., ``Step Bunching: Generalized Kinetics," J. Crystal Growth, in press.

Presentations:

Boettinger, W. J., “Prediction of Dendritic Growth Microstructures using the Phase-Field Method," Supercomputer Seminar Series, University of Minnesota, Minneapolis, MN, November 1996.

Boettinger, W. J.,”Prediction of Dendritic Growth Microstructures using the Phase-Field Method,” at Institute for Theoretical Physics Workshop, Quantitative Methods in Materials Research, University of California at Santa Barbara, Jan. 1997.

Boettinger, W. J., “Numerical Simulation of Dendritic Alloy Solidification Using a Phase Field Method," TMS-AIME, Sept. 1997.

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

Coriell, S. R., “Morphological Stability of Faceted Interfaces," Ames Laboratory, Iowa State University, Ames, Iowa, August, 1997.

Coriell, S. R., " Morphological Stability of a Vicinal Face: Effects of Anisotropic Kinetics and Fluid Flow," The Eastern Regional Conference on Crystal Growth and Epitaxy, Atlantic City, NJ, September, 1997.

Warren, J. A., "Phase Field Simulations of the Solidification of a Binary Alloy," Materials Research Society, San Francisco, April 2, 1997.

Warren, J. A., "Phase Field Simulations of the Solidification of a Binary Alloy," Second SIAM Conference on Mathematical Aspects of Materials Science, Philadelphia, PA, May 14 1997.

Warren, J. A., "Phase Field Simulations of the Solidification of a Binary Alloy," Seventh Conference on Computational Research on Materials, Morgantown WV, May 16th, 1997.

Warren, J. A., "Phase Field Simulations of the Solidification of a Binary Alloy," Solidification Processing 1997, Sheffield England, July 7th, 1997.

Warren, J. A.,"Phase-field Simulations of Solidification, Collision and Grain Boundary Formation" TMS, Materials Week, Indianapolis, September 1997.

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

Investigators: S. D. Ridder and F. S. Biancaniello

Objectives:

The primary focus of this project is to develop tools for the measurement and control of process conditions for plasma spray systems. This includes off-line analysis tools (e.g. high-speed cinematography, 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, once installed, will be the development of measurement tools to provide diagnostic and control capabilities for the production of industrially important spray coatings such as ceramic-based Thermal Barrier Coatings (TBC's) and metallic based corrosion and wear reducing layers.

The industrial use of thermal spray processes is as old as "fuel gas" welding and has become an integral part of the manufacturing art. In practice, thermal jets, generated by oxygen/fuel flames or plasmas (DC or AC) within a spray "gun" are used to melt or soften feed-stock materials and then propel the resulting particles onto various substrates. The geometry and operating parameters of the gun depend on the intended function of the resulting coated part. Due to the more reliable feed characteristics, there is growing interest in systems that use wire for the material feed stock, especially for the production of metallic coatings. However, many industrially important coatings are produced from ceramics and friable metallic materials that cannot easily be processed into a suitable "wire" shape.

Instrumentation packages for plasma spray systems currently incorporate user interface panels that provide indication and control of several process parameters: e.g., voltage, current, gas flow rates, powder flow rate, substrate position, and live video displays. Most commonly applied by skilled technicians, plasma spray is now being adapted for automatic control using robotics. NIST has capabilities in this area.

The switch to automatic control and robotics has created increasing demands for new sensors, diagnostics, modeling, and expert system controls. This project is designed to address these industrial needs. A DC plasma, powder feed, thermal spray system will be used to study new sensor and diagnostic systems. High-speed cinematography, multi-exposure laser holography, and high-speed video cameras will be developed to provide diagnostic tools for thermal spray systems. New Infra-Red (IR) thermal imaging sensors, currently capable of measuring the temperature of rough, variable emissivity surfaces, will be improved to provide on-line measurement of particle temperature and velocity.

Intelligent process control requires detailed understanding of the effects of process variables or parameters on the resulting coating characteristics. Process parameters must be identified, reduced (dimensional analysis and parameterization is used to identify the dependent and independent variables), and measured. 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.

Planned Outcome:

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

External Collaborations:

Current collaborative work on thermal spray processing includes the NIST SBIR funded research with Stratonics, Inc., The Cooke Corporation, and North Dancer Labs, Inc. all aimed at developing new sensor and diagnostics technology. A cooperative exchange of expertise has been initiated with scientists at Los Alamos National Laboratory. NIST has provided assistance in the design and operation of an inert gas atomization system for beryllium alloys and Los Alamos has provided technical assistance in the operation of the NIST D.C. plasma thermal spray equipment.

Accomplishments:

- The NIST thermal spray system has been installed and initial trials have been conducted. This system will be used to provide experimental thermal spray coatings for the NIST project on process modeling and control of thermal spray.
- A Phase I SBIR on developing a high speed video camera for spray diagnostics and control was awarded to The Cooke Corporation. During initial trials of this device in the NIST thermal spray system, multiple exposure images of thermal spray droplets in flight were demonstrated. The measured droplet sizes ranged from 40 to 100 µm with speeds from 80 to 190 ms^{-1}.
- A Phase II SBIR for developing a thermal imaging sensor for spray processing equipment was awarded to Stratonics, Inc.. This sensor, as currently configured, provides "real-time" temperature, emissivity, and surface roughness measurements on material coatings as they are formed. Development work is in progress on the use of image intensifying components with the intent of providing temperature measurements of particles/droplets "in-flight".
- A Phase I SBIR on developing a holographic diffuse light source for spray diagnostics was awarded and work was initiated with North Dancer Labs, Inc. This sensor, if successful, will provide illumination suitable for specularly reflective materials such as metal powder, droplets, and coatings. These measurement tools will be valuable for many materials processing systems. In particular, they will provide thermal and coating quality data for NIST process modeling and control software that is to be developed as part of the thermal spray project.

Impact:

Ongoing NIST SBIR funded research has resulted in a new imaging pyrometer with wide applicability in the materials processing area. This "Thermal Spray Imaging" sensor, available from Stratonics, Inc. of Laguna Hills, CA uses special IR optics to produce a high resolution two-color image of the material under test. This approach provides both temperature and emissivity data with spatial resolution as high as 15 µm. Equipped with a standard video CCD array, this device can measure real-time accurate surface temperatures (±10 K), emissivity, and roughness of such objects as plasma spray coatings, spray deposition substrates, and the surface of hot or molten materials. An image intensifying camera is currently under development that will provide similar results from thermal spray and atomization droplets in flight.

Outputs:

Publications:

Rosenthal, P. A., Cosgrove, J. E., Haigis, J. R., Markham, J. R., Solomon, P. R., Farquharson, S., Morrison Jr., P. W., Ridder, S. D., and Biancaniello, F. S. "FT-IR process monitoring of metal powder temperature and size distribution," *Optical Sensors for Environmental and Chemical Process Monitoring,* SPIE, **2367**, 183, (1995).

Presentations:

Ridder, S. D. "Metal Powder Research at NIST," TMS Symposium on P/M Current Research and Industrial Practices, Indianapolis, Indiana, Sept., 1997.

Project Title: **ELECTRODEPOSITION OF ALUMINUM ALLOYS**

Investigator: G.R. Stafford

Objectives:

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

Technical Description:

Aluminum and many of its alloys can impart excellent corrosion protection when applied as a thin coating to other materials. Typical coating technologies include hot-dipping, flame spray and physical vapor deposition (PVD). Electrodeposition may offer an inexpensive method for producing homogeneous and fine-grained aluminum-based thin films. Unfortunately, aluminum can only be electrodeposited from aprotic, nonaqueous solvents or molten salts. One of the more widely explored molten salt electrolytes consists of a mixture of $AlCl_3$ and an alkali chloride such as NaCl. The electrodeposition of alloys such as Al-Ti, Mn, Cr, Ni, Co and Cu have been demonstrated. Recent reports in the literature indicate that niobium may be electrochemically dissolved in chloroaluminate electrolytes and thus provide a means for electrodepositing Al-Nb alloys. Al-Nb alloys produced by PVD have shown excellent resistance to pitting in chloride media. Part of our effort this year has focused on the electrodeposition of Al-Nb alloys from the $AlCl_3$ - NaÇl electrolyte.

The $AlCl_3$ - alkali chloride systems have been widely explored and a continuous process for the electrodeposition of Al-Mn alloys onto sheet steel has been developed. Even so, physical properties such as high vapor pressure or high melting temperature make them unsuitable for many technological applications. Organic chloroaluminates, which are obtained when certain anhydrous organic chloride salts such as 1-methyl-3ethyl-imidazolium chloride

(MeEtimCl) are combined with $AlCl_3$, are viable alternatives since they are liquids at room temperature and exhibit negligible vapor pressure. Our remaining activities in this program have focused on the electrodeposition of pure aluminum and some of its alloys from the $AlCl_3$-MeEtimCl room temperature electrolyte.

Planned Outcome:

There are three primary goals to this work. The first is to verify reports in the literature indicating that niobium may be electrochemically dissolved in chloroaluminate electrolytes. This may be a significant result since refractory metals have generally been considered to be stable in these melts. The formation of an electroactive niobium species in solution may provide a means for electrodepositing Al-Nb alloys. We expect to gain information on the electroactive niobium species and demonstrate the deposition of Al-Nb alloys.

We plan to characterize the microstructure, morphology and chemical purity of pure aluminum, electrodeposited at room temperature from an $AlCl_3$-MeEtimCl molten salt electrolyte. It is likely that these deposits will have some chloride contamination. We anticipate that the addition of benzene will reduce the viscosity, increase the ionic conductivity of the melt and eliminate the chloride in the deposits. In addition, we expect to demonstrate the electrodeposition of Al-Ni, Co and Cu alloys from the room temperature $AlCl_3$-MeEtimCl molten salt electrolyte.

External Collaborations:

We are working with Geir Martin Haarberg of the Norwegian University of Science and Technology in Trondheim, Norway to understand the electrochemical behavior of niobium in chloroaluminate electrolytes. An understanding of niobium complex ion formation in this electrolyte is essential in our effort to electrodeposit Al-Nb alloys.

We are working with Professor Charles Hussey of the University of Mississippi to develop a chloroaluminate electrolyte which will allow us to electrodeposit pure aluminum and aluminum alloys at room temperature.

Accomplishments:

A study of the electrochemical behavior of niobium in a 52:48 mole ratio $AlCl_3$ - NaCl molten salt electrolyte was initiated. Niobium can indeed be electrochemically dissolved, however the solubility and electrochemical properties of the electroactive species have yet to be determined. Aluminum-niobium alloys, containing a Nb atomic fraction of up to 13.5 %, have been electrodeposited. Deposits containing less than 5 % Nb are face centered cubic (fcc) aluminum. As the Nb content increases, an amorphous phase is introduced into the structure. The exact composition of the amorphous phase as well as the phase distribution in the 5 % to 15 % Nb alloys have yet to be determined.

Pure aluminum electrodeposited from $AlCl_3$:MeEtimCl electrolytes is often contaminated with chloride. The viscosity of this room temperature system is higher than that of the high temperature analogs and electrolyte entrapment appears to be a significant adverse consequence of this high viscosity. We have demonstrated that the addition of benzene to the $AlCl_3$:MeEtimCl electrolyte reduced the viscosity and increased the ionic conductivity of the melt. Deposits made from benzene containing electrolytes are chloride-free and have much improved morphologies over those made from pure melt. It is likely that similar benefits can be obtained from the use of less hazardous aromatic solvents.

We have determined that Al-Ni, Al-Co and Al-Cu alloys can be electrodeposited from $AlCl_3$:MeEtimCl electrolytes at potentials positive of the aluminum deposition potential. The mechanism appears to be similar to that observed in the inorganic chloroaluminates where aluminum incorporation is driven by the free energy of alloy formation.

Outputs:

Publications:

Mitchell, J. A., Pitner, W. R., Hussey, C. L., and Stafford, G. R., "Electrodeposition of Cobalt and Cobalt-Aluminum Alloys from a Room-Temperature Chloroaluminate Molten Salt," J. Electrochem. Soc. **143**, 3448 (1996).

Liao, Q., Pitner, W. R., Stewart, G., Hussey, C. L., and Stafford, G. R., "Electrodeposition of Aluminum from the Aluminum Chloride-1-Methyl-3-Ethylimidizolium Chloride Room-Temperature Molten Salt + Benzene," J. Electrochem. Soc. **144**, 936 (1997).

Stafford, G. R., and Moffat, T. P., "The Electrodeposition of Corrosion Resistant Aluminum Alloy Coatings," Proc. of NACE Topical Symposium on Coatings and Surface Modification, Corrosion '97, New Orleans, LA (1997).

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

Presentations:

Stafford, G. R., "The Electrodeposition of Corrosion Resistant Aluminum Alloy Coatings," Norwegian University of Science and Technology, Trondheim, Norway, October, 1996.

Stafford, G. R., and Moffat, T. P., "The Electrodeposition of Corrosion Resistant Aluminum Alloy Coatings," NACE Topical Symposium on Coatings and Surface Modification, Corrosion '97, New Orleans, LA (1997).

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

Project Title: **ELECTRODEPOSITED COATING THICKNESS STANDARDS**

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

Objectives:

The objective of this work is to re-supply SRM Coating Thickness Standards numbers 1357, 1358, 1359, 1361a, 1362a, and 1363a used by the organic and inorganic coating industries.

Technical Description:

These standards have proven to be popular due to the diversity of industries which use them. The inventory kept by SRMP is low since the Electrochemical Processing Group last produced these SRMs in 1994. This production shutdown was necessary in order for us to replace obsolete primary standards and completely revise the production and certification protocols.

The uncertainties due to deficiencies in the certification methodology have been reduced by replacing the stage used for the certification of the secondary standards with one that completely automates the measurement process. Consequently, operator intervention and bias have been minimized. In addition, the operating range for each of the instruments as well as the mathematical models used to fit the data have been reviewed and optimized.

The production and thickness assignment of the primary standards, used for in-house calibration, represents the final task prior to continuing the production of the revised coating thickness standards. Assigning certified thickness values for these primary standards allows the certification of the secondary standards, which are sold to the general public, to proceed.

Planned Outcome:

The goal of this work is to replenish the stock of the following SRM's by a total of 953 units distributed in the following manner:

SRM 1358	479 units
SRM 1359	20 units
SRM 1362a	319 units
SRM 1363a	90 units
SRM 1364a	45 units
SRM's Total	953 units

Accomplishments:

- Work on the replacement primary standards used for the certification of the coating thickness SRM's listed above has been completed. Each of these primary standards has an average standard deviation which is less than 1.5% of the certified coating thickness.
- All of the 953 outstanding units of SRM's 1358, 1359, 1362a, 1363a, and 1364a have been fabricated. The thickness measurement has been completed on 550 of these 953 units.
- The packaging design for the new SRM's has been completed.

Outputs:

SRM's in production:

SRM#1357	Cu & Cr Coating on Steel
SRM#1358	Cu & Cr Coating on Steel

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

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:

The request for this standard has come mainly from the electronics industry where gold is electrodeposited on printed circuit board contacts. Also, the general plating industry for precious metals has requested the standard for process control of addition agents to Au electrolytes. This microhardness standard is expected to fill a void in the low hardness, low load standards presently offered. It will allow the electronics and precious metals plating industry to verify the proper operation of the microhardness measuring devices presently used for quality assurance.

Steps are now being taken to scale-up the fabrication of a low load microhardness standard prototype. This requires a scale-up of the Au electrodeposition process, a means to cut the material uniformly and accurately, a system to mount the samples in the mounting media and a jig to diamond turn up to eight samples at a time.

A non-uniform current density during Au deposition results in non-uniform grain size and hardness. We expect to reduce the hardness variation across the sample surface by scaling up the electrodeposition process and electroplating a large panel, perhaps eight inches square. This is analogous to a method successfully implemented to reduce the thickness variation in our electrochemically produced coating thickness standards.

In order to cut the larger panels into 1.5 cm square SRM samples, we propose to use a diamond saw blade on a table saw with a traversing table. Traditional methods of cutting using a silicon carbide abrasive wheel are unacceptable since these methods often introduce abrasive media into the gold electrodeposit.

Planned Outcome:

We expect to produce a 24K gold, low load microhardness standard, with an average Knoop hardness of 75 HK and overall uncertainty of less than 10%.

Accomplishments:

The Electrochemical Processing Group has produced a 24K gold, low load microhardness standard prototype. The surface area is 2.25 cm^2 and the deposit thickness is 200 μm. At a load of 25 grams, more than 1,000 indentations can be made on its surface. The average Knoop hardness is 75.5 +/- 10%. Conventional metallographic procedures were utilized to prepare the gold surface but proved unsuccessful. Large amounts of grinding and polishing media became imbedded in the gold and therefore rendered the surface unacceptable. An alternative method, diamond turning was developed. A single point diamond is used to turn the gold deposit to a mirror finish having a surface roughness of 63.5 nanometers peak to valley.

Outputs:

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

SRM's under development:

SRM#1870 Gold Microhardness Standard

Project Title: **ELECTROGALVANIZED COATINGS ON STEEL**

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

Objectives:

The object of this work is to develop the electrochemical expertise that will enable the production of mass per unit area standards to be used by the steel industry to calibrate on-line x-ray fluorescence instruments for process control of continuous strip plating of electrogalvanized coatings.

Technical Description:

The domestic electrogalvanizing market is approximately 2.5 billion dollars per year. Pure zinc still maintains about 82% of the domestic electrogalvanizing market, followed by alloy plating of Zn-Ni and Zn-Fe systems at 9% each. At the present, there is little accountability among sheet steel manufacturers with respect to zinc electrodeposited due to discrepancies between measurement methods. There is a critical need for standards of mass per unit area and composition for the electrogalvanizing industry, this is particularly accentuated by the industry's push to become compliant with regulations such as those self imposed under ISO 9000. The prototypes under development will serve to fill a void in the standards which are currently available, particularly for those manufacturers which require much improved reference coatings for on-line quality assurance.

Planned Outcome:

Zn/steel coating thickness standards will be developed that are applicable to the Zn coated sheet steel currently produced by the electrogalvanizing industry. These coatings must have a controlled microstructure including crystal orientation (for suitable mechanical properties) and uniform thickness (mass per unit area) to make them suitable for use as calibration standards for x-ray fluorescence and gravimetric test methods. These standards will be certified with respect to the coating mass per unit area. Prototype coupons, having an overall coating mass uncertainty of less than 5% will be fabricated in configurations which are acceptable to both the x-ray fluorescence and gravimetric measurement communities.

Accomplishments:

Zinc electrodeposited coatings with mass per unit area uniform enough to comply with the 5% uncertainty required for gravimetric testing methods (1 cm square coupons) were fabricated. Improvements to the cell geometry employed in the deposition process of these coatings are still being made with the objective of obtaining an overall coating distribution that is compliant with the tighter uncertainties required for the x-ray fluorescence instrumentation (10 cm x 15 cm panel). In addition, the algorithm employed for the selection of the coupons was optimized to increase the yield of coupons per plate while maintaining a low uncertainty.

Outputs:

Prototype plates capable of complying with the 5% uncertainty required for the gravimetric technique were prepared. In addition, the algorithm employed for the selection of the coupons was optimized to increase the yield of coupons per plate while maintaining uncertainties low.

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

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

Objectives:

The program is primarily focused on determining the effects of electrolyte composition and operating parameters on the composition, structure and properties of chromium electrodeposits in which a trivalent electroactive chromium species is used. The structure and properties of the chromium coatings from trivalent electrolytes will be compared to coatings from hexavalent electrolytes.

Technical Description:

Chromium is widely used as an electrochemically applied coating on metal for wear resistance, for reduced 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 applications where the coating thickness is on the order of 0.5 µm to 5.0 µm. The thicker deposits required for functional applications cannot be obtained from the commercial bath chemistry. A Cr^{+3} -based electrolyte, recently developed at NIST (U.S. Patent 5,415,763), allows one to electrodeposit chromium coatings which are thick enough (50 µm to 250 µm) to be suitable for engineering applications; however, the wear resistance is somewhat lower than coatings made from hexavalent electrolytes. This program focuses on the structural characterization of chromium coatings electrodeposited from the NIST trivalent electrolyte, paying particular attention to structural features which may lead to the observed lower wear resistance.

Planned Outcome:

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

External Collaborations:

As a result of the NIST “Workshop on Electrodeposition of Thick Chromium Coatings from Trivalent Electrolytes,” informal collaborations were initiated with Dr. John Dash of Portland State University to study the effects of chloride additions to a sulfate-catalyzed trivalent electrolyte on the adhesion of the chromium deposit on heat-treated steels.

An investigation into the use of amorphous alloy coatings of Co/Cr, deposited from a modified trivalent chromium electrolyte, as potential bearing surfaces for orthopedic implants is being carried out in collaboration with the Biomaterials Group of the NIST Polymers Division which is being partially supported by NIH.

Accomplishments:

It has been shown that chromium coatings from trivalent electrolytes are amorphous with a lamellar structure when viewed in cross-section, compared to a very small grained crystalline structure for deposits from hexavalent electrolytes. The conjecture is that the low wear resistance for the as-deposited coatings from the trivalent electrolyte is due to fracture along the lamellae. To support this conjecture, it is known that: (1) amorphous autocatalytic nickel deposits have a lamellar structure and when subjected to a bend test fail along the lamellae, and (2) the wear debris, generated by high load, unlubricated pin on disk type wear testing of tri-chromium deposits, is in flake form indicative of fracture normal to the applied load. It also appears that the wear resistance of heat-treated tri-chromium deposits does not exceed the hex-chromium deposits until the lamellar structure is minimized or lost even though the tri-chromium hardness is 1.3 times higher than the hex-chromium deposits. The influence of electrolyte chemistry and mass transport on the lamellar structure formation will be investigated.

An investigation into the effect of heat treatment on the microstructure and properties of trivalent chromium deposits from one electrolyte chemistry was completed. Significant results were: a maximum hardness of 1900 HK_{50}, compared to 1000 HK_{50} for deposits from hexavalent electrolytes, was obtained after heat treatment at 600 ^{o}C; DTA scans revealed a double exotherm around the glass devitrification temperature; and, TEM revealed, possibly for the first time, a structure modulated material consisting of alternating 20 nm layers of a BCC and amorphous structure.

Outputs:

Presentations:

Mullen, J. L., and Johnson, C. E., “Workshop on Electrodeposition of Thick Chromium Coatings from Trivalent Electrolytes,” NIST, January, 1997.

Johnson, C. E., and Mullen, J. L., “Structure and Properties of Functionally Thick Chromium Electrodeposits from a Trivalent Electrolyte-A “Green” Technology,” 126th TMS Meeting, Orlando, Florida, February, 1997.

Patents Granted:

Methods and Electrolyte Compositions for Electroplating Metal-Carbon Alloys
Christian E. Johnson, et al.
U.S. Patent 5,672,262 issued 09/30/97

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

Investigator: T. P. Moffat

Objectives:

The objective of this project is to develop an understanding of physical phenomena and processing parameters required for producing complex 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 heteroepitaxial deposition of 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 the processing parameters, the dynamics of nucleation and growth processes 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 by scanning probe microscopy, and morphology during homo- and heteroepitaxial growth has been explored.

Planned Outcome:

Electrodeposition is a convenient, low temperature, inexpensive 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 via electrochemical or CVD processes. Our specific findings are that the surface of the copper electrode is covered by an ordered layer of oxidatively adsorbed chlorine at electrode potentials typically associated with copper deposition and dissolution. The adlayer exerts a strong influence on the adatom binding and activation energy at steps and thus plays a dominant role in determining the evolution of surface morphology. Our scanning probe microscopy studies promise to provide considerable insight into the way these adsorbates influence microstructural evolution.

External Collaborations:

We are working with Professor L. Salamanca-Riba of the University of Maryland to explore the magnetic properties of electrodeposited strained-layer superlattices. Mr. Matsuhira Shima, a Ph.D. student at the University of Maryland, is involved in the synthesis and characterization of Cu/Co multilayers.

We are working with Dr. David van Heerden of Johns Hopkins University who is investigating the structure of electrodeposited Cu-Ni multilayers using cross-sectional TEM.

Accomplishments:

A firm scientific foundation for electrochemical deposition of alloys and multilayers requires a one to one correlation between coulometry and film thickness. This demands a knowledge of the current distribution and the current efficiency. In the last year we performed investigations into the current efficiency of iron group metal deposition as a function of film thickness (0-100 nm) and have designed a new electrochemical cell that optimizes the primary and tertiary current distributions so that coulometric control of film growth is directly related to film microstructure.

A scheme for depositing highly oriented copper seed layers on Si(100) and Si(111) has been adopted as a substrate for electrochemically growing oriented Cu-Co strained-layer superlattices for magnetic property investigations. In collaborations with the Magnetic Materials Group, M. Shima and L. Salamanca-Riba of the University of Maryland, $[Cu/Co]_N Si(100)$ films were shown to exhibit a dependence of the GMR on in-plane orientation, due to magnetocrystalline anisotropy of the epitaxy structure.

The capability was developed of using in-situ STM to study the structure and dynamics of the deposition/dissolution of Cu, and the influence of anion adsorption and metal underpotential deposition on step dynamics. Studies to date have focused on chloride adsorption and lead underpotential deposition on Cu(100), Cu(111) and more recently Cu(110). Step faceting due to the formation of an ordered, commensurate adlayer has been demonstrated. Likewise, the impact of adsorption on step-step interactions is being explored. Studies have been initiated for heteroepitaxial deposition of nickel and cobalt deposition on Cu(100).

An effort has been initiated to directly deposit metals onto semiconductor substrates.

Outputs:

Publications:

Moffat, T. P., “Electrodeposition of Strained-Layer Superlattices,” V-451, Electrochemical Synthesis and Modification of Materials, MRS Pittsburgh (1997).

Moffat, T. P., “STM Study of the Influence of Adsorption on Step Dynamics,” V-451, Electrochemical Synthesis and Modification of Materials, MRS Pittsburgh (1997).

Presentations:

Moffat, T. P., “Electrochemical Synthesis and Characterization of Novel Materials,” Swiss Federal Institute of Technology, Lausanne, Switzerland, September, 1997.

Moffat, T. P., “Electrodeposition of Strained-Layer Superlattices,” 192nd Electrochemical Society Meeting, Fundamental Aspects of Electrochemical Deposition and Dissolution Including Modeling, Paris, France, September, 1997.

Moffat, T. P., “STM Study of Adsorption and Electrodeposition Processes on Copper Single Crystals,” 191st Electrochemical Society Meeting, Third International Symposium on In-Situ Characterization of Electrochemical Processes, Montreal, Canada, May, 1997.

Moffat, T. P., “STM Study of the Influence of Adsorption on Step Dynamics,” MRS

Symposium on Electrochemical Synthesis and Modification of Materials, Boston, Massachusetts, December, 1996.

Moffat, T. P., “Electrodeposition of Strained-Layer Superlattices,” MRS Symposium on Electrochemical Synthesis and Modification of Materials, Boston, Massachusetts, December, 1996.

Moffat, T. P., “Electrochemical Synthesis and Characterization of Novel Materials, Louisiana State University, Baton Rouge, Louisiana, October, 1996.

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. The focus of this program is the development of improved dental restorative materials with greater durability, wear resistance and clinical acceptability.

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.

Dental research directions in support of the goals are established in collaboration with the American Dental Association(ADA), the National Institute of Dental Research (NDIR), 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 32 research associates at NIST. The collaborative relationship between that professional association and the federal government is unique, and continues to develop and transfer important new technologies to dentistry and medicine.

Project Title: **ADVANCED RESTORATIVE DENTAL MATERIALS**

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

Objectives:

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

Technical Description:

The 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 by common dental practice.

The approach 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 0.2µm to 2.0µm. The surface treatment involves the use of a dilute acid to remove the naturally occurring oxide layer on the powders. Subsequently, a slurry, consisting of the **wet** mixture of the surface treated powder particles, is placed and consolidated in a prepared dental cavity. The liquid film surrounding each particle serves both to maintain a clean surface, and to constrain the micron-size particles, so that they present no inhalation danger to the patient. The powders are consolidated into a solid mass using instruments normally employed in dental practice. The term “acid-assisted consolidation” was coined for the consolidation technique.

Planned Outcome:

The ability to condense surface-treated silver powder into a cohesive solid displaying reasonable mechanical strength values, as well as the established and approved use of silver as a dental restorative material, have the advantage of being mercury-free and thereby will provide an alternative 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.

A Cooperative Research and Development Agreement with L.D. Caulk Division of Dentsply aimed at identifying processing and placement aspects involved in the use of the alternative restorative was terminated by the industrial partner in April 1997.

Accomplishments:

An initial series of in vitro biocompatibility tests were completed on hand-consolidated and machine-pressed silver-based alternative restorative material. The tests included cytotoxicity, hemolysis, Ames' and Styles' Cell Transformation. The hemolysis, Ames', and Styles' tests did not reach the threshold level to be considered non-biocompatible. The cytotoxicity test result was considered severe. Based on the cytotoxicity test alone, this should not preclude the use of the silver alternative restorative since precedence has been set with other approved-for-use dental materials that are cytotoxic. The results of the initial biocompatibility testing thus far encourage further study and development of the mercury-free silver restorative.

By using appropriate chemical precipitation techniques and thermal anneal procedures, acid-assisted hand consolidation, using normal dental tools, is capable of producing silver compacts which are greater than 75% dense. With current state of the art, hand consolidated silver equals or exceeds the transverse rupture strength, shear strength, creep, toughness, corrosion resistance and microleakage properties of conventional silver amalgam. However, the compressive strength, elastic modulus, hardness and placement time are inferior to those of conventional amalgam. These issues are the basis for further study with emphasis on reducing the placement time.

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:

Publications:

Xu, H.H.K., Eichmiller, F.C., Guiseppetti, A.A., and Johnson, C.E., "Cylic Contact Fatigue of a Silver Amalgam Alternative," J. Dent. Res. **76** Special Issue, 198, 1997.

Patents Granted:

Electrochemical Fluidized Bed Coating of Powders
D.S. Lashmore, C.E. Johnson, D.R. Kelley and G.L. Beane
U.S. Patent 5,603,815 issued 2/18/97.

Patents Pending:

Acid Assisted Cold Welding and Intermetallic Formation
C.E. Johnson, and D.R. Kelley
NIST Docket Nos. 93-031 CIP2 and 95-037D

Acid Assisted Cold Welding and Intermetallic Formation and Dental Applications Thereof
C.E. Johnson, and D.R. Kelley
NIST Docket No. 95-038D

EVALUATED MATERIALS DATA

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

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

Database projects in MSEL include:

- Phase Equilibria Diagrams (PED), conducted in cooperation with the American Ceramic Society;

- the Structural Ceramics Database (SCD), a compilation of evaluated mechanical and thermal data for nitrides, carbides, and oxides of interest to engineers and designers;

- a ceramic machinability database, developed by the Ceramic Machining Consortium (see Ceramic Machining Program);

- a high T_c superconductivity database developed in cooperation with the Japanese Agency for Industrial Science and Technology (see High Temperature Superconductivity Program);

- development and implementation of the STEP protocol for the exchange of materials data, under the auspices of the ISO 10313 activity;

- the NACE/NIST Corrosion Performance Database developed by NACE and the Metallurgy Division to provide a means to select structural alloys for corrosive applications; and

- the Crystal Data Center developed by the NIST Center for Neutron Research which provides fundamental crystallographic data on inorganic materials.

Project Title: **NACE-NIST CORROSION DATA PROGRAM**

Investigators: C. D. Flanigan, E. N. Pugh, and C. P. Sturrock (SRMP/TS)

Objectives:

The NACE-NIST Corrosion Data Program is a long-standing collaboration between the NIST Metallurgy Division and NACE International (formerly the National Association of Corrosion Engineers). The program aims to disseminate evaluated corrosion data on the performance of engineering materials (primarily metals) in a wide variety of industrially relevant environments. The data are disseminated using a variety of information technologies, chiefly via databases and expert systems; the users of these computerized systems are primarily engineers and scientists in industry.

Technical Description:

Corrosion is a major problem for many industries, especially the process industries, which include the oil and gas, chemical processing, and electric power industries. Various national studies undertaken over the years in industrialized countries have estimated the annual losses attributable to corrosion to fall between 4 and 5 percent of the Gross Domestic Product. These studies have also concluded that many of these costs attributable to corrosion can be avoided or reduced through dissemination of existing corrosion knowledge. Yet there are few sources of widely available evaluated corrosion data, which are an essential ingredient of corrosion knowledge. The program was established to address this need, and has done so since the release of its first product in 1986, the Corrosion Data Survey ("COR•SUR") database.

Since the release of this first product the program has released numerous other corrosion informatics, most notably the CHEM•COR series of expert systems, which provide material selection and utilization advice for the handling of industrial corrosives, and the POWER•COR series, which address corrosion and materials performance problems encountered in the electric power industry. The program will conclude in fiscal year 1998 by coming "full-circle" with the release of a revised and updated version of COR•SUR, its original product.

Planned Outcome:

The revised COR•SUR database will include corrosion data on 50 metals/alloys and 36 nonmetallic materials in approximately 1000 aqueous environments. The user interface will take full advantage of the Windows™ operating system, with point-and-click input screens and high-resolution graphical output. Users of the revised COR•SUR database will also be able to use this product to develop and maintain their own corrosion databases for proprietary use. The original COR•SUR product accumulated a customer base of over 2,000 scientific and engineering professionals in its 11-year history. Most of these scientists and engineers are employed in U.S. industry, with a small contingent from outside the U.S. and/or in academia and government.

External Collaborations:

The principal partner with NIST in the program has been NACE International. The two organizations signed the original agreement to collaborate in 1982, and have renewed this agreement by mutual consent every three years thereafter. Since program inception, NACE has been responsible for coordinating the industry input and dissemination of the outputs, while NIST has overseen the technical issues involved in product development. The Materials Technology Institute of the Chemical Process Industries, Inc. was the chief industrial sponsor of the CHEM•COR series, while the POWER•COR series was funded by the Electric Power Research Institute. The chief collaborators with NIST on the revised version of COR•SUR have been Bijan Mashayekhi and C. Paul Dillon. Mashayekhi, a former employee of NACE International, has been retained by NACE under contract to do the programming of the COR•SUR user interface. Dillon, a NACE Fellow and distinguished corrosion expert with over 40 years of corrosion engineering experience in industry, is under contract to NACE to serve as the principal evaluator of the corrosion data in the COR•SUR database.

Accomplishments:

During FY 1997 the original COR•SUR data have been evaluated and revised extensively. By year-end, approximately 80% of the data had been input into the database, on schedule for planned completion at the end of calendar year 1997. The user interface was completely redesigned and developed under the Windows™ operating system, and tested extensively and independently by NIST staff not directly involved in the program. A technical paper describing the overall effort was presented at the NACE annual conference.

Impact:

The impact of the program on the scientific and technical community has been significant. Third-party industrial funding of the program, one measure of customer support, has exceeded $2 million. Since the release of the first product in 1986, over 2,000 corrosion data-bases and expert systems developed under the program have been purchased by third parties through NACE. It is difficult to assess the overall economic impact of these databases and expert systems, but one anecdotal unsolicited testimonial by an industrial user revealed cost savings of at least $100,000 from a single use of one of the CHEM•COR expert systems.

Output:

Publications:

Mashayekhi, B., Sturrock, C. P., and Flanigan, C. D., “Corrosion Data Survey: The Next Generation,” Paper No. 604, CORROSION/97, NACE International, Houston, TX (1997).

HIGH TEMPERATURE SUPERCONDUCTIVITY

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

The primary thrusts of the program are as follows:

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

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

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

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

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

Project Title: MAGNETIC PROPERTIES OF SUPERCONDUCTORS

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

Objectives:

This project seeks to improve present magnetic measurements and develop new measurements for superconductors, to provide support to the Ceramics Division in the determination of phase diagrams important for the processing of high temperature superconductors, and to determine the effect of various microstructural features such as inclusions, compositional modulation, and precipitates, on the flux pinning in high temperature superconductors.

Technical Description:

In collaboration with scientists from universities, industry, and other Divisions at NIST, superconducting materials are prepared and their microstructure and magnetic properties determined. The properties of impurities which form during processing of superconductors, or which are intentionally added to modify the properties, are also investigated. Measurements performed include AC and DC magnetization as a function of temperature and applied magnetic field, hysteresis loops, flux penetration and viscosity, critical fields, and critical temperatures. Microstructural studies are performed using scanning and transmission electron microscopy. Emphasis is on high temperature superconducting materials. When a Sn source becomes available, the structural and electronic properties of these compounds will be investigated by Mössbauer spectroscopy

Planned Outcome:

Results of this project will improve the ability of manufacturers and researchers to interpret magnetic measurements in high-temperature superconductors. It will also improve the ability of manufacturers to characterize and control the characteristics and quality of material they produce, will increase critical current densities by improvements in flux pinning, and provide better control over the flux pinning properties of materials for shielding and levitation bearings.

External Collaborations:

External collaborators include Dr. H.M. Seyoum at the University of the District of Columbia, Dr. M. Melamud of the Technion, Hiafa Israel, and M Rubinstein at the Naval Research Laboratory.

Accomplishments:

- Diamagnetic shielding measurements were performed on pure and Sn-doped GeCuO. It was found that the low temperature spin-Peierls transition of the pure material was modified by the Sn doping. The effects of composition on the superconducting properties of

$Sr_{4-x}Ca_xPtO_6$ were measured. This information was used to help determine phase relationships in this system. Compounds of (Sr,Ca)CuO prepared by the ceramics division were measured to determine if improved superconductivity could be achieved in this system by variations in the processing conditions.

Impact:

- Phase diagrams determined at NIST are being used by industry to fabricate improved high temperature superconducting materials. Commercial devices using high temperature superconductors are currently available. Many of these devices are being fabricated using laser ablation, a method which was developed by NIST in cooperation with the Johns Hopkins Applied Physics Laboratory.
- Our explanation of “inverse levitation” in terms of the effect of flux pinning on the magnetic properties of high temperature superconductors opens up many possibilities for the use of these materials in devices. An instrument, developed by NIST in cooperation with the Institute of Solid State Physics in Russia, for observing the flux distribution in superconductors and other magnetic materials won an IR100 award and has been commercialized by Phasemetrics, Inc.

Outputs:

Publications:

Effect of Barium Cuprate on High Temperature Superconductors, H.M. Seyoum, M. Melamud, W. Wong-Ng, L.H. Bennett, L.J. Swartzendruber, L. Cook, and H.J. Brown, J. Appl. Phys. 81, 4244 (1997).

ADDITIONAL OUTPUT

The following publicaitons and presentations by Metallurgy Division staff were not associated with a specific project, or resulted from work on projects which were no longer active in FY 1997.

Gayle, F. W., "Precipitation Hardening in the First Aerospace Aluminum: The Wright Flyer Crankcase," NIST Research Colloqium Series, 1997:Gaithersburg, July 25, 1997 and Boulder, July 18, 1997

Gayle. F. W., "The First Aerospace Aluminum: The Wright Flyer Crankcase," The Philosophical Society, Cosmos Club, Washington, DC, September 12, 1997.

Schaefer, R. J., "Research Opportunities at the National Institute of Standards and Technology," Fourth International Conference on Composites Engineering, Hawaii, July 10, 1997.

RESEARCH STAFF

Metallurgy Division Office

Handwerker, Carol A. carol.handwerker@nist.gov (301) 975-6158	• Interface thermodynamics and kinetics • Solder wetting and spreading • Microstructure evolution
Schaefer, Robert J. robert.schaefer@nist.gov (301) 975-5961	• Solidification of metals • Defects in castings • Consolidation of metal powders

Electrochemical Processing Group

Beauchamp, Carlos R. carlos.beauchamp@nist.gov (301) 975-6411	• Compositionally modulated alloys • Standard reference materials
Johnson, Christian E. christian.johnson@nist.gov (301) 975-6409	• Ultra-black coatings • Electroless deposition processes • Metallic glass alloy deposition • Microhardness SRM research • Chromium deposition • Pulse alloy deposition
Kelley, David R. david.kelley@nist.gov (301) 975-6410	• Microhardness SRM development • Dye penetrant SRM development • Precious metal electrodepostion • Plating on aluminum
Moffat, Thomas P. thomas.moffat@nist.gov (301) 975-2143	• Electrochemistry • Scanning probe microscopy •Nanostructures
Mullen, Jasper L. jasper.mullen@nist.gov (301) 975-4213	• Development of automated hardness testing • Electrochemical measurements for determining metal corrosion • Analytical spectroscopy
Stafford, Gery R. gery.stafford@nist.gov (301) 975-6412	• Electrochemical transients • Electrodeposition • Molten salt electrochemistry

Magnetic Materials Group

Brown, Henrietta J. henrietta.brown@nist.gov (301) 975-6042	• High T_c superconductors • Magnetic force microscopy • Magnetization measurements • Magnetoresistance
Egelhoff, Jr., W. F. egelhoff@nist.gov (301) 975-2542	• Giant magnetoresistance • Molecular beam epitaxy • Surface physics • Ultrahigh density data storage
McMichael, Robert D. rmcmichael@nist.gov (301) 975-5121	• Giant magnetoresistance • Micromagnetic modeling • Ferromagnetic resonance • Nanocomposites • Magnetocaloric effect
Shapiro, Alexander J. alexander.shapiro@nist.gov (301) 975-5970	• Mössbauer effect • Scanning electron microscopy (SEM) • X-ray microanalysis • Image analysis • Magnetic force microscopy
Shull, Robert D. robert.shull@nist.gov (301) 975-6035	• Nanocomposites • Magnetic susceptibility • Mössbauer effect • X-ray and neutron diffraction • Magneto-caloric and magneto-optical effects
Swartzendruber, Lydon J. lydon.swartzendruber@nist.gov (301) 975-6034	• Magnetic susceptibility • Magnetic methods, NDE • Mössbauer spectroscopy • Barkhausen effect

Materials Performance Group

Clough, Roger C. clough@enh.nist.gov 301-975-6143	• Micromechanical modeling • Acoustic emission • Mechanical properties

deWit, Roland roland.dewit@nist.gov 301-975-5707	• Fracture mechanics • Dislocation theory • Finite element analysis
Fields, Richard J. rjf@nist.gov 301-975-5712	• Mechanical properties • Mechanical testing • Powder consolidation • Metal forming
Foecke, Timothy J. tim.foecke@nist.gov 301-975-6592	• Nanostructured materials • Experimental fracture physics • SEM, TEM, SPM • Micro- and nano-mechanics of materials • Dislocation-based deformation mechanisms • Historical metallurgy
Hicho, George E. george.hicho@nist.gov 301-975-5707	• Mechanical properties • Failure analysis • Mechanical testing
Low, III, Samuel R. samuel.low@nist.gov 301-975-5709	• Hardness standards • Hardness testing • Mechanical properties of materials • Mechanical testing of materials
Pugh, E. Neville nev.pugh@nist.gov 301-975-4679	• Corrosion • Environment-induced fracture • Mechanical properties
Ricker, Richard E. richard.ricker@nist.gov 301-975-6023	• Corrosion • Electrochemistry • Chemistry and physics of fracture • Prediction of materials performance
Shepherd, Dominique A. dominique.shepherd@nist.gov 301-975-4798	• Titanium alloys • Mechanical testing • Mechanical properties • SEM, TEM

Smith, John H. jhsmith@nist.gov 301-975-5160	• Mechanical properties of materials • Fracture of materials • Structure integrity analysis • Pressure vessel technology • Mechanical testing standards
Stoudt, Mark R. mark.stoudt@nist.gov 301-975-6025	• Mechanical properties • Electrochemical measurements • Corrosion fatigue • Environmentally induced cracking

Materials Structure and Characterization Group

Adams, Jonice jonice.adams@nist.gov (301) 975-6007	• Nanostructured materials • X-ray diffraction
Bendersky, Leonid A. leonid.bendersky@nist.gov (301) 975-6167	• Functional ceramics • Analytical and high-resolution transmission electron microscopy • Intermetallics for high temperature applications; order-disorder
Bonevich, John, E. john.bonevich@nist.gov (301) 975-5428	• Electron holography • High resolution/analytical electron microscopy • Magnetic materials
Claggett, Sandra, W. Sandra.claggett@nist.gov (301) 975-6406	• Specimen preparation for electron microscopy • Digital Imaging
Drescher-Krasicka, E. dre@nist.gov (301) 975-6141	• Scanning acoustic microscopy • Tomography of internal residual stresses • Ultrasonics
Gayle, Frank W. frank.gayle@nist.gov (301) 975-6161	• Structure/property relationships • Transmission electron microscopy • Aluminum metallurgy

	• Solder science
Josell, Daniel daniel.josell@nist.gov (301) 975-5788	• Thermal diffusivity measurement and theory • Creep of thin films • Modelling of grain boundary effects on multilayer equilibra • Modeling of solder joint geometries
Powell, Adam, C. adam.powell@nist.gov (301) 975-4936	• Electron beam melting and evaporation • Modelling of liquid free surface shape and capillary force • Lattice gas automata models
Smith, Leonard leonard.smith@nist.gov (301) 975-5713	• Solder joint failure analysis • Optical microscopy and microstructure characterization
Warren, James A. james.warren@nist.gov (301) 975-5708	• Computer simulations of solidification • Dendrite pattern formation • Modelling of solder/substrate wetting processes

Metallurgical Processing Group

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

Coriell, Sam R. sam.coriell@nist.gov (301) 975-6169	• Modeling of solidification processes • Interface stability • Convection and alloy segregation during solidification
Hardy, Stephen C. (retired)	• Solderability measurements • Capillary effects • Wetting balance tests
Jiggetts, Rodney D. rodney.jiggetts@nist.gov (301) 975-5122	• Hot isostatic pressing • Electron beam welding • Quantitative metallography
Kattner, Ursula R. ursula.kattner@nist.gov (301) 975-6044	• Alloy phase equilibria calculations • Solder alloy evaluations • Casting of aerospace alloys
Manning, John R. manning@nist.gov (301) 975-6157	• Metals processing • Diffusion kinetics • Interface reactions
Napolitano, Ralph E. ralph.napolitano@nist.gov (301) 975-6146	• Solidification • Defects in single crystal castings • Computational physical metallurgy
Ridder, Stephen D. stephen.ridder@nist.gov (301) 975-6175	• Spray dynamics and deposition • Thermal spray processes • Process modeling and control
Simmons, John A. (retired)	• Ultrasonic interface characterization • Defects and internal stress • Modeling of microstructure evolution
Williams, Maureen E. maureen.williams@nist.gov (301) 975-6170	• Differential thermal analysis • Powder x-ray diffraction • Solder wettability