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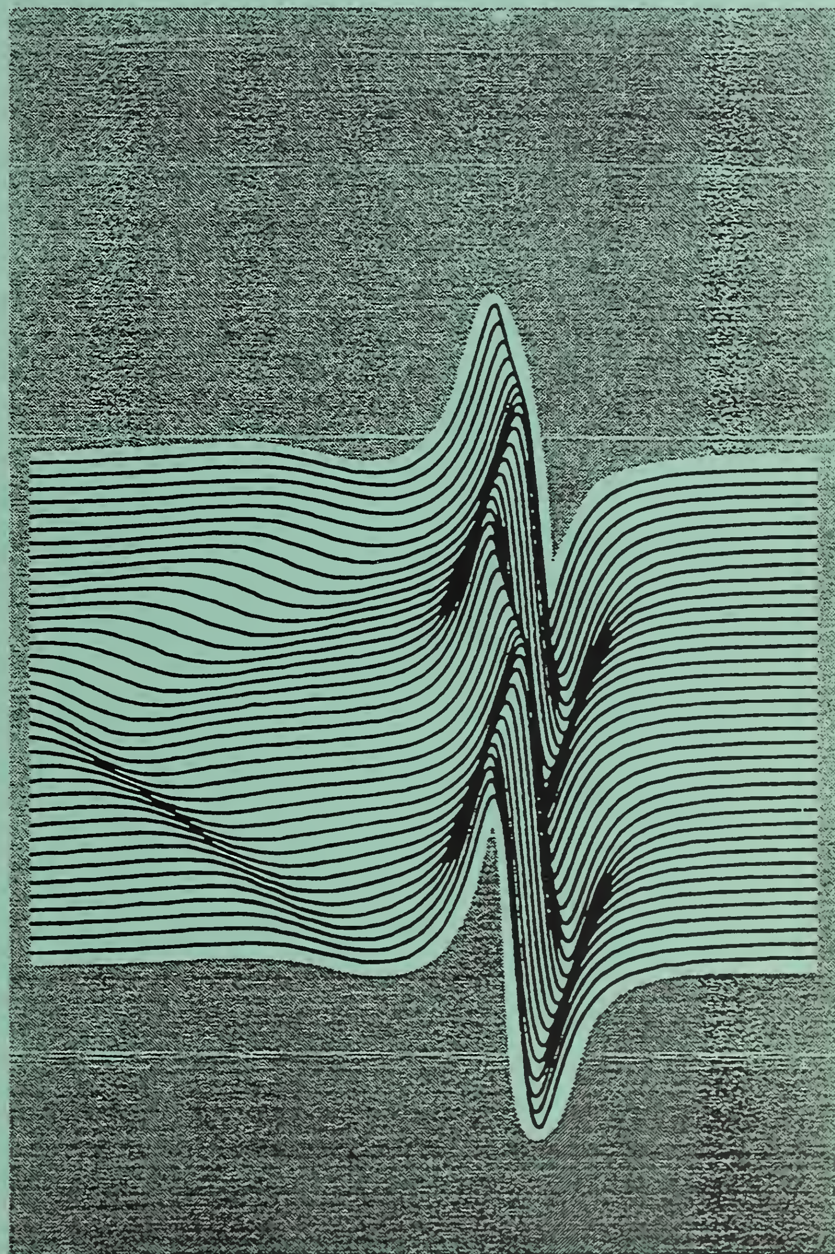
METALLURGY



NAS-NRC
Assessment Panel
April 6-7, 1995

NISTIR 5582
U.S. Department of Commerce
Technology Administration
National Institute of Standards
and Technology

Technical Activities
1994

The cover shows the ferromagnetic resonance peaks in a multilayered spin valve. For each curve, the field is applied in the plane of the film at angles from 0 to 360 degrees.

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E. N. Pugh, Chief
S. C. Hardy, Deputy

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Technical Activities 1994

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ABSTRACT

This report summarizes the FY 1994 activities of the Metallurgy Division, National Institute of Standards and Technology (NIST). These activities center on structure-processing-properties relations of metals and alloys, on methods of measurement, and on the generation and evaluation of critical materials data. Efforts comprise studies of metals processing and process sensors; advanced materials - including metal matrix composites, intermetallic alloys, and superconductors; corrosion and electrodeposition; mechanical properties; magnetic materials; and high temperature reactions.

The work described also includes cooperative programs with a professional society (the Corrosion Data Program with the National Association of Corrosion Engineers); with a trade association (the Temperature Sensor Program with the Aluminum Association) and several with industry including the Powder Atomization Consortium with five companies.

The scientific publications, committee participation, and other professional interactions of the 53 full-time and part-time permanent members of the Metallurgy Division and its 30 guest researchers are identified.

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OVERVIEW

METALLURGY DIVISION (855)

E. Neville Pugh, Chief
Stephen C. Hardy, Deputy Chief
June Toms, Secretary

The primary mission of the Metallurgy Division is to assist US industry in improving its competitiveness, and, to meet this objective, the Division brings to bear its traditional strengths in measurement science and materials characterization on industrial problems with significant competitive and economic impact. Major thrusts have grown about these strengths in the areas of materials processing, particularly in casting, powder processing and process sensing, and in nanostructured materials and electronic packaging. Each of these activities benefitted significantly in FY94 from the Division's growing competence in modeling, which is part of a concerted Materials Science and Engineering Laboratory (MSEL) effort to strengthen and broaden this essential capability. The Division also has maintained strong programs in the traditional NIST areas of standards and data which are essential to maintaining the nation's technological infratructure. In the former, we have continued to collaborate with the American Society for Testing Materials (ASTM) and manufacturers of hardness measuring machines and hardness calibration blocks to establish a hardness standardization facility at NIST. Collaboration with other national laboratories has been initiated to ensure that the US national hardness standard is compatible with hardness standards worldwide. In the area of data, the National Association of Corrosion Engineers (NACE)-NIST Corrosion Data Program has continued successful collaborative programs with industry to develop computerized databases and expert systems for use in materials selection and corrosion control.

Some indications that the Metallurgy Division is effectivly helping US industry are provided by examining a few mature programs and the results they have achieved. For a number of years the Division has had a collaborative program with the Aluminum Association to develop a non-contact method of measuring the temperature of aluminum sheet during the hot rolling process. This year a prototype eddy current sensor was operated for a four month period at the Alumax Mill Products plant in Lancaster, Pennsylvania. This trial was successful and the commercialization of the device is now being explored. In another long term collaborative program, the NIST/Industrial Consortium on Intelligent Processing of Rapidly Solidified Metal Powders by Inert Gas Atomization has completed its work to develop control systems for atomizers. The Expert System Control Shell (ECSS) technology developed in this program is being transferred to a commercial atomizer at Crucible Research. In a third program which was initiated in FY93, NIST, Xerox Corporation, and Cornell University collaborated in the study of magnetic nanocomposites of γ-Fe_3O_4 and a polymer. As a result of the developments in these materials achieved in the collaboration, Xerox Corporation is setting up a pilot plant for large scale production of these nanocomposites.

The details of the research in each project in the Division are described in this report under sections corresponding to the Division's seven groups:

CORROSION
ELECTRODEPOSITION
HIGH TEMPERATURE MATERIALS CHEMISTRY
MAGNETIC MATERIALS
MECHANICAL PROPERTIES AND PERFORMANCE
METALLURGICAL PROECESSING
METALLURGICAL SENSING AND MODELING

Highlights of the Division's research activities are summarized below. More extensive descriptions of these and other Division projects may be found in the project summaries.

- The NACE-NIST Corrosion Data Program continued to collaborate with industry to produce personal computer based corrosion information and advisory systems. During FY94, three systems were released for public distribution and four more systems were distributed to industrial review committees for evaluation prior to public release.

- The Electrodeposition Group has made significant progress in the development of mercury-free dental restoratives. The approach being used is based on the premise that ductile silver and silver coated intermetallics will cold-weld to form a dense filling, under moderate pressure and ambient temperature, if the surface has undergone appropriate treatment to remove the native air formed oxide. The transverse rupture strength of silver which has been consolidated after treatment in 2% fluoroboric acid was six times greater than that of identical silver powder consolidated without treatment.

- Measurements on ultra-low carbon, low-carbon, and high-strength-low-alloy indutrial sheet steels has succeeded in establishing an excellent correlation between Vickers hardness and the magnetic Barkhausen signal for these steels.

- Ferromagnetic resonance measurements have shown that the magnetic layers in giant magnetoresistance spin valve structures maintained their distictive character after annealing at 400 °C for 30 minutes, but the FeMn pinning layer showed irreversible changes after 20 minutes at 250 °C.

- As part of the National Aging Aircraft Research Program, an extensive research project was carried out to study the manner in which cracks propagate in the presence of multiple site damage. The project involved ten tests of the largest structural aluminum panels ever tested in tension. Analyses of the results by two different procedures indicated a reasonably good capability for predicting the critical fracture stresses.

- In work with the Consortium on Casting of Aerospace Alloys, crystallographic characteristics of grain defects in single crystal turbine blades were identified. A model was developed to describe dendrite growth in complex containers, identifying some of the conditions leading to formation of these defects.

- In other work with the Consortium on Casting of Aerospace Alloys, measurements of unsurpassed accuracy have been made of selected thermophysical properties of Inconel 718 and Ti-6Al-4V alloys at high temperatures in both solid and liquid phases up to about 300K above the melting region.

- Simulations of dendritic growth and resulting microsegregation patterns during cooling of a binary alloy were obtained using a phase-field approach.

- In collaboration with Advanced Technololgy Program Awardee MicroFab Technologies and a consortium including Delco, AMP, Universal Instruments, Texas Instruments, and Motorola, means have been identified to overcome technical barriers to good mechanical and electrical contacts in solder joints fabricated by solder jet technology.

- Precision measurements of certain vibrational resonant frequencies of a cylinder have been used to demonstrate the feasibility of instruments for measuring the case depth in drive shafts, the stress in cylindrical load cells, the pressure inside piping and the recrystallization process in aluminum alloys.

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CORROSION

Richard E. Ricker

Corrosion control enhances industrial competitiveness by improving manufacturing efficiency and product quality. In addition, the application of reliable advanced materials and corrosion prevention methods to manufacturing processes, products, or to containers for hazardous materials or wastes improves the safety of employees, consumers and the general public. The Corrosion Group works with industries, universities, government agencies and consumers to enhance industrial competitiveness and promote safety by: (1) collecting and disseminating information on materials and methods for corrosion failure prevention; (2) developing improved corrosion measurement science, corrosion prevention methods, and life prediction methods; and (3) assisting industry to develop more competitive products through the application of corrosion measurement science and the development of improved corrosion testing standards.

The Corrosion Group collects and disseminates information on corrosion failure prevention through the NACE-NIST Corrosion Data Program. This program is the result of an agreement between NIST and NACE International to work together to achieve this common goal. The NACE-NIST Corrosion Data Program uses the latest advances in computer information science and technology to provide industry with convenient and reliable information on materials performance and corrosion control. Working with industry through consortia such as the Materials Technology Institute of the Chemical Process Industries, the Electric Power Research Institute, and the International Copper Association, NACE-NIST software engineers develop expert systems, databases, and hybrid programs that are distributed to industry through NACE.

The Corrosion Group develops improved corrosion measurement science, corrosion prevention methods, and life prediction methods by investigating and modeling the mechanisms of corrosion failure. During the past year, greater emphasis was placed on developing the elements which will eventually be used in life prediction models and the development of measurement techniques appropriate to these models. For this purpose, research focused on corrosion failure mechanisms, their rate determining steps, modeling of the electrochemical processes, and the development of means for estimating service life from laboratory measurements.

The Corrosion Group assists industry in the development of more competitive products by applying their understanding of corrosion mechanisms and corrosion measurement science to the design of improved corrosion evaluation technique methodologies, and standards and in the application of these to the development of better products and processes.

FY 1994 Significant Accomplishments

- The NACE-NIST Corrosion Data Program continued to collaborate with industry to produce personal computer based corrosion information and advisory systems. During FY94, three systems were released for public distribution and four more systems were distributed to industrial review committees for evaluation prior to public release. This brings the total number of systems developed by this joint activity and in public distribution to 12 (includes two demo programs for main projects worked on).

- The NACE-NIST Corrosion Data Program continued developing a multi-year international research project with the Katholieke Universiteit Leuven (Belgium) under the sponsorship of a consortium of the domestic chemical process industry. The ultimate objective of the research is to develop an expert system that will predict the likely performance of candidate stainless steel alloys in aqueous environments over a wide pH range. During FY94, a first prototype was demonstrated to representatives of the sponsoring industry consortium, the Materials Technology Institute of the Chemical Process Industries, Inc.

- Working with the Fire Science Division of the Building and Fire Research Laboratory, the Corrosion Group evaluated the potential for failure of fire suppressant storage and handling systems due to corrosion of the metals when they are exposed to the non-ozone depleting alternatives to the CFC Halon 1301.

- Developed two electrode electrochemical impedance techniques and a three electrode electrochemical polarization technique for the evaluation of the corrosivity of low conductivity, low dielectric constant electrolytes such as the none-ozone depleting alternatives to the CFC Halon 1301.

Corrosion Mechanisms, Measurement Science, and Life Prediction
E. Escalante, J. L. Fink, E. N. Pugh, R. E. Ricker, and M. R. Stoudt

Many industries are finding that existing corrosion testing standards are unacceptable as they either fail to accurately predict performance or they have an unacceptably high degree of uncertainty associated with their predictions especially when applied to a new (advanced) material or product. This places the manufacturer who selects a new advanced material or design for his product in a position where his competitiveness and profitability are at increased risk due to the possibility of increasing warranty repairs, liability claims, product recalls, or customer dissatisfaction. The only way to reduce the uncertainty associated with the prediction of performance in actual service is to increase our understanding of failure mechanisms, the origins of uncertainties in predicting service lifetime from laboratory measurements, and the development of improved corrosion testing standards.

During FY94, the Corrosion Group worked to improve our understanding of corrosion failure mechanisms and their measurement by (1) investigating the film-induced cleavage mechanisms of stress corrosion cracking, (2) investigating electrochemical techniques for the measurement of corrosion rates in low conductivity electrolytes, (3) investigating the origins of discrepancies between measurements of corrosion rate by electrochemical means and exposure (mass loss) measurements, (4) investigating the origin of discrepancies between different techniques for the measurement of crack propagation rates.

Mechanism of Stress Corrosion Cracking - One of the mechanisms proposed to explain stress corrosion cracking is the film-induced cleavage (FIC) mechanism. According to this mechanism, a film is produced by corrosion reactions at the tip of a crack which induces brittle "cleavage-like" crack extension. Previous work in the Corrosion Group confirmed the hypothesis that a brittle film can "induce" brittle "cleavage-like" crack propagation. However, prediction of component lifetimes based on this mechanism and laboratory measurements will require a better understanding of the kinetics of film growth and the relationships between these films and the extent or rate of crack extension. Understanding the kinetics of film growth and the relationship between the nature of the surface film and the extent of crack propagation will enable the development of test methods for predicting performance.

Electrochemical Measurement of Corrosion Rates in Low Conductivity Electrolytes - In order to facilitate the development of non-ozone depleting fire suppressants, alternative fuels for automobiles, and processes for safe destruction of hazardous wastes in supercritical water, the Corrosion Group began investigating the measurement problems associated with conducting electrochemical experiments in low conductivity electrolytes both above and below the supercritical point. Special chambers, samples and electrodes were developed for conducting experiments at elevated temperatures and pressures. Experiments have been conducted in high purity ethanol, fire suppressant candidates, and other environments.

Life Prediction Modeling - Laboratory corrosion measurements are frequently poor indicators of performance in service. It is crucial that the origins of these discrepancies be analyzed and understood. To develop a better understanding of the origins of the difference between mass laboratory exposure tests (considered the best indicator of in service behavior) and relatively quick electrochemical measurements, the Corrosion Group has been comparing measurements made on Al alloys in different pH environments by these different techniques. The Corrosion Group demonstrated that the discrepancy between measurements can be explained by a model for the time dependent variation of the corrosion rate in the exposure tests and assuming that the initial corrosion rate was equal to that measured by the electrochemical techniques.

A similar discrepancy was found between stress corrosion crack velocity measurements made by the load pulsing technique and other techniques for measurement of crack length. In the load pulsing technique, the constant load used to propagate the stress corrosion crack is periodically pulsed by a small (typically 10%) increase which deforms the metal at the crack tip and leaves a line of deformation on the fracture surface. These lines mark the position of the crack front and by measuring their spacing, the crack velocity can be calculated from the time between pulses. Since load pulsing always resulted in a slightly higher crack velocity measurement than other types of measurements, there was concern that the load pulsing was accelerating crack propagation. However, then it was recognized that classical crack velocity measurements actually determine the average crack tip velocity in some pre-determined axis while the load pulsing techniques measured the crack tip velocity in the direction of crack propagation. The discrepancy is related to angle of deviation between the direction of crack propagation and the axis used for classical crack propagation measurement. To analyze the effect of deviations in crack propagation from the direction perpendicular to the applied load, the Corrosion Group developed a technique for analyzing the distribution of crack path deviations and estimating their effect on the difference between the actual crack tip velocity and the extent of propagation in the measurement axis.

Corrosion Data Program

C. P. Sturrock, C. D. Flanigan, P. Karras*, B. Mashayekhi*, and R. E. Ricker
* NACE Research Associate

The Corrosion Data Program was established in 1982 as a joint program between the NIST Corrosion Group and NACE International. The objective of this program is to use the latest advances in information science and technology to provide industry with convenient and reliable information on materials performance and corrosion control. During FY94 activities in the Corrosion Data Program centered on:

1. The development of the CHEM•COR series of materials advisory systems which guide material selection for storage and handling of hazardous chemicals. Three systems were released for public distribution during this fiscal year and four more are in review by committees of industrial experts (sponsored by the Materials Technology Institute of the Chemical Process Industries).

2. The development on the POWER•COR series of software modules to guide electric utilities in such diverse areas as corrosion control in condenser systems, environmentally induced fracture, intergranular corrosion in steam generators, corrosion of critical components in flue gas desulfurization systems, microbiological influenced corrosion and corrosion in service water systems. All six modules have been released for public distribution.

3. The development of an expert system that predicts the performance of stainless steels in aqueous environments. This project is being done in conjunction with researchers at the Katholieke Universiteit Leuven (Belgium) and is sponsored by the Materials Technology Institute of the Chemical Process Industries.

The Corrosion Data Center remains the focal point for addressing complex issues in the collection and dissemination of reliable corrosion data using the latest advances in artificial intelligence and information science. The Center receives substantial financial support and technical input from industry in carrying out its mission.

Corrosion Behavior of Magnesium Alloys

A. C. Fraker

The low density of Mg makes alloys based on this element desirable for applications where reducing weight results in improved performance or fuel economy. However, Mg has a large thermodynamic tendency to corrode and Mg alloys do not readily passivate in neutral pH solutions. The poor corrosion resistance of Mg alloys keeps these alloys from being used in applications where other properties make them ideal. As a result, Mg producers have been working with the automotive industry and other potential users to develop more corrosion resistant alloys. This development effort has been hampered by the lack of convenient and reliable test methods. The Corrosion Group has been working with Mg alloy suppliers to develop a better understanding of the corrosion behavior of Mg, Mg alloys, and Mg matrix composites and, thereby, develop better test methods that enable and promote the development of more corrosion resistant Mg alloys and Mg based composites.

Previous work in this project showed that reproducibility was achieved in tests of magnesium materials in 0.05 mol/L sodium borate solution with a pH of 9.3. The sensitivity of the electrochemical tests can be useful in the development of magnesium alloys if microstructural and other factors are controlled. Work continues to establish appropriate electrochemical testing for magnesium alloys that will produce data that can be correlated with the widely used salt spray test.

Recent studies have been conducted to evaluate the effectiveness of coatings on magnesium for protection against corrosion. If holes are present in the coatings, a local corrosive environment results, and the local corrosion rates can be greater than the rates for the uncoated condition. The corrosion potential is more negative (active) and these local areas are anodic to the coated areas and to the uncoated alloy. This electronegativity may result from the coating treatment and/or inability of the environment to reach the bottom of the hole. However, over time, on the order of hours or days, the potential of the coated specimen changes to a more positive potential than the uncoated material. At this point, the coated material is several orders of magnitude more corrosion resistant than the uncoated material when measured by the ac impedance method. Techniques applied in this study include anodic polarization and ac impedance. This work, on coatings on magnesium, is continuing with emphasis on utilizing the ac impedance technique.

Corrosion Behavior of Titanium Alloy, Ti-15 Mo-3Nb (Ti21SRx)

A. C. Fraker

The Titanium Metals Corporation of America (TIMET) developed a beta titanium alloy, TIMETAL 21S, (Ti-15Mo-3Al-3Nb) for use in the National Aero-Space Plane (NASP). The Air Force and the National Aeronautics and Space Administration have a joint program office (NASP joint program office) to transfer some of the technology developed for the NASP project. One example is this alloy, Ti21SRx, that has been altered by TIMET for consideration as a surgical implant material. A consortium has been set up that includes TIMET, the NASP office, implant manufacturers, biological testing laboratories, and NIST. This consortium will study all aspects of this alloy with reference to its use as a surgical implant material. Data obtained will be placed in a file at the Food and Drug Administration (FDA) and will be available to all implant producers.

The NIST role in this consortium has been to study the corrosion behavior of Ti21SRx. An initial investigation of the corrosion behavior of Ti21SRx in simulated physiological testing solution at 37 °C and pH of 7.4, has been completed and results were submitted to the NASP office. This study showed that, at this near neutral pH and at 37 °C, the Ti21SRx is comparable in corrosion behavior to the currently used alpha-beta Ti-6Al-4V alloy. Microstructural studies, using transmission electron microscopy, indicate that omega phase is present in the alloy. This needs further investigation because the presence of the omega phase causes a loss in ductility and changes in other mechanical properties of the material. Additional corrosion studies will be made under conditions of varying pH and surface treatment.

Waterline Corrosion of Nuclear Waste Tanks
E. Escalante and R. E. Ricker

Failures of the DOE nuclear waste tanks at Hanford, WA occur through poor tank design and construction or from corrosion of the tank wall. Improper design generally results in an immediate failure of the tank during initial filling (poor corner and weld design). Improper construction often results in short term stress corrosion failures (<5 y) from poor welding procedures or failure to stress relieve after welding. Unlike other forms of failure, corrosion attack of the steel container is an ongoing process that does not slow down with time. Figure 1 is a plot of cumulative failures as a function of time.

The results show that corrosion will not occur at the waterline unless the solution in this region becomes diluted. Conditions for corrosion develop when moisture evaporated from the hot liquid waste condenses on the inner wall of the dome, runs down the wall and re-enters liquid at the waterline. This reduces the concentration of wastes locally at the waterline. Our data show that dilution of the waste results in a significant drop in pH, sufficient to allow corrosion to initiate at the steel surface. The electrochemical potentials observed between the concentrated bulk solution and the dilute solutions is of the order of 150 mV, more than sufficient to form a corrosion cell.

The data shown were measured using A515 pressure plate steel in a simulated waste solution of 3.5 M sodium nitrate and 2.5 M sodium hydroxide. The composition of the simulated waste is made up of the major components found in a "typical" waste tank.[1]

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[1]Sutter, H., "Representative Chemical Composition of Current and Future HLW at Hanford," Handout at SST Interim Stabilization Technical Issues Program Review, SAIC: Richland, WA (1992).

Effect of dilution of simulated waste on pH - Six diluted solutions were made from the simulated waste. The pH of these solutions versus the concentration of sodium hydroxide is shown in Figure 2.

The effect of localized dilution of the simulated liquid waste on the potential of steel - Two samples of A515 steel were placed in containers of unlike concentrations of waste solution, connected through a fine fritted glass wall. The potential difference between the two steel specimens was monitored for 60 minutes when one specimen was in a concentrated waste solution and the second steel specimen was in a dilute solution of simulated waste. This experiment was repeated, using one of the six dilute solutions plotted in Figure 2 in one container and the concentrated solution in the second container. The difference in potential between the steel specimens was of the order of 150 mV as dilution was increased.

The effect of localized dilution of the simulated liquid waste on the "galvanic" current of steel - Following the potential measurements, the galvanic, or local-action, current between the steel specimens was measured, using a zero resistance ammeter. This current was measured periodically over a 60 minute period, reaching a steady state ranging from -0.28 to -0.47 $\mu A/cm^2$, where the specimen in the concentrated solution is anodic to the specimen in the dilute solution. Figure 3 is an example of a typical plot of galvanic current versus time.

Coupon tests - Four coupons of AISI 1018 carbon steel were partially immersed in simulated waste solution for periods of up to 60 days. These coupons were periodically examined for evidence of corrosion at the waterline. In the concentrated solution of simulated waste, there was no evidence of any corrosion attack at any time. Similar specimens that were placed in the most dilute solution of simulated waste showed evidence of corrosion attack within a few hours.

These preliminary experiments indicate that in the absence of dilution, corrosion of steel will not occur. The pH of the concentrated waste solution is sufficiently high ($\approx$13.7) to passivate the steel surface. As the pH decreases through dilution, its ability to passivate the steel decreases. Other work performed in this laboratory, has shown that once corrosion is initiated, repassivation of the steel becomes difficult, because the corrosion process further reduces the pH locally, and the corrosion product that forms acts as a temporary barrier to the bulk, high pH solution.[2]

[2]Escalante, E. and Ito, S., "Measuring the Rate of Corrosion of Steel in Concrete," ASTM STP 1065, ASTM: Philadelphia, PA, pp. 86-102 (1990).

Evaluation of the Corrosion Behavior of Alternative Fire Suppressants

M. R. Stoudt, R. E. Ricker, J. L. Fink, and J. F. Dante

Halon 1301 (CF_3Br) is one of several in-flight fire suppressants that possess sufficient stratospheric ozone depletion potentials to warrant limitations on its production and use. The Corrosion Group is continuing to assist both the Fire Science Division of BFRL and the US Air Force in the identification of a suitable alternative to Halon 1301. The role of the Corrosion Group in this effort is to assess the compatibility of the possible Halon alternatives with the broad range of structural materials used in the engine nacelles and in dry bays on board high performance jet aircraft. In Phase I, the Corrosion Group developed test methods to screen the corrosion behavior of the original thirteen potential replacement candidates. A general ranking of the corrosion behavior of these agents was generated from this data and then used to determine suitable replacement candidates for further evaluation. Phase II is focused on evaluating the corrosion behavior of the remaining candidates over a broader range of environmental conditions. The experimental methods used for this analysis were specifically designed to measure the general corrosion and the stress corrosion cracking susceptibility of representative aircraft materials in these agents both at ambient temperatures and at temperatures comparable to in-flight conditions. Experiments were also conducted to further evaluate the corrosion compatibility of these aircraft materials with the range of combustion by-products formed by the agents. The results of this on going evaluation will be compiled and used to further reduce the list of replacements for Halon 1301. In addition to these experiments, the Corrosion Group has developed a reproducible electrochemical measurement technique designed to evaluate the corrosion behavior and predict the potential for component failure over a broader range of conditions and temperatures in these non-aqueous, low conductivity, organic compounds.

Figure 1. Cumulative Tank
Failure versus Time

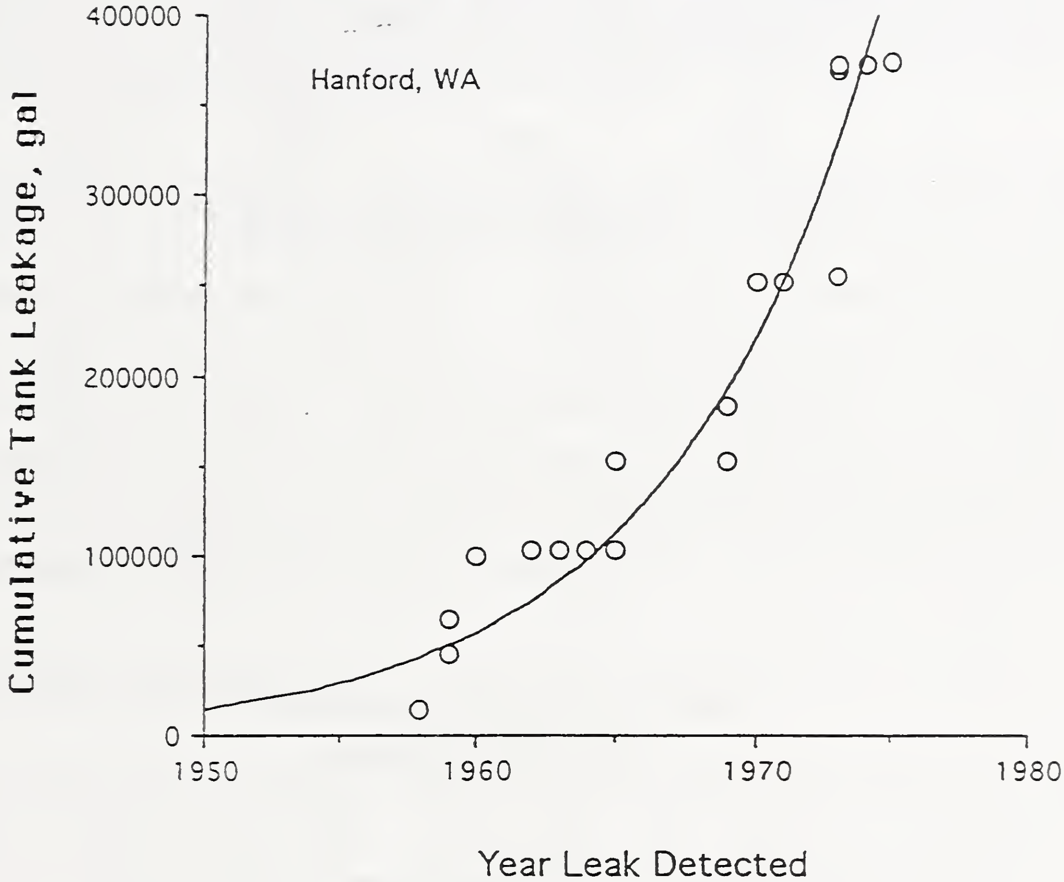


Figure 2. pH vs Conc of Simulated Waste

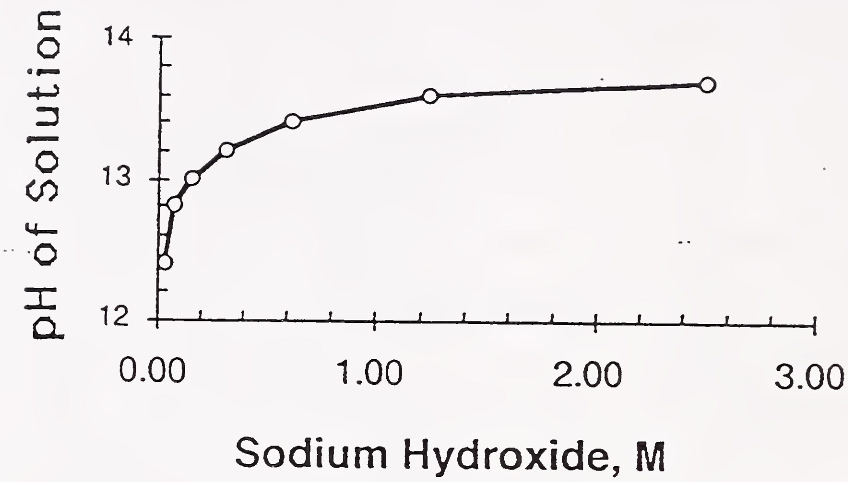
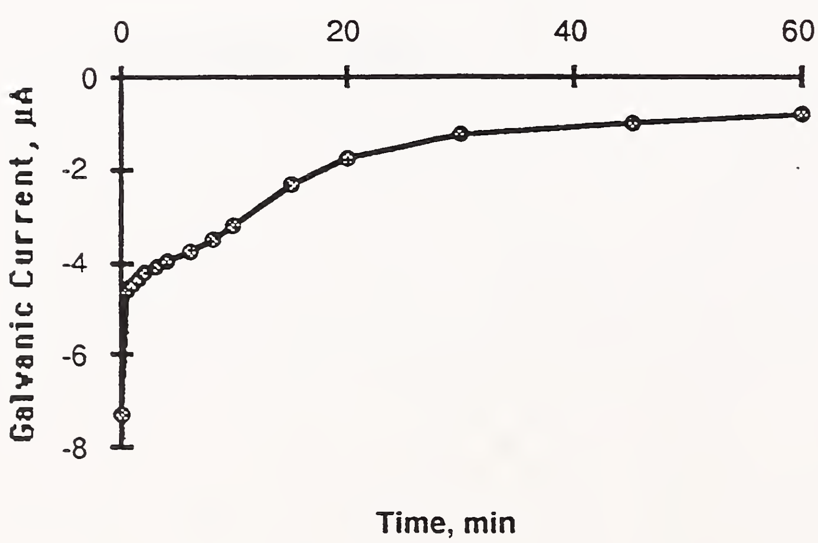


Figure 3. Galvanic Current vs Time (32:1 dilution)



ELECTRODEPOSITION Gery R. Stafford

The electroplating industry contributes $42.4 billion to the gross national product in the United States and employs almost 500,000 workers in 12,400 associated companies. Numerous thin-film and low-dimensional structures, such as corrosion/wear resistant coatings, interconnects in electronic packaging, magnetic recording media, and low noise magnetic multilayer read/write heads, currently are being fabricated by electrochemical technology. Electrodeposition is an attractive option, particularly for the production of large-area and non-planar devices. It also has the advantage of not requiring high-purity starting materials, being an isothermal process controlled primarily by chemical and electrical parameters and being readily adapted to large-scale production.

The Electrochemical Processing Group is responsible for the processing and characterization of electrochemically formed thin films. The objectives of the group are: (1) the determination of the critical mechanistic, chemical and process variables controlling the structure/property relationships of electrodeposited thin films; (2) the development of approaches which will result in improved materials and processing controls for industry; (3) the fabrication of standard reference materials which are certified to coating thickness, chemical composition or properties, such as microhardness; (4) the identification and development of new standards reference materials; (5) the provision of NIST expertise to voluntary standards organizations; (6) the provision of NIST expertise to industry, through research associates, appropriate contracts and consulting arrangements; and (7) the provision of NIST expertise to other government agencies through other agency contracts.

FY94 Significant Accomplishments

- The composition of aluminum-titanium alloys electrodeposited from a 2:1 $AlCl_3$:NaCl electrolyte containing Ti(II) is independent of current density and is fixed at 25-27 atomic percent titanium. This can be explained if we introduce the notion of a single electroactive species having the structure and stoichiometry of $[Ti(AlCl_4)_3]^-$ which has been proposed recently in the literature. The ability to electrodeposit alloys from a single electroactive species may eliminate many of the problems traditionally associated with alloy deposition such as variation in alloy composition due to non-uniform current distribution. In addition, it would guarantee compositional homogeneity on a molecular level.

- Investigated the potential for making Al-Ni, Al-Cr, Cu-Ni and Cu-Co alloys from chloroaluminate electrolytes. Developed some insight into the connection between the thermodynamics of alloy formation and the electrochemical potential for alloy formation. This resulted in a paper which was recently published in the Journal of the Electrochemical Society.

- A series of metastable Al-Cr alloys was synthesized electrochemically. These included a metallic glass that is known to exhibit enhanced aqueous corrosion resistance relative to conventional aluminum alloys. The possible application of this material as a high temperature coating remains to be explored. Of special note was the similarity between phase evolution in the Al-Cr system and the extensively developed Al-Mn system.

- Continued the examination of the passivation of transition metals such as chromium and nickel. Recent experiments reveal a clear electrochemical signature associated with the activation of chromium. This is the first such observation for this system. The scanning tunneling microscopy studies continue to yield remarkable information regarding the structure and dynamics of passive films.

- Demonstrated the ability to perform scanning tunneling microscopy at the electrode/electrolyte interface with atomic resolution. The $\sqrt{2} \times \sqrt{2}$ R45° adlattice of Cl on Cu(100) was imaged in 10 mmol/L HCl.

- One hundred and twenty microhardness standard reference materials were produced this year, comprised of 85 SRM 1906 and 35 SRM 1394. In addition, 1605 coating thickness standards (Cu on steel) ranging in thickness from 2 to 2000 µm were supplied to industry. Manufacturers of equipment and quality control laboratories depend on these standards to maintain uniformity in their products.

- Developed the capability to electrogalvanize steel sheet, simulating the process used by industry to coat zinc on steel for the automotive industry. Similarly, tin plating has been performed successfully using electrochemical plating techniques used by industry. These capabilities allow us to develop zinc and tin coating thickness standards useful to industry.

- Significant progress has been made in the development of mercury-free dental restoratives. Our approach is based on the premise that ductile silver and silver coated intermetallics (Ag_3Sn or Ag_4Sn) will cold-weld to form a dense filling, under moderate pressure and ambient temperature, if the surface has undergone appropriate treatment to remove the native air formed oxide. We have shown that the transverse rupture strength of silver which had been consolidated after treatment in 2% HBF_4 was six times greater than that of identical silver powder consolidated without treatment.

- A process was identified and developed to precipitate silver powder from an aqueous solution of silver and tin as a result of Sn^{+2} to Sn^{+4} oxidation with possible formation of a AgSn alloy and/or Ag_4Sn intermetallic compound. This should improve the packing density of consolidated powders.

- The agglomeration of silver coated silver-tin intermetallic powders was minimized with the redesign of the plating chamber for the fluidized bed (vibratory) plating apparatus. In addition, modifications in the electrolyte chemistry now allow us to routinely coat particles as small as 25 µm.

- The CRADA with Atotech, USA to develop an understanding of the electrochemistry of trivalent chromium electrolytes and characterize physical and mechanical properties of deposits from such electrolytes was completed. A final report was submitted to Atotech, USA.

- A U.S. Patent assigned to NIST has been allowed for "Methods and Electrolyte Composition for Electrodepositing Chromium Coatings". The patent encompasses the deposition of functional chromium from trivalent electrolytes as an alternative to the toxic hexavalent electrolytes.

- Thermally fired liquid noble metal resinate and electrodeposition were used in combination to metallize SiC/Al Alloy composites to promote solderability. The metallized thermal management devices maintained their integrity through soldering and thermal cycling tests up to 450 °C.

The Electrodeposition of Aluminum-Titanium Alloys

G. R. Stafford

The excellent high temperature properties, low density and corrosion resistance of several aluminum-based intermetallic compounds has led to the consideration of these ordered alloys for structural applications, with applications envisioned for monolithic and, more likely, composite materials. Electrodeposition is an attractive method for fabricating intermetallic compounds since undesirable compositional inhomogeneities are very limited in scale and grain sizes are typically very small. Aluminum-titanium alloys can be electrodeposited from a 2:1 $AlCl_3$:NaCl molten salt electrolyte containing Ti(II). We always have considered the deposition process to involve two electroactive species, $Al_2Cl_7^-$ for the deposition of aluminum and $Ti[AlCl_4]_x^{2-x}$ for the deposition of titanium (until recently, x has been considered to equal 2). The concentration of $Al_2Cl_7^-$ in 2:1 $AlCl_3$:NaCl is about 4.0 mol/L. When the electrolyte contains sufficient Ti(II) to avoid mass transport limitations, alloy composition is independent of current density and is fixed at 25-28 atomic percent titanium. Electrodeposits are single phase and reveal electron diffraction patterns that are consistent with the ordered face-centered cubic (fcc) $L1_2$ structure. The grain size is typically 0.1 to 0.5 µm. High resolution transmission electron microscopy (TEM) analysis shows that these alloys have a very high anti-phase boundary density, with the $L1_2$ domains on the order of 5-10 nm in size. Alloy compositions greater than 28 atomic percent Ti have not been observed at deposition temperatures of 150 °C.

The addition of Ti(II) to the chloroaluminate electrolyte results in dramatic changes in the deposition voltammetry on polished tungsten, Figure 1. When no titanium ions are present, curve (a), the deposition wave, is nearly identical in the cathodic and anodic direction. Pure aluminum deposits with minimal, if any, nucleation overpotential. In electrolytes containing greater than 150 mmol/L Ti(II), curve (b), both the deposition and stripping overpotentials are increased by about 60 mV over that of pure aluminum. In addition to the increased deposition overpotential, a rather large nucleation overpotential (25-50 mV) is required to deposit on polycrystalline tungsten. Chronoamperometric analysis as well as microscopic analysis of the early stages of potentiostatic deposition suggest that the deposit forms by instantaneous 3-dimensional nucleation followed by hemispherical diffusion controlled growth. Equally important, these nucleation transients appear to result from the diffusion of a single electroactive species to the electrode, i.e., the diffusion of Ti(II).

It is apparent from the voltammetry in Figure 1 than the presence of Ti(II) in the electrolyte inhibits the aluminum deposition reaction; otherwise, one might expect to observe a pre-wave for pure aluminum prior to the alloy reduction wave. Aluminum is known to form an under potential deposition (UPD) layer onto tungsten. It appears that Ti(II) in the melt alters the surface of the tungsten and inhibits the deposition of pure aluminum, perhaps by interfering with aluminum UPD. This may be an indication that Ti(II) specifically adsorbs onto tungsten, yet no direct evidence is available at the present time.

The independence of alloy composition on current density is quite unusual for the deposition of alloys and suggests that the two electroactive species are not electrochemically independent. Recent reports in the literature indicate that Ti(II), in a 2:1 $AlCl_3$:NaCl melt, is bound to six chlorine atoms in the first coordination sphere and to three aluminum atoms in the second coordination sphere, suggesting the complex ion to be $Ti[AlCl_4]_3^-$.

The alloy composition (Al_3Ti), its independence of current density, and the dependence of the nucleation transients on Ti(II) can be explained if we introduce the notion of a single electroactive species having the structure and stoichiometry proposed in the literature. The electrodeposition of alloys resulting from the discharge and decomposition of a single complex containing both components has previously been reported in the literature (Ni_3S_2 from $Ni_3(S_2O_3)_3$ as well as Ni-Cu alloys from heteropolymetallic complexes); however, this is the first report for such behavior being observed in chloroaluminate electrolytes. The ability to electrodeposit alloys from a single electroactive species may eliminate many of the problems traditionally associated with alloy deposition such as variation in alloy composition due to non-uniform current distribution. In addition, it would guarantee compositional homogeneity on a molecular level.

Electrochemical Synthesis of Nanostructural Materials

T. P. Moffat

A variety of nanostructural materials may be synthesized by electrochemical deposition. Our effort is currently focused in three areas, nanocrystalline alloys, low dimensional structures such as multilayers, and the electrochemical synthesis and in-situ characterization of materials via proximal probes such as scanning transmission microscopy (STM) and atomic force microscopy (AFM).

Nanograined Materials

T. P. Moffat, T. Foecke and U. Admon*

* Guest Scientist - Israeli Atomic Energy Commission, Beer-Sheva, Israel

Currently there is tremendous scientific and technical interest in the mechanical properties of nanograined materials. Thin films as well as three dimensional near net shape objects may be formed electrochemically. By the appropriate choice of processing parameters we have been able to produce thin films of nickel which exhibit grain sizes ranging from 10 nm to 100 nm as shown in Figure 2. The use of grain refining organic additives appears to be central to the process. In fact many of these agents are used as generic brightening and leveling additions in many commercial plating operations. Establishing the proper additives most often determines the success or failure of a given plating process. However the mechanism by which such additions influence structural evolution remains unresolved. This program addresses the role of such additives by examining the relationship between as-formed microstructures, processing parameters and the consequential mechanical properties. From the processing perspective we are exploring the utility of in-situ STM/AFM for examining the adsorption of organic additives at the electrode/electrolyte interface and the impact of such layers on the charge transfer reaction and microstructural evolution of both copper and nickel deposits.

Multilayers

T. P. Moffat, C. R. Beauchamp, S. Hua*, D. S. Lashmore*, Y. Zhang**, T. Foecke, D. Van Heerden, L. Bennett, R. D. McMichael, L. J. Swartzendruber

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** Guest Scientist - University of Maryland, Baltimore, MD

The Electrochemical Processing Group has established the ability to produce multilayers of Cu-(Ni-Cu, Co-Cu, Ni-Co-Cu) from a single electrolyte via pulse plating. An x-ray pattern exhibiting satellites associated with the compositional modulation is shown in Figure 3. The scientific and technical interest in these materials stems from the observation of giant magnetoresistivity as well as the effects of compositional modulation on mechanical properties. Our current effort is focussed on refining the synthesis methodology and developing a clearer connection between the processing parameters and the structural evolution of such materials. For example, the mechanical characteristic of Cu-Ni multilayers are thought to be dominated by the transition from coherent to incoherent interfaces which occurs with increasing wavelength. This relationship is being carefully examined by x-ray, diffraction, TEM and straining stage TEM experiments with an eye toward the influence of processing conditions on the amplitude of the compositional wave as well as interfacial roughness and sharpness. An effort is underway to broaden the scope of this processing technique to enable synthesis of multilayers incorporating other noble and transition metals. Issues concerned with metal on metal epitaxy are central to such developments. A variety of means are available for examining such issues. Most notably we recently have obtained the ability to image metal surfaces in an electrolyte with atomic resolution STM while the substrate is controlled electrochemically. For example, the $\sqrt{2} \times \sqrt{2}$ R45° Cl adlattice on Cu(100) in 10 mmol/L HCl was resolved as shown in Figure 4. In the coming year, we hope to be able to perform in-situ dynamic studies related to metal on metal epitaxy using STM as well as other proximal probes.

Scanning Probe Microscopy

T. P. Moffat

In addition to the applications outlined above, namely, metal on metal epitaxy and the role of organic species in the microstructural evolution of electrodeposits, proximal probes such as STM/AFM may be used in nanofabrication. A variety of possible applications exist that center on probe-induced chemistry. We are able to perform such functions in an electrochemical cell. For example, Figure 5 shows an image of a rectangle, two monolayers deep, that was selectively etched in the surface of graphite via tip-induced chemistry. The etching process only occurs above a certain substrate oxidation potential which demonstrates the electrochemical selectivity of the process. In the coming year we hope to use such schemes to perform selective metal deposition either by tip catalyzed deposition or via patterning of a resist for subsequent metal deposition, i.e., lithography.

Standard Reference Materials

E. Escalante, C. R. Beauchamp, E. C. Soltani, J. L. Mullen, H. B. Gates, P. N. Sharpless, S. W. Claggett, D. R. Kelley and C. E. Johnson

Zinc on Steel and Tin on Steel Standards - Our efforts were focused on providing tin and zinc thickness standards to calibrate coating thickness measuring equipment that use a radioactive isotope or an x-ray fluorescence beam with a cross section of approximately 10 x 15 cm. Potential users include the automotive industry, users of zinc coated steel sheet for automobile bodies, the canning industry, and users of tin coated steel sheet. Typically, 1.5 m wide rolls of steel sheet are electroplated on a continuous feed line, and the thickness of the metallic coating is monitored on-line.

To accommodate the large beam size used in industrial production, we have produced three 10 x 15 cm prototype zinc on steel thickness standards, covering a range of thickness from 1 to 8 μm. Characterization of the thickness of these prototypes has been performed by destructive techniques such as chemical stripping and atomic absorption which were then correlated to nondestructive x-ray fluorescence measurements. The same approach is being used to produce the tin on steel prototype thickness standards.

Related to these large prototypes are smaller versions of these reference coupons directed at laboratory and quality assurance users, which represent a much larger population than that expected for the large prototypes. Typically, these coupons are 3 x 3 cm in size.

Microhardness Standards - Microhardness standards are one of a continuing line of standards that this group has provided the national and international market for over a decade. This year, two microhardness standard reference materials, a low hardness (125 kg/mm^2) copper reference (SRM 1894) and a higher hardness (600 kg/mm^2) nickel reference (SRM 1906) were produced to meet the demand for these certified standards. SRM 1894 is certified at three indentation loads (25, 50, and 100 g) with five Vickers indentations per load. SRM 1906, on the other hand, is indented at only one load (500 g) with five Knoop indentations per load.

Coating Thickness Standards - State of the art coating thickness gauges approach the measurement uncertainty of secondary standards produced in the past. Our activities have focused on reducing the uncertainties of future SRMs by addressing the measurement procedure and material properties.

Modification to hardware and software used in the certification process was directed at minimizing uncertainties associated with the measurement procedure. This was accomplished through measurement automation which provided precise and reproducible sample positioning, allowing meaningful statistical characterization of uncertainties. Other modifications to procedures included elimination of false triggering during the measuring operation, an alternative calibration algorithm which optimized correlations between primary standards and the calibration curves of the instruments used for the certification, and a new assembly procedure for the SRMs which duplicates the measurement conditions of the primary standard during the calibration process. In addition, a new database of measured SRM values for process control and trouble shooting is being created. These data will assist in rapid and more efficient customer support.

Uncertainties associated with material properties were addressed by optimizing substrate parameters such as coating thickness, composition, surface finish, and substrate size. Criteria for specifying steel substrate material were established and suppliers were contacted. Candidate steel samples were received and evaluated using established magnetic and metallographic methods, in a collaborative effort with the Magnetic Materials Group. Efforts now are directed toward fabrication and certification of primary standards.

Development of a Metallic Mercury-free Alternative to Dental Amalgams

G. R. Stafford, C. E. Johnson, D. R. Kelley, J. L. Mullen, D. S. Lashmore*, M. P. Dariel**, U. Admon***

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*** Guest Scientist - Israel Atomic Energy Commission, Beer-Sheva, Israel

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 the objective of this program. The approach chosen by the Electrochemical Processing Group is based on three main premises: (1) the cold-welding of oxide-free silver; (2) the in-situ formation of Ag_xSn_y intermetallics by the room temperature fast interdiffusion of silver and tin; and (3) the homogeneous precipitation of silver by Sn(II) in solution.

Cold-welding can occur across appropriately cleaned metal surfaces from which oxide or absorbed layers have been removed. We have found that efficient surface cleaning of silver occurs by immersion in a mild acid. Ductile silver and silver coated intermetallics (Ag_3Sn or Ag_4Sn) will cold-weld to form a dense filling, under moderate pressure and ambient temperature, if the surface has undergone appropriate treatment to remove the native air formed oxide. For example, the transverse rupture strength of silver which had been consolidated after treatment in 2% HBF_4 was six times greater than that of identical silver powder consolidated without treatment.

Intermetallic compounds form at silver-tin interfaces even at room temperature due to the fast interdiffusion of silver and tin. By taking advantage of the immersion deposition process whereby a more noble metal, e.g. silver, deposits from a solution in which a less noble metal, e.g. tin, has been immersed in the form of solid powder particles, a large interfacial area, equal to the surface area of the tin particles, provides an extensive area over which fast diffusion can occur. X-ray diffraction and transmission electron microscopy have identified Ag_4Sn and Ag_3Sn resulting from the interdiffusion of silver, immersion deposited onto tin. By properly adjusting the initial amount of solid tin and the concentration of silver ion in solution, the final amount and composition of the intermetallic compound formed can be controlled.

Finely divided silver particles can be precipitated homogeneously by Sn(II) in solution. This precipitation will occur in the voids between silver coated intermetallic particles, thereby filling the void with metal and improving the overall packing density of the consolidated alloy. The final alloy will then consist of pre-alloyed intermetallic, immersion-formed intermetallic and silver. Current efforts are focusing on structure/property relationships as the relative amount of these constituents is varied.

Trivalent Chromium

C. E. Johnson

Research has focussed on a NIST developed process to electrodeposit chromium from a trivalent chromium (Cr^{+3}) electrolyte. The program originally began with sponsorship from Sandia as part of a DOE Waste Minimization Program and continued with support from a one-year Cooperative Research and Development Agreement (CRADA) with Atotech, USA. With recent interest in seeking alternatives to hexavalent chromium (Cr^{+6}), this new process can be substituted for the highly toxic hexavalent chromium electrolytes that are presently in use. The resultant coating from the trivalent electrolyte is an alloy of 94.7 chromium, 2.5 carbon, 2.5 oxygen, and 0.3 hydrogen reported as weight percent. Unlike many commercial processes, this process is capable of producing very thick coatings. To date, coatings greater than 500 µm have been produced.

As-deposited coatings from the trivalent electrolyte are bright, amorphous and microcracked up to 75 µm thickness and become semi-bright at greater thicknesses. Differential Thermal Analysis (DTA) revealed a transformation from amorphous to crystalline BCC chromium structure beginning at ~300 °C and peaking at ~375 °C as well as a peak at ~600 °C associated with the precipitation of chromium carbide, Figure 6. The chromium carbide phase can be either Cr_7C_3 or $Cr_{23}C_6$ depending on the heat treatment temperature, Figure 7. Measurement of Coefficient of Thermal Expansion (CTE) on chromium deposits from the trivalent electrolyte from 25-1100 °C resulted in significant permanent contraction (3.4%). The majority of the contraction occurred with the transformation from the amorphous state to the crystalline BCC structure occurring between 25-400 °C. The contraction was due to the loss of free volume associated with an amorphous structure. The as-deposited coating hardness, nominally 750 Knoop or Vickers, can be increased to 1800 with heat treatment at 450 °C. The increase in hardness is associated with precipitation hardening with the formation of a chromium carbide phase. Maximum hardness was obtained when the coatings were heat treated within a range of 400-500 °C for one hour. However, the precipitated phases were not detected by x-ray diffraction until the heat treatment temperatures were in the range of 600-650 °C. Wear performance of chromium deposits from the trivalent electrolyte increases significantly with heat treatment due to the formation of the hard chromium carbide phase. Wear data of heat treated (650 °C) coatings in a lubricated abrasive wear environment have shown the coatings to be 2-3 times more wear resistant than hard chromium deposits from hexavalent electrolytes.

No inherent toxicology problems exist for chromium deposition from the trivalent electrolyte except for the possible evolution of chlorine at the anode which to some extent is redissolved in solution. However, future work is planned to eliminate or suppress this reaction.

Future work on chromium deposition from the trivalent electrolyte will depend on new funding support. The CRADA with Atotech, USA was terminated on September 30, 1994. A joint proposal was written with Dr. N. Wheeler (Guest Scientist - University of Virginia) and submitted to EPA-Environmental Technology Initiative for "Plating Technology for a Cleaner Environment: Electrodeposition of Functionally Thick Chromium Coatings from Trivalent Electrolytes".

Coating of Metal Matrix Composites

C. E. Johnson

High performance thermal management and structural components for the electronics industry comprised of a silicon carbide (SiC) and aluminum (Al) alloy composite are metallized to promote solderability. The present method of choice by industry is to deposit nickel by autocatalytic deposition followed by an electrodeposited layer of gold. The adhesion attained by this approach is dependent only on mechanical "keying or locking" to surface imperfections which in some cases result in blistering of the coating during thermal cycling up to 450 °C.

A different approach was taken by depositing a "seed" layer of metal using a noble metal resinate prior to electrodepositing the nickel and gold coatings. Liquid metal resinates (metallo-organic formulations) are air-fired (500-600 °C) to form essentially pure films of gold, platinum, palladium or silver. Base metals such as nickel, chromium, or tin are added to the formulations to promote bonding between the coating and substrate either by oxygen linkages or direct chemical reactions with the substrate. Platinum, gold and palladium metal resinate also could be applied by traditional spin coating techniques, silk screening or dipping. After firing at 400 °C, the resulting metal film thickness was estimated to be 0.1-0.3 micrometers. Subsequent nickel and gold coatings were electrodeposited to a thickness of 2.0 micrometers, respectively. The low firing temperature of 400 °C for the resinate was dictated by the melting point of an eutectic in the aluminum matrix which restricted the firing to 500 °C and below. Composite coupons treated with the platinum resinate maintained their integrity through soldering and thermal cycling tests while those treated with palladium and gold eventually blistered. This may in part be due to the similar coefficient of thermal expansion (CTE) of platinum and the SiC/Al alloys composite; palladium and gold have somewhat higher CTEs. The optimum bonding between the film and substrate may not have been attained with the firing at the lower temperature of 400 °C since these particular resinate formulations were designed for firing temperatures between 500-600 °C. New resinate formulations designed to be fired at lower temperatures will be investigated. This work has created an interest in examining the liquid metal resinates further since they may provide a viable route for metallizing non-conducting or "difficult to plate" surfaces.

Microstructural Characterization of Co-W Coated Graphite Fibers

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** Guest Scientist - Materials Innovation Inc., West Lebanon, NH

The present research concerns an electrodeposited cobalt alloy coating containing 7.1$\pm$0.4 at.% tungsten, which was designed to serve as a diffusion barrier coating on graphite fibers. As previously reported, the coating extended the maximum temperature for use of graphite-nickel metal matrix composites from 600 °C to 800 °C for up to 24 hours. This represents a seven-fold increase in the useful lifetime of this composite at 800 °C. Although full protection was not imparted at higher temperatures, the interdiffusion was slowed. For example, at 1100 °C, the lifetime of the composite was extended five-fold. The focus of this year's research was a microstructural study to identify the reason for failure of the coating at higher temperatures. X-ray diffraction (XRD) and transmission electron microscopy (TEM) were the tools used in this investigation.

XRD showed the as-deposited coating to contain hexagonal close packed (hcp) cobalt, whereas only the face centered cubis (fcc) phase was observed after annealing at 1100 °C for 1.5 hours. The annealed alloy was found to contain 5.3$\pm$0.3 at.% tungsten carbide, WC, on the annealed fiber surface after acid stripping to remove the coating, indicating that carbon had diffused out and reacted with tungsten in the alloy at the coating-fiber interface. Inspection of the f.c.c. peaks showed each to be convoluted. Peak profiling, followed by lattice parameter determination for the peaks indicated that three Co-W-C alloy phases may have formed upon annealing the coated graphite fibers at 1100 °C for 1.5 hours. It appears that small differences (i.e., 0.19 to 0.66 $\pm$ 0.09 at %[3]) in carbon composition, (and possibly in the tungsten composition, as well) correspond to distinct phases in the Co-W-C phase diagram. Although it is not possible to identify these phases in the alloy without further experimentation, it appears from the phase diagram that their differences may arise due to precipitated co-phases and to differences in magnetic properties (eg., ferromagnetic f.c.c. vs paramagnetic f.c.c.).

TEM analysis showed the WC phase to be present at the interface as flat triangular crystals, with sides of approximately 100-300 nm in length. In many cases, the WC crystals seem to form an overlapping network, lying flat against the fiber surface and stacked like bricks. This could explain why the coating increases the lifetime of the fibers but does not protect them completely. Where the crystals are formed, they appear to lie flat along the fiber surface, forming a protective barrier. The fibers that appeared unchanged by the annealing process had this type of protective networks of overlapping WC crystals. However, those fibers with no apparent WC crystals at the interface had irregular borders arising from diffusion of the carbon into the alloy. Presumably, the carbon content of the alloy immediately surrounding the irregular fibers would be higher than that just outside the fibers/WC interface, due to the large quantity of carbon that was dissolved. This possibility suggests itself as an explanation for the origin of three separate Co-W-C phases, which were indicated by the XRD analysis.

A convergent beam electron diffraction (CBED) study of the changes in the carbon and tungsten concentrations and their relative proportions in various regions of the alloy could prove fruitful and may be undertaken in the future. For the present, the results of this Co-W alloy as a prototypical diffusion barrier is a mixed success. The upper temperature for use of graphite fibers in a nickel matrix was extended. This improvement, although not sufficient yet to warrant the use of graphite-nickel composites for high-temperature applications, suggests that this approach might be refined and used with other alloys to extend the useful temperature range still further.

This research, which was a joint project between NIST and University of Virginia, was sponsored by a grant from the National Science Foundation.

Deformation Induced Martensites

R. M. Waterstrat*

*Guest Scientist

Incommensurate structure modulations and a shape-memory effect have been observed in the compound ZrRh. The crystal structure of martensitic ZrRh and of the isostructural martensitic ZrIr compound have been determined from x-ray and neutron powder diffraction data. The temperature at which the shape-memory effect occurs in ZrRh is, perhaps, the highest yet observed for this phenomenon.

Our previous work has shown that the deformation of certain metallic B2-type compounds, such as equiatomic Zr (Pd, Ru) alloys, can produce tough, wear-resistant martensitic structures. Such alloys may find important applications in long-lasting biocompatible hip and knee implants and in many other industrial applications that require resistance to wear and corrosion. Some of these alloys also exhibit desirable shape-memory characteristics and super-elastic behavior. Such behavior is observed, for example, in the well-known "Nitinol" (NiTi) alloys at or near room temperature.

In order to develop expanded applications for such alloys it is desirable to find alloys of this latter type which operate effectively at higher temperatures. The compound ZrRh has been reported to exhibit a shape-memory effect when heated between 590 ° and 680 °C. In collaboration with Dr. Richard Fields, we have confirmed this by direct observation of shape recovery in a cast rod of ZrRh that was initially bent in the metastable austenitic condition at 550 °C. A similar rod of ZrIr composition did not exhibit a shape-memory effect but showed a pronounced bend ductility in the metastable austenitic condition at 850 °C. The compounds ZrRh and ZrIr are isostructural and differ only in their martensitic transformation temperatures.

In a collaborative effort with NIST staff members Drs. Judy Stalick and Leo Bendersky, X Meng-Burany and A. Curzon of the Simon Fraser University in British Columbia, Canada and M. Estermann of the ETH-Zurich Laboratory in Switzerland, we have determined the martensitic crystal structure of the isostructural ZrRh and ZrIr compounds. The structure is a new orthorhombic type that can be derived from the austenitic B2-type structure by a faulting mechanism. It is also related to the CrB-type structure.

Structure modulations having a wavelength of approximately 60 nm have been observed in the martensitic phase of ZrRh. These are incommensurate with the underlying crystal structure planes. We will attempt to learn whether such structures can be correlated with or have an important influence on the mechanical properties of this compound.

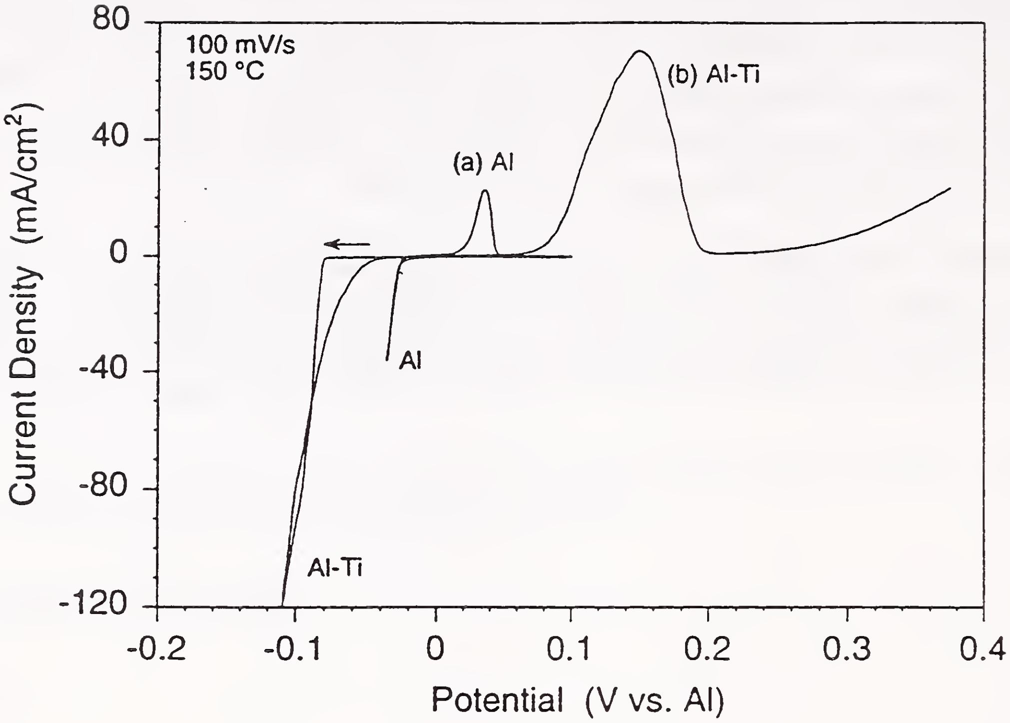


Figure 1. Linear sweep voltammogram in (a) 2:1 $AlCl_3$:NaCl (b) 2:1 $AlCl_3$:NaCl containing 225 mmol/L Ti(II) at 150 °C. The working electrode was a 0.005 cm^2 polished tungsten wire; sweep rate was 100 mV/s.

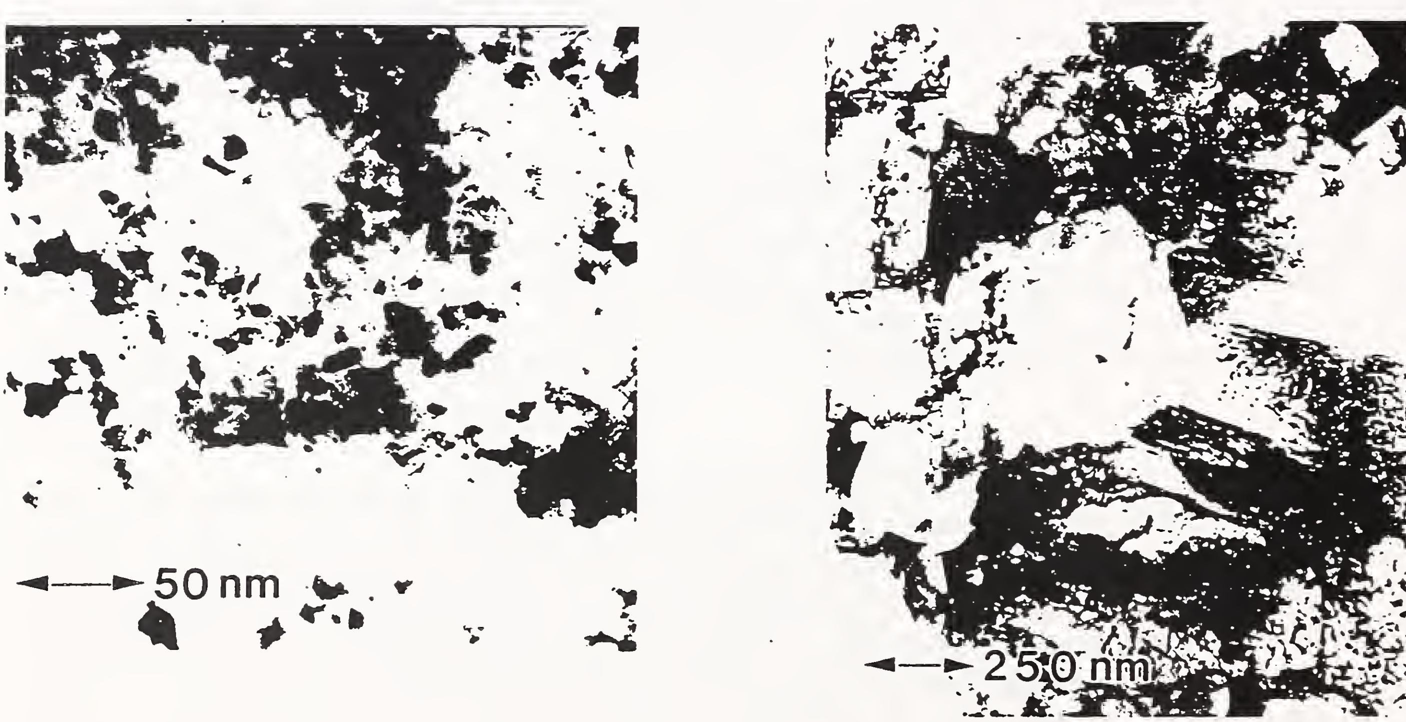


Figure 2. Influence of electrochemical processing on the grain size of electrodeposited nickel.

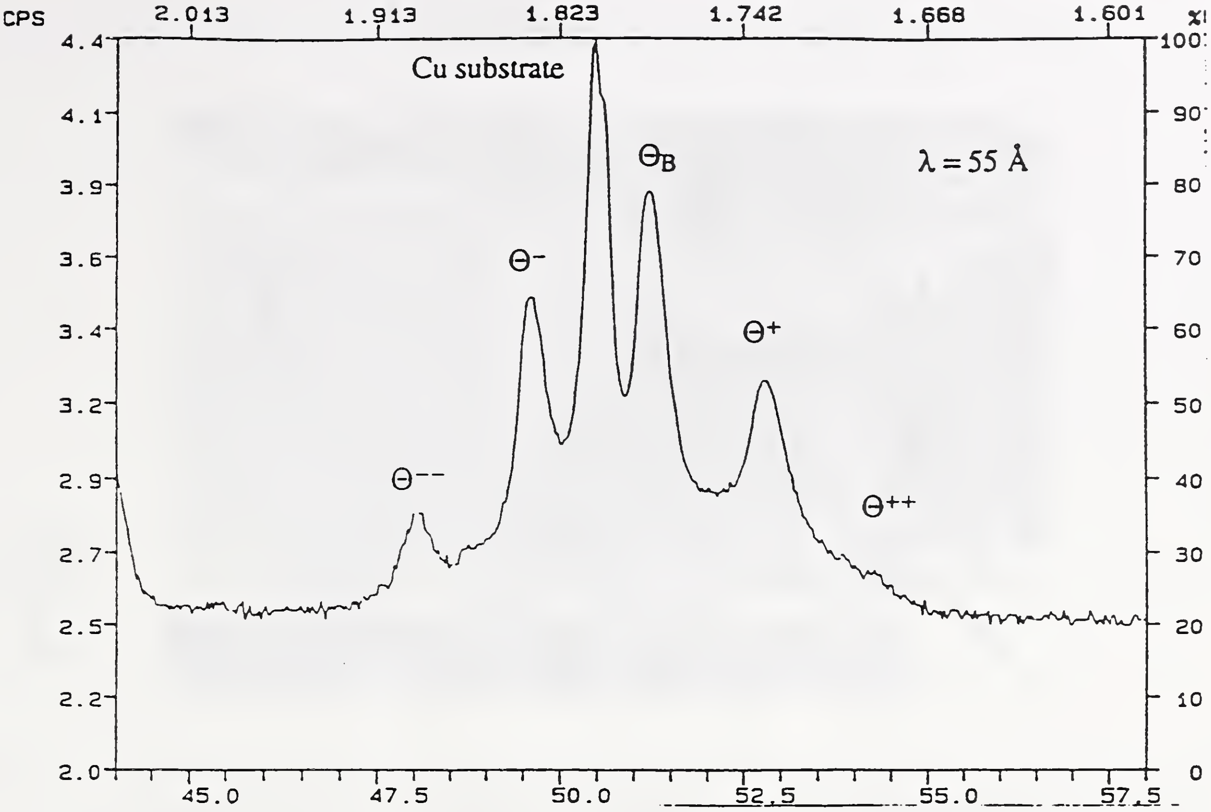


Figure 3. X-ray satellite structure for a Cu-Ni superlattice grown on Cu (100).

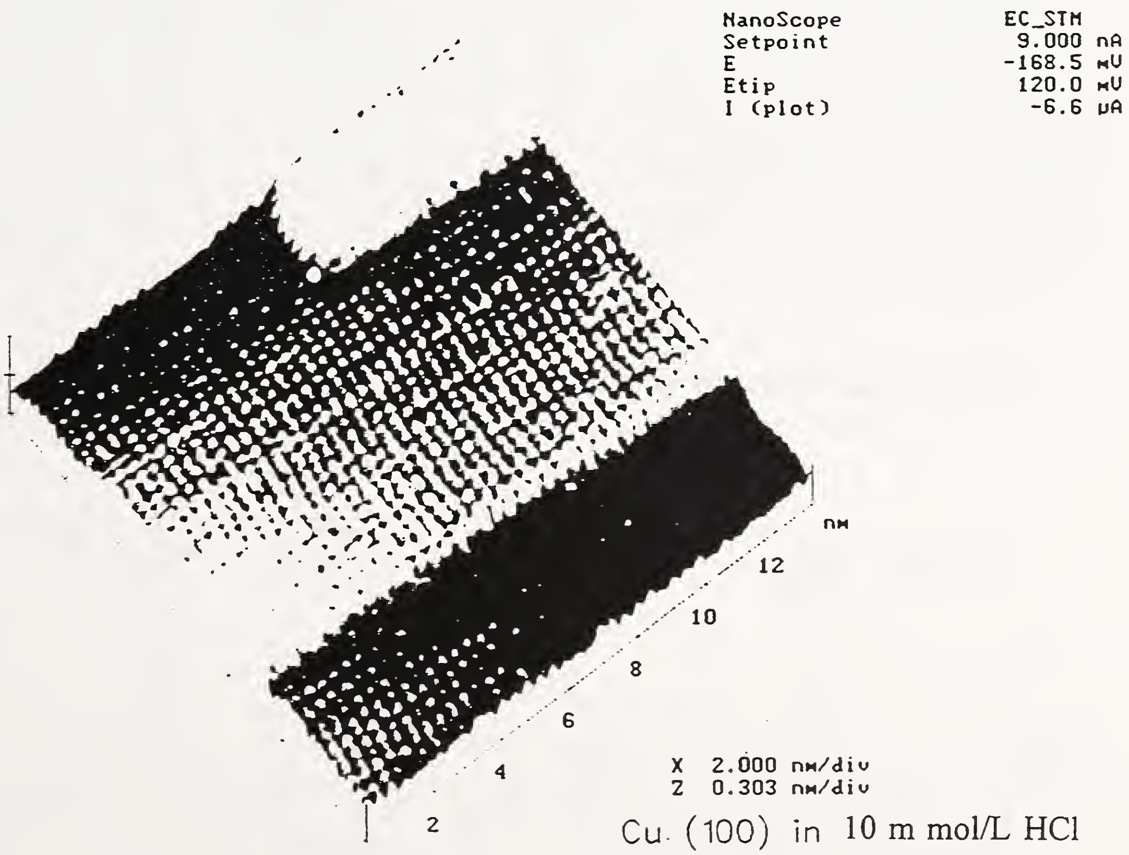


Figure 4. An in-situ ATM image of the $\sqrt{2} \times \sqrt{2}$ R 45° chloride adlattice on Cu (100) in 10 m mol/L HCl

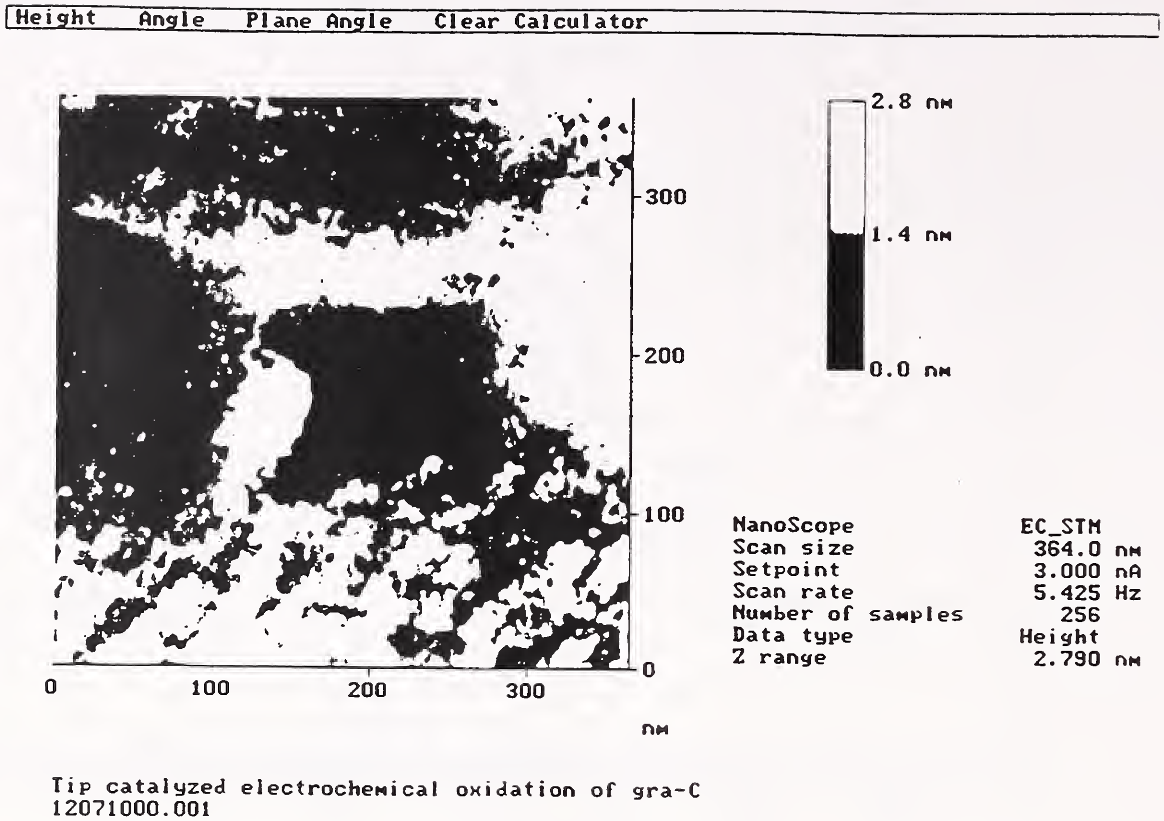


Figure 5. Tip catalyzed electrochemical etching of graphite.

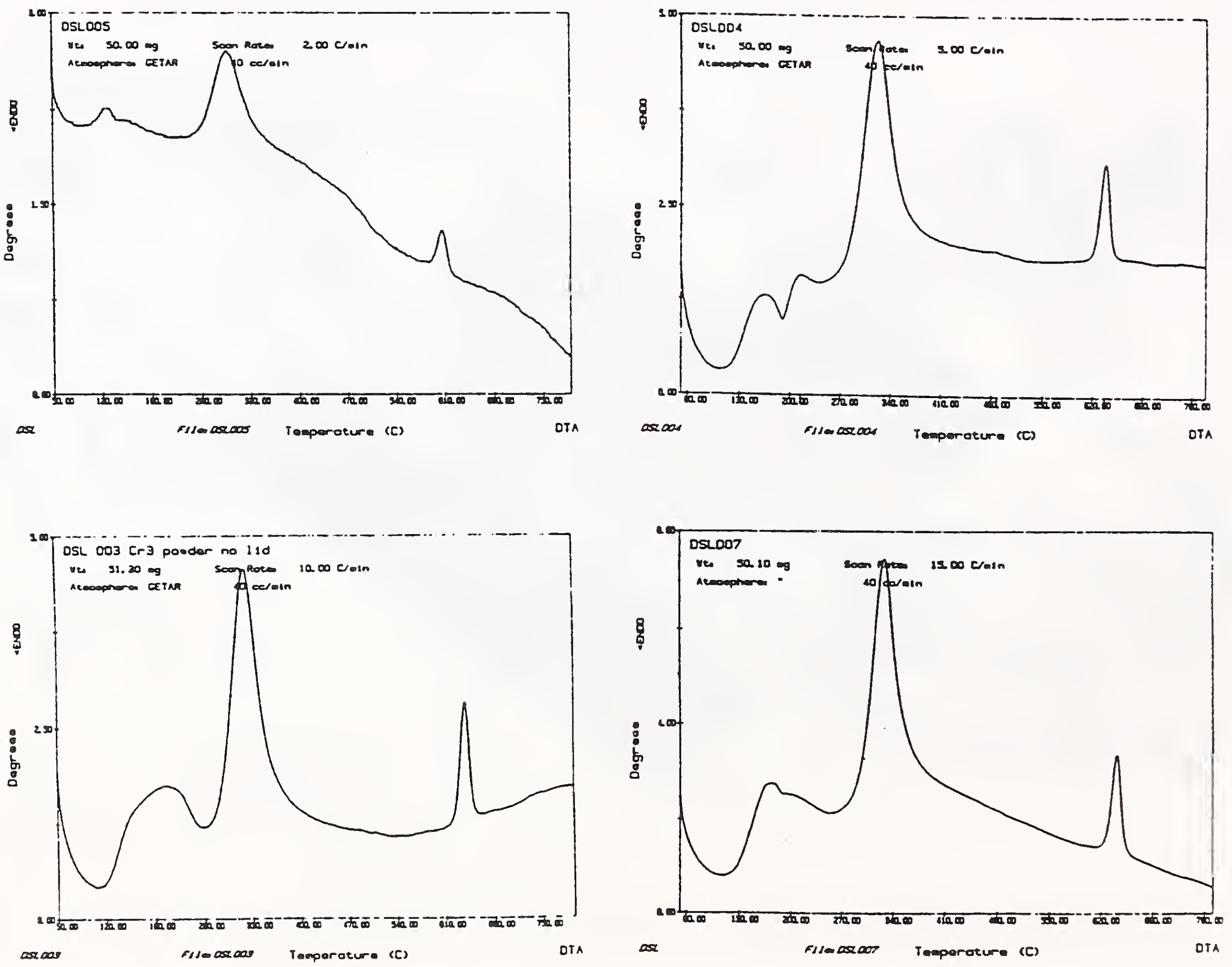


Figure 6. Differential Thermal Analysis of NIST tri-chrome samples at various scan rates (heating). 50 mg samples were analyzed. The test environment was argon flowing at a rate of 40 cc/minute.

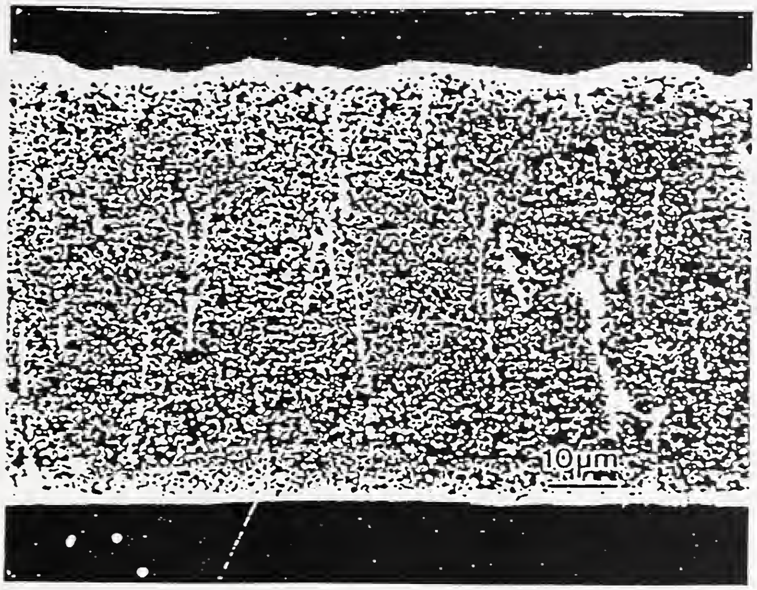


Figure 7. Light micrograph of etched section of heat treated 65 μm (2.6 mils) thick NIST tri-chromium deposit which reveals the precipitated chromium carbide phase. Heat treatment was carried out in a vacuum at 800 °C for 1 hour.

The research focus in materials processing and performance emphasizes, in general, the high temperature thermodynamic, chemical-kinetic, interfacial reaction, and molecular-level behavior of inorganic materials, including ceramics, metallics, and composites. Current program elements and objectives are listed below, where the main focus over the past year has been on the first three elements:

(1) To develop and apply a unique facility for *in situ*, real-time molecular-level determination of process mechanisms involved in the controlled production of thin films by vapor deposition; materials systems of recent interest include superconducting, ferroelectric, magnetic, and other advanced electronic and nano-structured films;

(2) To develop gas phase models of the pulsed laser deposition (PLD) process in support of efforts to improve process control and film quality;

(3) To develop, validate, and apply new molecular-specific methodologies for obtaining thermal and chemical stability data at ultra-high (2000 - 5000 K) temperatures; these data are needed for diverse applications such as: (a) the development of chemically-based models for vapor deposition, (b) the design of high performance refractory materials for use in hypersonic transport vehicles, (c) nuclear power generation, and (d) combustion-based applications such as turbine engines;

(4) To develop a new NIST competence in the area of "*In Situ* Characterization of Thin Film Deposition," with particular emphasis given to the widely used commercial process of ion-sputtering. Initial work is being carried out in collaboration (via a CRADA) with the DuPont Company, which has an ATP project in sputter deposition of complex oxide films.

(5) To deposit nano-structured magnetic thin films, using the recently developed pulsed laser deposition (PLD) process, and to correlate the film magnetic properties (determined by R. Shull, Magnetic Materials Group) with observed molecular-level characteristics of the vapor/plasma phase.

FY 94 Significant Accomplishments

- For a series of pulsed laser depositions of $BaTiO_3$ films, a parametric correspondence has been demonstrated between film oxygen deficiency, chamber oxygen pressure, and the *in situ*, real-time spectral emission intensity of the atomic oxygen plume intermediate. This study demonstrates the applicability of non-perturbing *in situ* monitoring for process control and optimization.

- Using a recently industry-developed, and N.I.S.T. acquired, very fast, high dynamic range camera/spectrometer system, which utilizes an intensified charge-coupled device (ICCD) detector, we have demonstrated a unique application to *in situ* particulate detection in laser plumes during thin film deposition. By imaging the actual ejecta trajectories, and correlating the observations with the inclusion of particulates in the film, we were able to establish the laser-target interaction conditions that lead to particulate ejection during deposition of $PbZr_{0.53}Ti_{0.47}O_3$ (PZT) films.

- Using a NIST-developed high pressure sampling, molecular beam mass spectrometer system, we have determined plume species velocity distributions for $BaTiO_3$ and PZT PLD systems, and have correlated the results with species-specific gasdynamic models and the spatial/temporal images obtained using the ICCD system. These results provide a new molecular-level understanding of PLD plumes prior to their deposition as films and the insight gained should enable further development of models of the film deposition process.

- A gasdynamic analysis of the mass spectrometrically determined post-expansion laser plume species velocities and temperatures has been used to determine the near-target plume pressure and temperature characteristics. This analysis has been carried out for a wide variety of materials and laser conditions. The good correlation found between the pre- and post-expansion conditions for all materials supports the applicability of the gas dynamic model used.

Laser Deposition of Electronic Thin Films

P. K. Schenck, D. W. Bonnell, J. W. Hastie, and A. J. Paul

The principal objective of this project which incorporates the program elements (1) and (2), is to demonstrate the general utility of pulsed laser deposition for producing thin films, particularly for complex oxide and nano-dispersed composite materials. Emphasis is given to the measurement science issues of process control and optimization -- requiring development and application of *in situ*, real time process monitors coupled with the development of process models. There is a growing industrial requirement for devices comprised of complex oxide thin films, particularly high T_c oxides, $PbZr_{0.53}Ti_{0.47}O_3$ (PZT) and $BaTiO_3$. With conventional commercial deposition approaches (e.g., sputtering), stoichiometry and, particularly, phase control have been difficult to manage for such complex structures. These limitations have led to a concerted effort by us, and others, to develop new deposition approaches such as PLD.

During the past year, we have continued systematic PLD studies of $BaTiO_3$ and PZT. In addition, new work has begun on high T_c oxides under a CRADA agreement with DuPont. In connection with these studies, major improvements in our PLD facility were made, first, in the form of an ICCD-image analysis and optical multichannel analysis spectroscopy system and, second, with the coupling of excimer laser beams with molecular beam mass spectrometry. With these improvements, we have been able to monitor PLD plume chemistry and dynamics over the pertinent process time scale of nano- to milli-seconds (Figure 1). A typical sequence of plume images, obtained at various times following the laser pulse is given in Figure 2. Frames such as these have been linked to form stop-action "movie-like" sequences, animating the plume evolution process. In addition to providing fundamental insight into the PLD process dynamics, these *in situ*, real-time observations have potential for process control--even for processes other than PLD such as magnetron sputtering and chemical vapor deposition.

ICCD imaging experiments have revealed conditions under which particulates are ejected from the targets. Figure 3 shows a case where these particulates have appeared and at times well after dissipation of the luminous (film depositing) plume. A systematic study of the PZT system indicated that the appearance of the particulates correlated with the frequency with which the laser pulse impacted the same area of the target. Because of the design of the target translation system, the region of highest laser damage was at the target center. Modifications are in progress to provide a more uniform laser strike pattern over the target surface. The nature of the laser target damage is noteworthy as nodules, or cones, are formed (see Figure 4) with dimensions similar to those of the film particulates (see Figure 5).

Thermodynamics and Kinetics of Refractory/Electronic Materials and Processes at Ultra-High Temperatures

J. W. Hastie, D. W. Bonnell, A. J. Paul, P. K. Schenck, J. Yeheskel*
* Guest Scientist, Nuclear Research Centre-NEGEV, Beer-Sheva, Israel

This project addresses, primarily, the goals of the program element (3) and, secondarily, elements (1) and (2). Coupling laser heating with mass spectrometric and optical spectroscopic analysis has the potential for providing quantitative thermochemical and kinetic data for inorganic materials and processes at temperature and pressure extremes inaccessible by conventional techniques. In addition, degradation processes of materials illuminated by high- powered lasers are important; e.g. in laser processing of ceramics (most recently, superconducting, ferroelectric, and diamond films), laser etching of semiconductor components, laser annealing of surface alloys, laser welding, and in the durability of refractories in defense, space, and other high technology applications.

In the past year, emphasis has been given to experimental and model investigations of thermodynamic, chemical kinetic, and gasdynamic processes occurring in the pulsed laser plumes used for thin film deposition. Our multistage high pressure sampling mass spectrometer system (MS) has been modified (see Figure 6) to provide far-field, species-specific determinations of velocity distributions for both neutrals and the stable ionic species arising from PLD plumes. Models are being developed and tested by comparison with the observed species distributions, and with the results obtained from optical emission imaging and spectroscopy. The gasdynamic component of the models assumes that the vapor expands adiabatically; this leads to a velocity enhancement, local cooling, and strong forward-peaking of the plume, features that greatly influence film structure.

Coupled with the gasdynamic effects are underlying thermochemical and gas kinetic forces that affect the species identities and concentrations in the plume. Efforts are underway to model these contributions to the pulsed laser material transport process. Chemical equilibrium and chemical kinetic models presently are being developed by us, using the quantitative species concentrations observed with the upgraded mass spectrometric system to estimate the early plume formation conditions, and to indicate the extent of chemical reaction that can occur during the plume lifetime. Chemical equilibria calculations provide a reference point for the degree of departure from equilibrium behavior prior to eventual simulations of spatial or temporal domains within a more comprehensive model. Gas phase and gas-target equilibrium compositions have been calculated using a NIST modified Solgasmix code for the target materials: $BaTiO_3$ at 4500 - 7500 K/0.1MPa-5MPa; and PZT at 5500 - 7500 K/0.1 MPa-5MPa. Pressures up to 50 bar have been considered in light of recent studies suggesting that instantaneous pressures may approach the material's critical point for relatively high laser fluence conditions. Comparison with the results of the mass spectrometric observations of the downstream free-flight region, indicates species identities and concentrations similar to the model values. Our measurements and calculations show that in thermal vaporization (i.e. moderate fluence) PLD, pressures corresponding to the material's *normal* boiling point are attained near the target surface, as shown in Figure 7. From the good correlation, shown in Figure 7, between the final (beam) and initial (target) temperatures it follows that each of the systems represented followed a well-behaved gasdynamic expansion.

Kinetic calculations have been initiated using the CHEMKIN-II (Sandia Labs.) software package, with the aim of rationalizing any discrepancies found between experimental and calculated equilibrium compositions. These kinetic considerations are needed to allow for possible chemical changes that may occur during the limited residence time in the high pressure, near-surface (target) layer and for any chemical reactions that may occur during the initial stage of adiabatic expansion. Kinetic models also are key to an eventual description of the plume condensation process at the substrate.

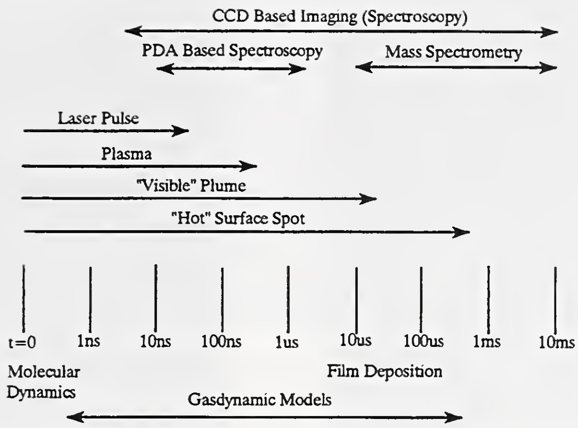
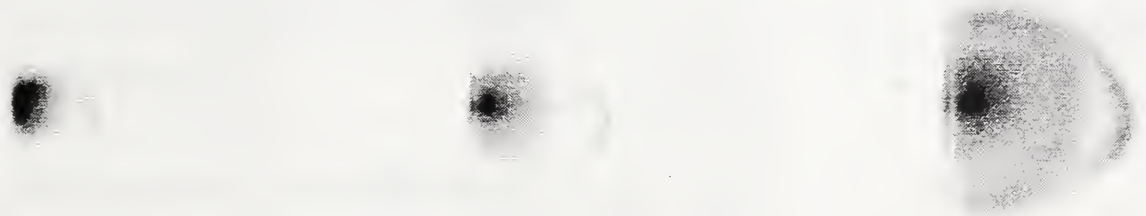


Figure 1. Time scale for pulsed laser depostion of films



a). 100ns b). 200ns c). 300ns

Figure 2. $BaTiO_3$ plume, negative images (self-scaled) obtained with 40 Pa added O_2. Target and substrate positioned at LHS and RHS, respectively

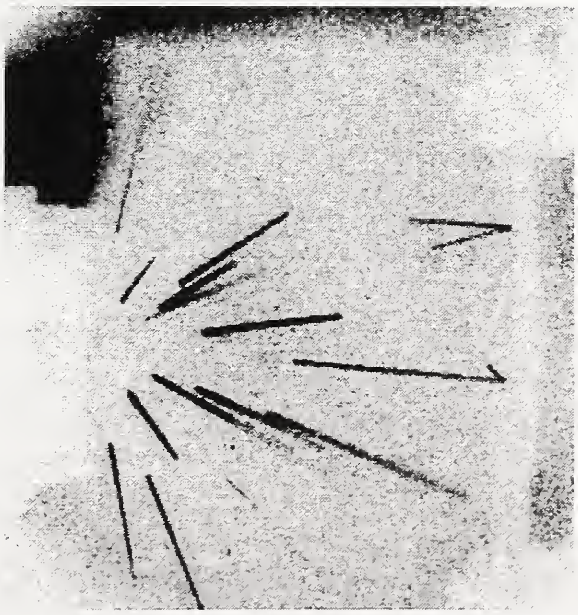


Figure 3. ICCD image (negative) of PZT particulates with a 1 ms exposure, 85 μs after the laser pulse (5 cm field-of-view).

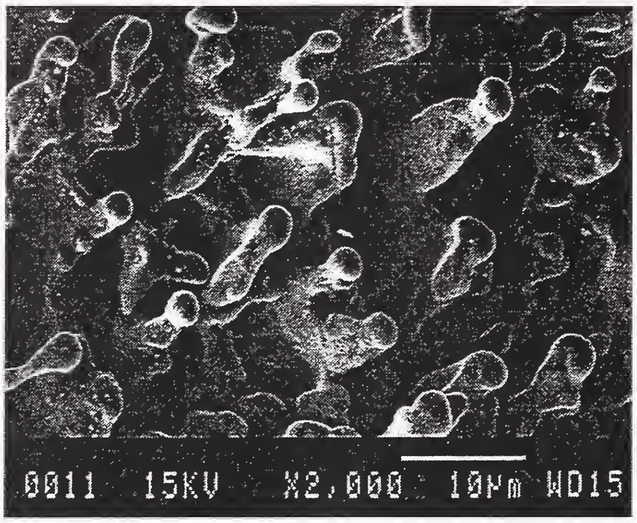


Figure 4. SEM image of PZT target near center.

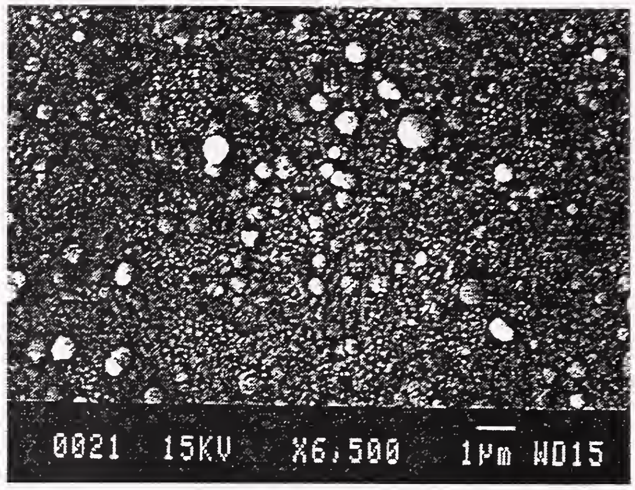


Figure 5. SEM image of PZT film corresponding to the conditions represented by Figure 4.

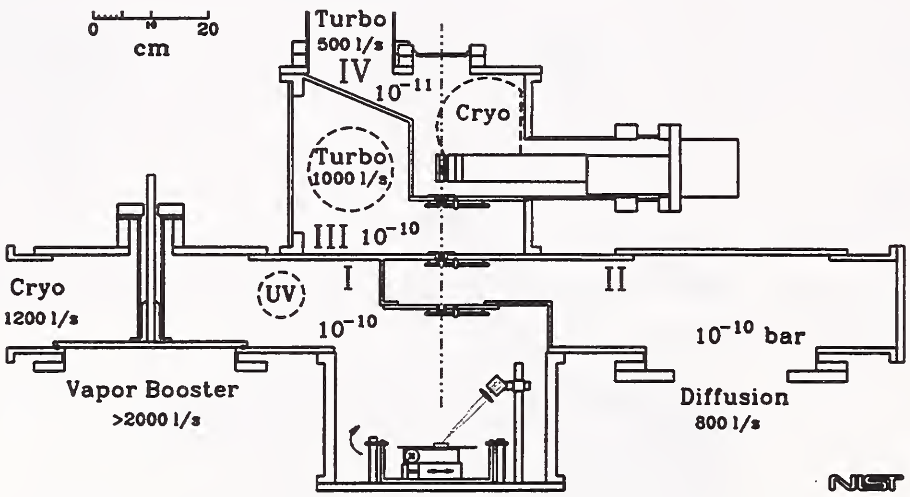


Figure 6. Scale schematic of molecular beam sampling mass spectrometric apparatus for plume species analysis.

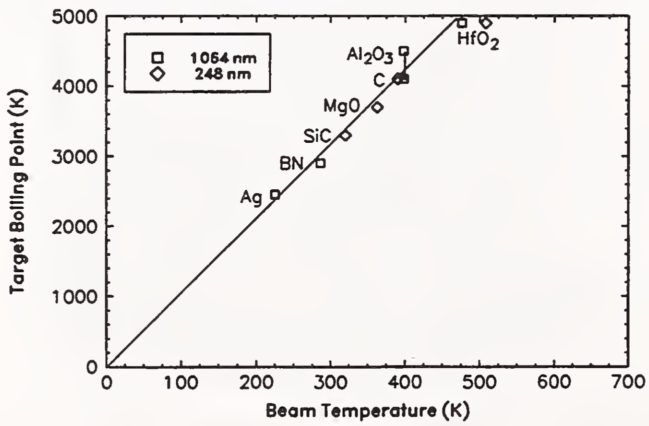


Figure 7. Gasdynamic correlation of initial and final temperature conditions. Target materials are labeled on the figure.

MAGNETIC MATERIALS

Lawrence H. Bennett

The Magnetic Materials Group studies advanced magnetic and superconducting materials to characterize their properties and performance, and promotes their economical processing and efficient use; develops and maintains competence in (1) metallurgical, magnetic, and electronic structure of materials and their correlation with processing conditions, (2) magnetic measurement methods, (3) magnetic reference standards, and (4) magnetic techniques of nondestructive evaluation of materials and structures; and provides expertise to industry, universities, standards organizations, and government agencies.

Magnetic materials are important to the commerce of the nation. The world market for magnetic technology in information storage and electrical equipment (e.g., motors and power transformers) exceeds $83 billion/year. Magnetic nondestructive evaluation methods are used for quality control wherever steel is used. Conventional superconductors have many commercial uses, including for medical magnetic resonance imaging (MRI) technology, and the new high-temperature superconductors have important potential applications, both near-term and future.

FY 94 Significant Accomplishments

- A large number of measurements on ultra-low carbon, low-carbon, and high-strength-low-alloy industrial sheet steels has succeeded in establishing an excellent correlation between Vickers hardness and the magnetic Barkhausen signal for these steels.

- Using ferromagnetic resonance, we found that the magnetic layers in giant magnetoresistance spin valve structures maintained their distinct character after annealing at 400°C for 30 min, but the FeMn pinning layer showed irreversible changes after 20 min at 250°C

- A method utilizing a field gradient to measure the value of Meissner fraction in high temperature superconducting samples of any shape was developed.

- In a collaboration with Xerox Corporation, engineered a liquid magnetic nanocomposite containing nanometer-size γ-Fe_2O_3 particles embedded in a polymer having a five-fold increase in magnetic strength over that of conventional ferrofluids, and showed that the interparticle distance in these ion-exchange resins changes with the addition of water to them.

- Showed that nanometer-sized spherical Fe_3O_4 particles are formed on the inside surfaces of silica beads in such a manner as to maximize the separation distance between the Fe_3O_4 particles, when prepared in a combustion flame.

- Found that magnetic nanocomposites containing nanometer-sized particles of Fe_2P can be prepared by sol-gel techniques. This material exhibited superparamagnetism with an unusually high blocking temperature of 250 K.

- Showed that annealing the vapor-condensed Fe_3O_4 + Ag magnetic nanocomposites in inert and oxygen environments changes the magnetic moment per iron atom.

- Magnetic nanocomposites could be prepared from Dysprosium Aluminum Garnets by incorporating iron into the lattice similar to the way the earlier $Gd_3Ga_{5-x}Fe_xO_{12}$ nanocomposites were prepared by incorporating iron into the lattice of Gadolinium Gallium Garnet. The new $Dy_3Al_{5-x}Fe_xO_{12}$ nanocomposites possessed the enhanced magnetocaloric effects expected for magnetic nanocomposites, with magnitudes similar to the gadolinium gallium iron garnet magnetic refrigerants.

- Showed that the magnetic domains in electrodeposited multilayers that exhibit giant magnetoresistance can be imaged using a new magneto-optical indicator film technique.

Granular Magnetic Nanocomposites

R. D. Shull, R. D. McMichael, L. J. Swartzendruber, L. H. Bennett, R. Brown, R. Drew
J. Weissmüller, Universität des Saarlandes, Saarbrücken, Germany

Composite materials containing nanometer-sized magnetic species have been shown to possess unique properties, new magnetic states, and unusual property combinations. Through variation of the relatively easily controlled variable of composition, these materials also permit the atomic engineering of specific material properties. Progress has been made on many fronts. Included is proof that large quantities of these materials, as will be required by industry, may be prepared by a variety of techniques. Through extensive interaction with industry the utility of these materials for magnetic refrigeration, magnetic recording, and color reproduction are being examined. In addition, magnetic methods at NIST have been used to optimize the industrial processing of these materials.

In a collaboration with Xerox Corporation and Cornell University (CRADA signed in FY93), magnetic nanocomposites of γ-Fe_2O_3 and a polymer have been examined via vibrating sample magnetometry, Mössbauer spectroscopy, and transmission electron microscopy (TEM) with the Materials Structure and Characterization group. These materials are prepared by ionically exchanging Fe^{2+} ions with H^+ ions in a cross-linked divinylbenzene polystyrene polymer, and subsequently reacting the Fe^{2+} ions with oxygen. This process results in the formation of bulk quantities of nanometer-size γ-Fe_2O_3 particles embedded in the polymer. These materials can then be made into a sol by the appropriate addition of liquids like water. The NIST measurements have enabled Xerox Corporation to design and engineer a magnetic nanocomposite having a five-fold increase in magnetic strength over that prepared before the interaction with NIST (see Fig. 1). These materials are particularly interesting for their use as advanced toner materials for high quality color copiers and printers. Xerox considers itself at the leading edge of this new technology and credits NIST for helping them stay there. This year NIST scientists also showed by electron microscopy observations that the interparticle distance between the γ-Fe_2O_3 particles changes when the material is prepared as a sol. This information is helping Xerox Corporation continue to engineer this material for their applications. As a result of the developments in these materials achieved in this collaboration with NIST, Xerox Corporation is setting up a pilot plant for large scale production of these nanocomposites.

We have examined the microstructure and the magnetic properties of mechanically alloyed FeNi, $FeNi_3$, and $(FeNi_3)_{1-x}Ag_x$ prepared by Lazlo Takacs of the University of Maryland, Baltimore County. The high permeability of $FeNi_3$ ('permalloy') and the fact that both Fe and Ni are immiscible in Ag make the system a candidate for achieving a high sensitivity magnetoresistance element consisting of nanometer-sized particles of $FeNi_3$ embedded in a matrix of Ag. Indeed, good magnetoresistive properties have been observed recently in granular $(FeNi_3)_{1-x}Ag_x$ produced by annealing multilayer samples. These structures are being investigated by IBM corporation because of their potential for application in magnetic recording media (Science 261 1021 (1993)). The production of nanometer-sized grains in our mechanically alloyed samples was confirmed by x-ray line broadening and by transmission electron microscopy. X-ray measurements indicated, that a small amount (~7%) of Ag could be alloyed into the Fe-Ni and that considerable lattice strain was present. Mössbauer and magnetic measurements found no evidence for superparamagnetism in these alloys. These results will appear in Acta Metallurgica. We presently are investigating the magnetoresistance of our samples.

Magnetic nanocomposites prepared by three additional methods which are potentially capable of providing bulk quantities of material (as will be needed for industrial application) were also studied during FY94. These material routes were selected partially because of the potential they possessed for incorporation of rare earth species into the composite. Rare earth species are desirable in order to increase the magnetic spin of the entities in the magnetic clusters. The magnetocaloric effect scales with the magnetic cluster size, and so rare earth magnetic clusters in the magnetic nanocomposites would be advantageous. Through collaboration with Rutgers University, Osaka Prefecture University, and Darmstadt University bulk magnetic nanocomposites for the first time were prepared by co-condensation of species from the vapor onto a cold finger. Mössbauer effect data, magnetic measurements, and electron microscopy observations were used to show that bulk composites of Ag and Fe_3O_4 with nanometer-sized magnetite particles could indeed be prepared by this technique. Magnetization measurements showed that the as-prepared material was superparamagnetic. During FY94 the stability of these materials was examined during heat treatment at 250°C in helium and in oxygen. Despite remaining superparamagnetic during these thermal treatments, the material's magnetization varied. X-ray absorption spectroscopy (XAS) and Mössbauer spectroscopy were used to show that the form of the iron-oxide changed to predominately γ-Fe_2O_3 after annealing in oxygen, but remained primarily Fe_3O_4 after annealing in helium.

A collaboration with the Reacting Flows Group of Chemical Science and Technology Laboratory (CSTL) has resulted in the production of large quantities of iron oxide + silica nanocomposites prepared by flame combustion. Electron microscopy observations showed "spherical" 10 nm diameter iron oxide particles inside silica spheres. The high temperatures of the combustion flame serve to lower the nucleation rate of the iron oxide and to promote rapid sintering. It was found in FY94 that these iron-oxide particles were Fe_3O_4 and that they were located on the inner surface of the silica spheres. This finding suggests the Fe_3O_4 formed first and subsequently floated to the outer surface of the growing silica bead during cooling. In addition, magnetization data for a 50 wt.% Fe sample showed this material was superparamagnetic at temperatures larger than 170 K. Increased Fe loading resulted in ferromagnetic material at room temperature, indicating the loss of independent magnetic-particle behavior.

In collaboration with Vanderbilt University, a fine dispersion of nanometer-sized Fe_2P particles in a silica gel was prepared using sol-gel techniques. Magnetization data, displayed in Fig. 2, and ac susceptometry measurements, showed this nanocomposite was superparamagnetic, with a surprisingly high blocking temperature of 250 K. Low temperature magnetic measurements ruled out magnetic spin-glass behavior. To utilize superparamagnetic magnetic nanocomposites for high density recording media, their blocking temperature needs to be above room temperature. Consequently, work is in progress to increase the blocking temperature for this material.

Magnetic Refrigeration

R. D. Shull, R. D. McMichael, L. J. Swartzendruber, L. H. Bennett, R. Brown, A. Schindler

The U.S. Patent Office has informed us that our disclosure "Nanocomposite Material for Magnetic Refrigeration and Superparamagnetic Systems Using the Same" will be granted as a patent.

Al Schindler, formerly of NRL, NSF, and Purdue University has joined us as a guest scientist to measure the magnetic heat capacity of potential magnetic refrigerants. This data, which is mostly absent from the literature, is an important parameter needed to engineer a practical refrigerator.

Using the experience gained from our previous development of the magnetically clustered garnet, $Gd_3Ga_{5-x}Fe_xO_{12}$ (GGIG), we were successful in FY94 at preparing another magnetically clustered garnet, $Dy_3Al_{5-x}Fe_xO_{12}$ (DAIG), $0 \leq x \leq 5$. In this material the total magnetic moment of the rare earth atom was increased from 7 to $10\mu_B$ in order to increase the total magnetic entropy contained by the system. In order to maintain the garnet structure, the group IIIA element was changed to Al. Lattice parameter measurements show a continuous variation with Fe content indicating the Fe is going in substitutionally for the Al atoms. Mössbauer effect data on an x=2.5 material showed only a central doublet at room temperature, showing that the material is indeed comprised of small magnetic clusters. Magnetization measurements performed as a function of field and temperature showed that the original Dysprosium

Aluminum Garnet (DAG) changed from being paramagnetic to superparamagnetic upon the addition of the Fe. This is similar to what occurred in the earlier invented GGIG magnetic nanocomposites, and shows that the DAIG material is comprised of nanometer-sized magnetic clusters. Magnetocaloric measurements on the DAIG nanocomposites showed the enhancements expected for magnetic-cluster materials, but the magnitude of the effects were comparable to that measured earlier for $Gd_3Ga_{5-x}Fe_xO_{12}$. This lack of improvement over GGIG is probably because of the presence of an orbital contribution to the total angular momentum possessed by the Dy atom, a contribution not present for Gd. Preliminary SANS measurements on the DAIG nanocomposites show no large magnetic scattering until $x \geq 2.5$. For $x=2.5$, strong magnetic scattering, indicating correlations between magnetic spins, was observed at temperatures less than 70 K. Work is proceeding to understand the origin of the magnetic scattering, and to determine the size of the magnetic scatterers.

Our work in magnetic refrigeration materials under a CRADA with General Motors Corporation has been extended to look at a different class of magnetic transitions. While previous work has concentrated on the magnetization of superparamagnetic or superferromagnetic nanocomposites, our recent work investigates $Fe(Hf_xTa_{1-x})$ Laves phase compounds which exhibit a ferromagnetic-antiferromagnetic transition with an abrupt change in magnetization with temperature. The large value of $\partial M/\partial T$ gives a large value of $\partial S/\partial H$, albeit over a narrow temperature range.

Recent advances in permanent magnet materials have made possible devices which can use mechanical rotation to produce the large varying fields needed in magnetic refrigeration. An example is the so-called magic ring illustrated in Fig. 3. This device consists of rings with magnetization directions arranged to produce concentrated fields in their center. By using two such concentric rings and rotating them with respect to each other, the fields can either add to exhibit a large field (Fig. 3a), or subtract to show a near zero field (Fig. 3b). Recognizing the potential of such devices, a Small Business Innovation Research (SBIR) request for proposals to engineer such a system for use in room temperature magnetic refrigeration has been issued.

Magnetic Multilayer Nanocomposites
R. D. McMichael, L. H. Bennett, L. J. Swartzendruber, H. J. Brown, R.V. Drew, W. F. Egelhoff (CSTL)

Our effort in multilayer magnetic nanocomposite materials grew dramatically in FY94, with renewed emphasis on giant magnetoresistance (GMR) and magnetic imaging of multilayered materials. Our increased activity in GMR materials is largely due to formation of a close collaboration with W. F. Egelhoff Jr., who was in CSTL in FY94, but joined our group at the beginning of FY95. Our work with Bill has been in studying the details of the manufacturing process for GMR "spin-valve" materials in collaboration with ATP-supported U.S. companies such as Nonvolatile Electronics, Inc. and the National Storage Industry Consortium (HP, IBM, Kodak, Maxtor, NVE, Seagate, Read-Rite, Censtor, Quantum, and Applied Magnetics). These field-sensor materials find applications in areas as diverse as automotive cam shaft position sensing and read heads for high-density magnetic recording. Our role in the GMR "spin-valve" work has been characterization of layered structures (produced at HP and at NIST) by magnetoresistance, magnetometry, and ferromagnetic resonance (Illustrated on the cover of this Report) and in exploring the thermal stability of the films, which is a critical issue in processing the films into devices. Using ferromagnetic resonance, we found that while spin valve structures tend to fail at temperatures between 250 and 300 °C, the magnetic layers maintained their distinct character after annealing at 400 °C for 30 min, but the FeMn pinning layer showed irreversible changes after 20 min at 250 °C. (See Fig. 4)

We have continued our work on electrodeposited magnetic multilayer materials with further measurements of GMR, and a new emphasis on magnetic imaging of magnetization reversal processes using two distinct techniques. (i) The magneto-optical indicator film (MOIF) technique developed by visiting Russian scientists, Valerian Nikitenko, and his colleagues from the Institute of Solid State Physics, Chernogolovka, Russia permits the imaging of stray fields from magnetic domain walls by means of the Faraday effect induced in a magneto-optically sensitive garnet film placed on the surface of the sample in a polarizing light microscope (see Fig. 5). The MOIF technique has been important for studying the underlying magnetization reversal mechanisms responsible for differing GMR values in CoNi/Cu multilayers as a function of Cu layer thicknesses. A report of this work will appear in Applied Physics Letters. (ii) A magnetic force microscope permitting the imaging of stray fields from magnetic materials has been acquired, and is being used to study steel, magnetic multilayers, and magnetic thin films.

High-Temperature Superconductors

L. J. Swartzendruber, L. H. Bennett, H. J. Brown, R. V. Drew
M. Seyoum, University of the District of Columbia

Soon after superconductivity was discovered it was found that a superconductor cooled through its transition temperature will expel magnetic flux and attain a negative magnetization. This is called the Meissner effect. Since the discovery of high temperature superconductors a number of authors have reported on a so-called "paramagnetic Meissner effect (PME)," wherein flux is not expelled but is attracted by the superconductor. A number of theories have been proposed to explain this effect. The PME is often observed in SQUID magnetometers. We have shown how an apparent PME arises from the presence of a field gradient in the magnetometer (i.e., there is in fact no PME). We have also shown how the field gradient may be taken advantage of to determine the Meissner effect magnitude at low fields even when the demagnetizing factor is unknown (the case for most high T_C samples). The method is illustrated in Fig. 6.

We have added the capability of measuring the temperature dependence of the resistivity to our SQUID apparatus. We are attempting to explain the origin of re-entrant behavior in high temperature superconductors. Our discovery of re-entrant superconductivity in a multiphase Tl-Ca-Ba-Cu-O system, appeared in Physics. Letters A (**190**, 483 (1994)).

Measurements of magnetic properties of single crystals of $Ba_2Y_1Cu_3O_7$, before and after indentation and before and after neutron irradiation, were carried out for the Ceramics Division. Irradiation effects on Li-doped Bi tape were also studied.

Modeling of Magnetic Materials

R. D. McMichael, M. Donahue, L. H. Bennett, L. J. Swartzendruber, F. Y. Hunt*, Hai C. Tang*, M. Melamud**, and F. Z. Vajda***
*Computational and Applied Mathematics Laboratory
**Guest scientist - Nuclear Research Centre - Negev, Beer Sheva, Israel
***Guest scientist - The George Washington University

New results in micromagnetic modeling of Barkhausen signals were produced in collaboration with Fern Hunt of CAML, and published in the IEEE Transactions on Magnetics. (See Fig. 7.) Using discretized versions of the Barkhausen model of hysteresis, which describes motion and pinning of a domain wall element in an inhomogeneous material such as polycrystalline steel, we calculated analytical expressions for the distribution, $P(\tau)$, of Barkhausen jump lengths, τ. For a pinning field which obeys the statistics of a bounded random walk, the $P(\tau)$ is a sum of exponentials which is numerically close to truncated exponentials of the form $P(\tau) \approx \tau^{-\alpha}\exp(-\tau/\tau_0)$. The scaling exponent changes from $\alpha \approx 1.5$ for small jumps to $\alpha \approx 1.0$ for jumps longer than the correlation length of the pinning field. For a pinning field which is an unbounded random walk, $P(\tau) \approx \tau^{-3/2}$, showing that the scaling exponent shift and the exponential cutoff are caused by correlations in the pinning field.

Michael Donahue joined this group as an NRC postdoctoral research associate in September, 1994, and began work in micromagnetic modeling. In connection with this work he will collect and analyze magnetic force microscopy data and construct computer simulations. Materials to be examined include steels and various thin films, which will be studied in collaboration with the Barkhausen signal and magnetic storage projects (described elsewhere).

In order to increase our understanding of the relationships between microstructural properties, mechanical properties, and the magnetic Barkhausen effect, a series of "Barkhausing" seminars have been held with members of both the Magnetic Materials Group and the Materials Performance Group presenting research results and/or journal club style reports of results from the literature. The "Barkhausing" seminars have come to focus mainly on the role of dislocations in both structural performance and in domain wall pinning.

We have continued our cooperation with Ed Della Torre and his students at the George Washington University in the area of domain-wall-motion modelling in support of the ATP awardee, the National Storage Industry Consortium.

Magnetic Methods for Intelligent Processing and NDE

L. J. Swartzendruber, R. D. McMichael, D. E. Mathews, G. E. Hicho, and G. Kohn*
*Guest researcher, Nuclear Research Centre - Negev, Beer Sheva, Israel

The mechanical properties of a steel are closely related to composition and microstructure. We are attempting to exploit this relationship for on-line measurement of mechanical properties in an industrial environment. This project is being carried out in cooperation with LTV Steel Company and Weirton Steel Corporation, who are providing sheet steel samples, and with the Industrial Materials Institute in Canada, who are developing laser ultrasonics for the measurement of grain size in the same materials.

Results to date have consistently shown that when a mechanical property of the sheet steel is related to hardness, then the same mechanical property can be related to a magnetic property. Our recent efforts have concentrated on three types of steel, high-strength low-alloy (HSLA), low-carbon (LC), and ultra-low carbon (ULC), produced in the LTV and Weirton mills. Some recent results are summarized in Fig. 8. This figure plots the hardness as a function of the jump sum rate (JSR) first moment (which is derived from the material's magnetic Barkhausen signal). An excellent correlation between hardness and JSR is evident. Statistical analysis of the data in Fig. 1 gives a correlation coefficient (R value) of 0.98. Since the JSR can be readily measured to 5 μT, the slope of the line in Fig. 1 shows that hardness can be determined with a resolution of better than 1 Vickers hardness unit. This is sufficient resolution to make the technique quite valuable in an industrial environment. The American Iron and Steel Institute is considering filing a patent on the method developed for extracting the JSR first moment and relating it to hardness value.

Developments to expedite industrial application of our magnetic method of mechanical property determination are currently underway. Because the magnetic response changes with tensile stress, we are determining correction factors covering the range of stresses expected in a rolling mill. The effect of electrical and acoustic noise present in a steel mill is being tested to determine the extent of instrumentation shielding that will be needed. New probes are being developed to reduce the effect of lift off and external noise. The relationship between Barkhausen signal and mechanical properties is also being investigated from a theoretical point of view. The Data Measurement Corporation has applied for a cooperative effort with AISI and NIST to develop a commercial system for direct use on the production line in a steel mill.

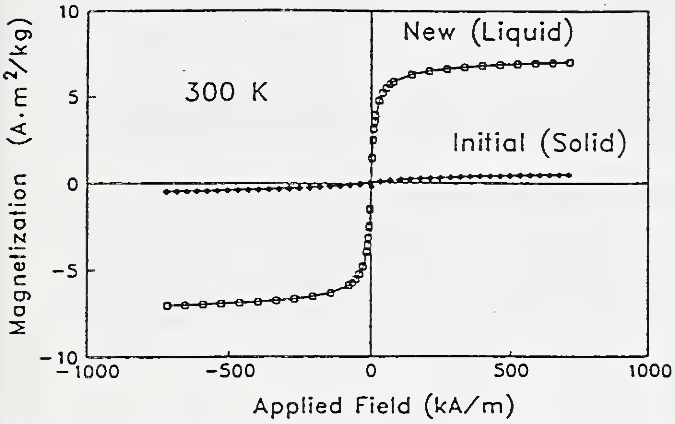


Fig. 1. Room temperature magnetization vs magnetic field for the initial γFe_2O_3/polymer nanocomposite measured at NIST (filled symbols) and a recent one (open symbols) prepared as a result of a NIST/Xerox collaboration, showing the large improvement in saturation magnetization.

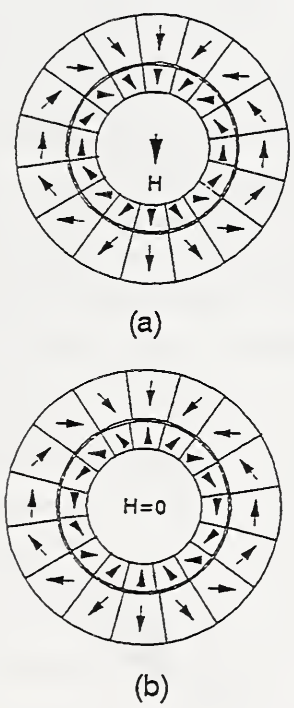


Fig. 3. "Magic ring" device for rapidly turning on and off a large field. Two concentric rings with permanent magnets set with the directions shown by the arrows can be rotated with respect to each other to produce (a) a large field or (b) a near zero field. Such a device could be useful in room temperature magnetic refrigeration.

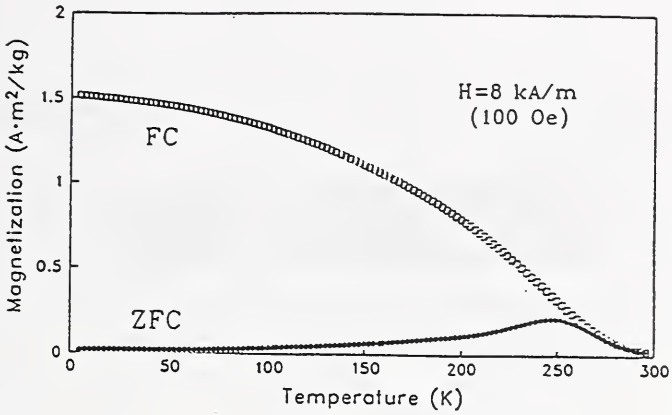


Fig. 2. Magnetization vs temperature of an Fe_2P+silica magnetic nanocomposite measured during cooling (FC, open symbols) and heating after cooling in zero applied field (ZFC, filled symbols). This thermomagnetic history is indicative of superparamagnetism. The blocking temperature is the temperature above which the curves coincide.

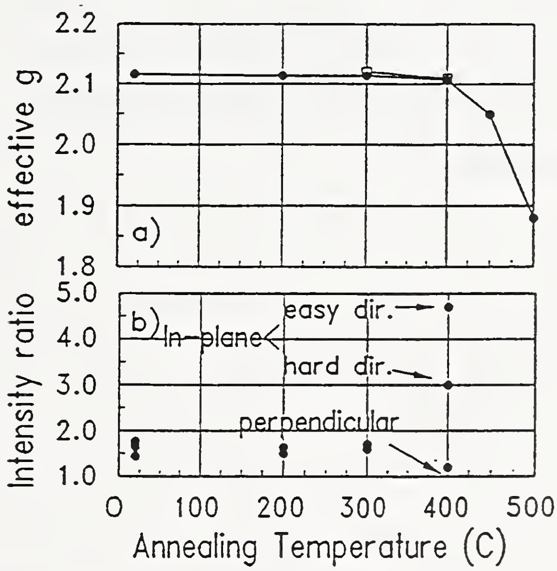


Fig. 4. a) Effective gyromagnetic ratio, g, and b) ferromagnetic resonance intensity ratio, I, for two magnetic layers in an unpinned spin valve separated by a 2.5nm Cu layer. Changes in I indicate increased film-film coupling. The sudden decrease in g indicates inhomogeneity. These results show that thermal degradation of the spin valve occurs by pinhole coupling through the Cu.

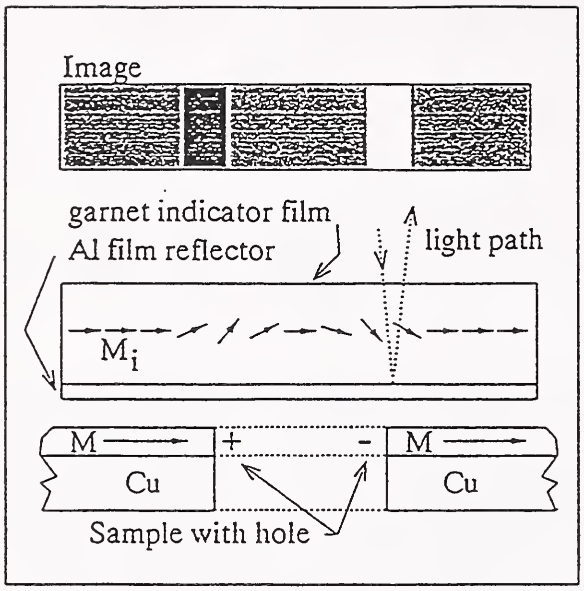


Fig. 5. Schematic illustrating the magnetooptical indicator film (MOIF) technique for investigating stray magnetic fields emanating from a magnetic material. Here the fields around a hole are represented.

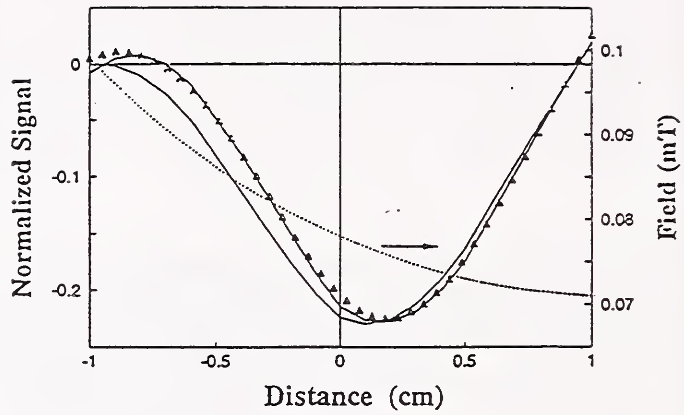


Fig.6. Data and fits obtained in a SQUID magnetometer after cooling a BYCO sample in a field of 0.1 mT from 95 K to 75 K. The triangles are the measured signal from the coil pickup system (left scale). The dotted line shows the measured field profile (right scale). The light solid line is a fit to the data assuming no Meissner fraction, and the heavy solid line is a fit to the data assuming a Meissner effect of the correct sign and of magnitude 0.08.

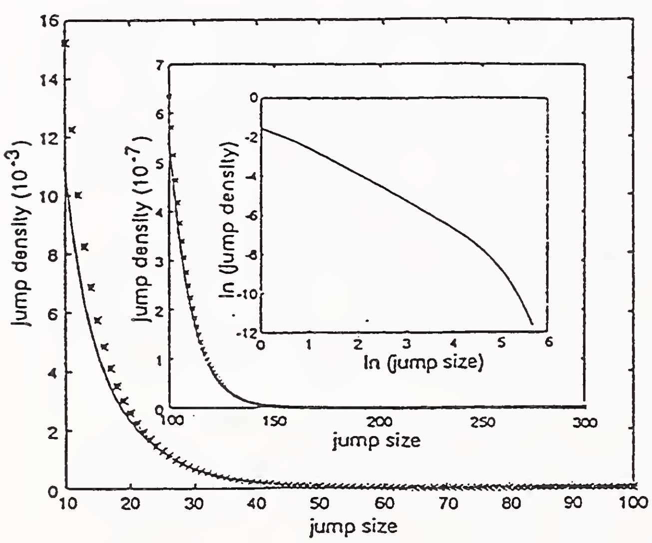


Fig. 7. Results of a calculation of a one dimensional analytical micromagnetic model of the Barkhausen effect, showing the relation between the jump density and jump size distributions. The ln-ln plot (inner inset) is over the whole range of jump size.

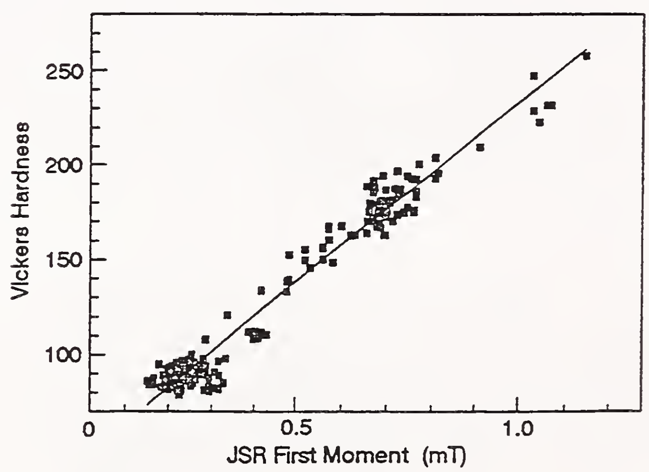


Fig. 8. Vickers hardness vs. magnetic Barkhausen JSR First Moment measured on a series of HSLA, LC, and ULC sheet steels.

MECHANICAL PROPERTIES AND PERFORMANCE

Leonard Mordfin

The Mechanical Properties and Performance group develops new and improved mechanical test methods and standards; characterizes, analyzes, and models the mechanical properties and performance of engineering materials under the kinds of environmental conditions that are experienced both in processing and in service; and relates these properties to microstructure. The Group also provides expert consultation and testing services relating to the mechanical behavior of materials and structural components, including failure analysis, for other government agencies and, under appropriate conditions, for the private sector as well.

The first part of this mission statement covers the Group's research program, which normally constitutes some 80 to 90 percent of its total activities. A principal area of emphasis in the research program is **fracture**. NIST's unique facilities for doing advanced fracture research, together with the Group's established competence and reputation in this area, continue to draw support from other agencies for new and challenging projects. A second area of research emphasis for the Group, selected because of the tremendous potential it holds for American industry, is **discontinuously reinforced metal-matrix composites** (MMC). After pursuing this topic on a shoestring for several years, it is satisfying to report that the potential benefits of the Group's efforts are finally being recognized and that significant support for a major project in collaboration with the auto industry is scheduled for FY95. The third area of research emphasis for the Group is the **mechanics of metal processing** which, this year, included projects dealing with the residual stresses in welds, on-line measurements of the mechanical properties of sheet steel, and others. A major new effort in this area is investigating the long-term strength of lead-free solder connections in copper tubing.

The second part of the Group's mission, providing expert consultative and testing services to government and industry, represents only a minor portion of the overall program, but one which is taken very seriously. The principal activity in this area, this year, was a detailed evaluation of the standard test methods used by the Department of Defense for bolts, nuts, and other fasteners. Other activities included consultation on fracture for the Transportation Department's Office of Pipeline Safety, tests of large marine hawsers for NOAA in support of a failure analysis project, development of a stress corrosion test method for miniature specimens, and preliminary arrangements for a workshop on processing and mechanics of layered nanoscale materials.

On the administrative side, some personnel actions merit mention. Dr. Leonard Mordfin, who served as the Group's leader since 1989, retired but remains on the rolls as a guest researcher. Dr. Tim Foecke, an NRC post-doctoral associate in the Materials Science & Engineering Laboratory for the past two years, joined the Group. Foecke strengthens the Group's capabilities in areas such as electron microscopy and experimental fracture physics, and is studying deformation and fracture in nanoscale materials.

FY 1994 Significant Accomplishments

- As part of the National Aging Aircraft Research Program, an extensive research project was carried out to study the manner in which cracks propagate in the presence of multiple site damage. The project involved ten tests of the largest structural aluminum panels ever tested in tension (see cover photo, ASTM Standardization News, Sept. 1994). Analyses of the results by two different procedures indicated a reasonably good capability for predicting the critical fracture stresses.

- To quantify the fracture toughness of shallow flaws in reactor vessels, tests were carried out in the 12M-lbf universal testing machine on full-thickness clad beams cut from the wall of a nuclear pressure vessel. The beam specimens, which have a cross section of 225 mm square, are loaded to failure in three-point bending over a 1120-mm span at -25 °C following fatigue precracking at room temperature. These tests are investigating the influence of metallurgical gradients and the cladding process on the fracture toughness.

- In a research project on the mechanics of nanoscale multilayered materials, a new sample configuration was perfected, which allows observation of deformation and fracture in the cross-sectional orientation. Several mechanisms were revealed which may contribute to the observed tensile characteristics of high yield strength and low fracture ductility.

- Experimental methods for evaluating residual stress states usually are limited by difficulties in determining reliable values of stress-free lattice parameters (d_0). NIST researchers have perfected a technique for determining d_0 in-situ in single phase, stressed bodies, and are now developing a method which yields the total stress tensors in both phases of a stressed, two-phase body with d_0 determined directly from only one of the two components.

- The Group has initiated two new long-range research programs in direct support of American industry. In collaboration with the U.S. Council for Automotive Research, NIST will provide car makers with working models for the consolidation of particle-reinforced aluminum alloys, and in collaboration with the Copper Development Association, NIST is establishing pressure ratings for copper tubing systems joined with lead-free solders.

Fracture Behavior of Large-Scale Thin-Sheet Structural Aluminum Alloy Panels
R. deWit, R. J. Fields, L. Mordfin, S. R. Low, III, D. E. Harne, and T. Foecke

The aging of the commercial transport fleets around the world is of constant concern because of the loss of structural integrity through fatigue cracking. In one design approach for aircraft fuselages using semi-monocoque construction, circumferential rings or frames are intended to steer dangerous longitudinal cracks--if they appear--in the less threatening circumferential direction around the fuselage. It has been hypothesized, however, that in the case of aging aircraft in which multiple site damage, such as short fatigue cracks emanating from rivet holes, is present, cracks that start running longitudinally may continue to do so because the cracked rivet holes may provide a path of lesser resistance. Our research was intended to provide some of the information needed to better understand this crack propagation process. In this work we were aided by the advice of David Broek. Also, a team from NASA Langley under leadership of James C. Newman and David Dawicki assisted with additional measurements.

We carried out a series of fracture tests on large-scale, pre-cracked, aluminum alloy panels for the Federal Aviation Agency to examine and to characterize the process by which cracks propagate and link up in this material. Ten panel specimens, each consisting of a single sheet of 2024-T3 aluminum alloy, 3988 mm high (the loading direction), 2286 mm wide, and 1.016 mm thick were fabricated with simulated through-cracks oriented horizontally at mid-height. The simulated cracks were saw cuts, ending with the sharpest jeweller's saw cuts available, having a final tip radius of 0.076 mm. Extended grips and test fixtures were specially designed to enable the panel specimens to be loaded in tension in a 1780-kN-capacity universal testing machine.

Using existing information obtained from tests with smaller specimens, we set up a test matrix that explores regions of failure that are controlled by fracture mechanics, with additional tests near the boundary between plastic collapse and fracture. In addition, a variety of multiple site damage (MSD) configurations were included to distinguish between various proposed linkage mechanisms. All tests used anti-buckling guides, except one which helped assess the effect of buckling.

During the fracture tests, each event was recorded on film, video, computer, and magnetic tape, and the NASA team occasionally also added light microscopy. Using flat sheets without stiffeners, these tests were aimed more at obtaining basic material properties than simulating fracture in an airplane fuselage. The properties sought were the basic fracture properties and linkage criteria for the MSD cracks.

We analyzed the data by two different procedures, (1) the plastic zone model based on the residual strength diagram and (2) the R-curve. The first three test specimens contained a single central crack and the collected data were used to determine the basic material properties, namely, the collapse stress and the effective fracture toughness for the residual strength diagram, and the R-curve. These results were subsequently used in the analysis of the tests with MSD cracks. There was good agreement between the measured values and the results obtained from the analysis. It was found that the critical fracture stress can be approximately predicted by using either the plastic zone criterion or the R-curve; the results were virtually the same. Refinements in the analysis are being worked out and are expected to further improve the agreement.

Short segments of the video recordings presented at scientific meetings created substantial interest and requests from universities for teaching purposes. We are collecting and annotating portions of the tests into a video show that will subsequently be available for distribution.

Full-Thickness Clad-Beam Fracture Toughness Tests
R. deWit, R. J. Fields, S. R. Low, III, and D. E. Harne

Current reactor pressure vessel (RPV) life assessments are based on data from deep-flaw fracture toughness specimens. These specimens are tested in the L-T orientation, which means that the crack-plane is perpendicular to L (L = direction principal deformation or maximum grain flow), and the expected fracture direction is T (T = direction of least deformation). They are taken from the central, homogeneous, region of the source plate which yields a toughness significantly different from the actual material toughness in an RPV. The limiting condition of the RPV is most often governed by pressurized-thermal shock (PTS) accident conditions. Reactor vessel analyses are based on the Marshall flaw distribution and Reg. Guide 1.154. The Marshall flaw distribution predicts more small than large flaws while Reg. Guide 1.154 requires that all flaws be considered as surface flaws. The shallow-surface-flaw is therefore of major importance in RPV life assessments.

Shallow-flaw specimens cut from homogeneous plate material have been shown to exhibit an effective toughness greater than that shown in deep-crack specimens. Shallow flaws in an RPV, however, are located near the plate surface where large metallurgical gradients exist. Axial flaws in an RPV are oriented in the L-S material direction (S = third orthogonal direction) rather than the L-T orientation. These metallurgical differences may have a significant impact on the resulting fracture toughness.

To quantify the fracture toughness of shallow flaws in reactor vessels, we are testing several full-thickness, clad beams under prototypic PTS conditions. The flaws in these beams are located in weld and plate material in which metallurgical conditions are prototypic of those found in RPVs. These tests will investigate the influence of metallurgical gradients and the cladding process on the fracture toughness of material with flaws prototypic of those found in an RPV. Comparison of results from these tests with those from homogeneous shallow-flaw test specimens will provide a quantitative definition of the effect of near surface conditions on fracture toughness. The effective fracture toughness from these large beams will also be compared with the toughness as estimated by current ASME Section XI rules.

This project examines the effect of crack length on the fracture toughness of full-thickness clad beams extracted from an unirradiated nuclear pressure vessel. The initial effort is directed at cracks of different depths located in a longitudinal weld. The geometry of the test artifacts corresponds to the arc-bend chord-supported test described in ASTM E 399 with certain exceptions that are not expected to invalidate the tests. The nominal dimensions of the test specimens are 225 by 225 mm in cross section with a loading span of 1,120 mm. The outer radius of curvature is 2,590 mm and the inner radius is 2,362 mm.

Fatigue precracking at room temperature and testing to failure at -25 °C are carried out in the 12 Million Pound Universal Testing Machine at NIST. The samples are not moved after fatigue precracking to avoid the possibility of warm prestressing. In order to carry out the tests to these specifications, the following test systems were designed, fabricated or set up, and tested:

1. A three-point loading jig satisfying the requirements of ASTM E 399 and having a span of 1,120 mm with a load capacity of at least 15 MN.

2. A fatigue system with a load capacity of 2.6 MN that can be removed before fracture testing without moving or otherwise disturbing the precracked test specimen.

3. A cooling system capable of uniformly cooling the test specimen to -60 °C.

4. Crack opening and load line displacement gages suitable for the full thickness beams and satisfying the requirements of ASTM E 813.

5. Two data acquisition systems to collect redundant data sets in case one system failed.

In addition, all critical measurements are made with instruments with calibrations traceable to NIST.

The specimens are instrumented with crack opening clip gages, load line displacement gages, and strain gages. A cooling system is built around each specimen. Sixteen thermocouples mounted on and in each beam are monitored every few seconds as liquid nitrogen is sprayed on the beam in the cooling chamber.

The results of testing five beams is shown in the table below:

Test No	Crack Depth (mm)	Toughness MPa$\sqrt{m}$	Date of Test
1	118	179	4/6/93
2	10.8	219	1/13/94
3	23.7	377	2/24/94
4	22.6	133	8/24/94
5	12.1	437	9/1/94

We are now preparing to test base metal properties.

Mechanical Properties of Nanoscale Multilayered Materials
T. Foecke

Work is in progress to determine the micro-/nano-mechanisms that operate during deformation and fracture of nanoscale multilayered materials. In situ transmission electron microscopy deformation studies performed on plan-view samples of Cu/Ni electrodeposited multilayers reveal several mechanisms that may contribute to the observed macroscopic tensile characteristics of high yield strength and low fracture ductility. Slip was seen to be localized immediately in front of the crack tip, with a very narrow, intense plastic zone preceding the moving crack. It was seen by energy dispersive spectroscopy analysis of the plastic zone that the deformation localized within the Cu layers, shearing them to failure, while the Ni layers remained as ligaments. After the crack front progressed several tens of micrometers, the Ni ligaments failed in a brittle fashion. Fracture was seen to be transgranular at large (> 100 μm) in-plane grain sizes, and exhibited a transition to intergranular cracking at smaller grain sizes. Interactions of crack tip emitted dislocation arrays with misfit dislocations also were observed. An experimental sample configuration to allow the observation of deformation and fracture in multilayers in the cross-sectional orientation has been perfected, and observations are in progress in this geometry.

Residual Stresses in Welds, II
G. E. Hicho

The fracture safety of welds may be compromised by the residual stress state, which is usually unknown. Researchers at the US DOT's Volpe Center in Boston identified welding residual stress as a potential fatigue risk at certain attachments in railroad tank cars. Preventing excessive distortion of the shell often requires that pad-to-shell welds be skip welds. A theoretical analysis by the Volpe Center showed that significant tensile residual stresses may occur in the shell near the ends of the skip welds. Experimental work by the Oregon Graduate Institute confirmed this general picture of the theoretical analysis and also showed that these adverse stresses are likely to be retained in service. Neither of the efforts was able to provide any information about the stress gradient through the shell thickness. These gradients are suspected to exist because of bending effects induced by the skip-type weld, which is always configured as a bead or a fillet at the outer surface, with a transition to low tension or even compression at the inner surface. Stress-gradient information can be obtained by means of nondestructive measurements, namely, x-ray diffraction for the measurement of the residual stresses present on the surface, and neutron diffraction for the measurement of both surface stresses and those that exist through the plate's thickness.

Research has been conducted on the determination of the surface residual stresses, those located at the mid-thickness, and those on the opposite surface of a plate using neutron diffraction methods. Initial neutron diffraction measurements indicate that the residual stresses at these three locations are compressive. Research was conducted on the measurement of surface residual stresses located in four welded plate samples using x-ray diffraction, in order to verify the surface measurements made by neutron diffraction. The x-ray diffraction measurements were in good agreement with the neutron values with the exception of one entire location in one specimen. This has been attributed to the fact that x-ray measurements are much more likely to pick up local distortions in the material.

Residual Stresses in Welds, I
R. J. Fields

Stimulated by three previous years of Office of Naval Research (ONR) funded research on residual stress in welds, NIST has developed a unique, world-class instrument at the NIST nuclear reactor's cold neutron research facility for measuring the complete residual stress tensor in each phase of minute, yet reproducibly positioned volumes. As part of the ONR research, the in-situ sample size has been significantly reduced. New in-situ methods for obtaining the stress-free lattice parameter have been developed here as well. The welding process, by its very nature, generates residual macrostresses. The macrostresses are partitioned on the microscale between the various metallurgical phases which are present as a result of solidification, transformation, and precipitation, as well as inclusions. This partitioning may result in undesirable high levels of residual microstresses in brittle particles that can trigger cleavage fractures even under normal service conditions. Predicting the extent of this partitioning by the theories of Eshelby[1] and Mura[2] usually involves assumptions for which the justification is unclear and which reduce confidence in the prediction. Experimental measurements are needed to investigate the partitioning. If the stress-free lattice parameters (d_0) were known, neutron or x-ray diffraction techniques could easily determine the stress in each phase. However, reliable values for d_0 are difficult to obtain.

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[1]J. D. Eshelby, "Elastic Inclusions and Inhomogeneities," in Progress in Solid Mechanics 2, eds. I. N. Sneddon and R. Hill, North Holland Publishers, Amsterdam, pp. 89-140 (1961).

[2]T. Mura, Micromechanics of Defects in Solids, Martinus Nijhoff, The Hague (1982).

Winholtz and Cohen[3] have provided a formalism by which the deviatoric stress tensor can be measured in each phase without knowing values of d_0. While the deviatoric stress is important for deformation or shear fracture, brittle fracture responds to the normal stress, and hydrogen diffusion is driven by pressure. As part of previous research on this program for ONR, we developed a method of determining d_0 in-situ in single phase, stressed bodies. We are now developing a method which yields the total stress tensors in both phases of a stressed, two-phase body with d_0 determined directly for only one of the two components. This approach is applicable to most real systems in which the major phase is well known and standard methods to obtain d_0 may be used. The method relies on a combination of diffraction measurements for at least six sample orientations (impossible with x-rays) and a resourceful application of the equations of stress equilibrium on both the macro- and microscale.

The accuracy obtainable using this method will be tested by performing experiments on a model two-phase weldment in which the d_0 values can be measured independently for each phase. We intend to investigate the possibility of determining the d_0 values in-situ by using the additional information in the Eshelby and Mura equations to supplement the measurements.

In addition to this research, we would like to understand how the various welding parameters conspire to generate specific residual stress states. Using some of the methods developed above, as well as the totally nondestructive nature of neutron residual stress measurements, we have measured the micro- and macro residual stress state in an electron beam weld possessing an easily modeled geometry. These results and all other necessary information are being examined by a modeling group. The close interaction between welder, metallurgist, and stress analyst are expected to advance our understanding of how certain stress states develop, how to model them, and how to control them.

<u>**On-line Properties Measurements of Sheet Steels**</u>

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During the production of coiled sheet steels, quality control and customer specifications require that destructive mechanical property tests be conducted on these materials. Normally, mechanical property test specimens are taken from the beginnings and ends of coils, and no test specimens are taken from inner areas because coil continuity would thereby be destroyed. Stringent quality control requirements by prospective buyers dictate that the coils be uniform in mechanical properties from end to end. To help fill this industrial need, research is currently underway on a nondestructive magnetic approach to on-line measurement of selected mechanical properties of entire coils as they are being processed. Three steels were selected for the study; a low carbon, an ultra-low carbon, and a high-strength low alloy steel.

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[3] R. A. Wineholtz and J. B. Cohen, <u>Adv. X-Ray Anal.</u> <u>32</u>, 341-353 (1989).

Mechanical property and magnetic evaluations were conducted on samples taken from the supplied steels. Approximately 23 heats of steel were used for the study. Exhaustive mechanical and magnetic test results for the three steels indicated that correlations could be improved if they were concentrated on a single chemical composition. Our initial results now verify this proposition. Tests are now being conducted on individual heats of the ultra-low carbon and high strength alloy steels to confirm our observations.

This project is supported by the American Iron and Steel Institute and the NIST Office of Intelligent Processing of Materials. Magnetic property measurements and their correlation with mechanical properties are being performed by the Magnetic Materials Group. In addition, IMI of Canada is performing ultrasonic measurements on these same steels. Their results will complement our findings.

Pressure Ratings for Lead-Free Solder Joints in Copper Tubing
R. J. Fields, G. E. Hicho, R. B. Clough, D. J. Pitchure, and D. E. Harne

The rated internal working pressures that are currently in effect for copper tube joints are based upon test data generated at this agency (then the National Bureau of Standards) more than fifty years ago. The copper industry currently believes that these rated pressures may be overly conservative for the lead-free solders that are now required for drinking water. Research was initiated here in order to provide a comprehensive and reliable database of test results that will enable ASME Committee B 16 (on Valves, Flanges, Fittings, and Gaskets) and B 31 (on Code for Pressure Piping) to establish rated internal working pressures for today's copper tube joints.

Solder joints were fabricated in accordance with ASTM methods from standard copper tubes and wrought couplings using two compositions of solder, ASTM B 32 types HB and E. For phase one of the program, it was necessary that failures be in the joints and that the observed separation strengths exhibit reasonable statistics among the samples tested. Technicians at NIST's plumbing shop prepared a series of test specimens using available material and the specified solders. Copper Development Association representatives instructed NIST personnel on the proper method currently used to solder tubing. Inconsistency in joint preparation for the specimens soldered with type E solder were observed. Statistical analyses revealed that good solder joints using type E solder have not yet been obtained and the work is continuing. Test results for joints using HB solder revealed that failure did not occur in the joints and future tests using HB solder would have to be performed above room temperature to induce failures in the joints.

Metal Matrix Composites
R. J. Fields, R. Clough, and D. Harne

The U.S. Council for Automotive Research (USCAR) has identified the development of low cost technologies for the production of particle-reinforced aluminum as an important element in future car-making activities. An extensive program was developed by the Council, one phase of which is modeling. At USCAR's request, this phase will be addressed by NIST, under a CRADA with USCAR, based on the Metallurgy Division's previous research on modeling the consolidation of Al/SiC powders into shapes such as those used in automotive engines. The Division has advanced various scientific fronts in metal powder technology and metal matrix composites over the past decade.

Modeling provides car manufacturers and their suppliers with a rapid, inexpensive (compared to traditional methods) procedure for designing dies and establishing heating and pressing schedules for powder consolidation. The proposed effort includes extensive university collaboration, development of instrumented powder consolidation systems and advanced measurements and methods. The goal is to provide industry with working models for the consolidation of particle reinforced aluminum alloys and associated validated data bases.

Review and Upgrading of Military Fastener Test Standard MIL-STD-1312
S. R. Low, III

A study was carried out for the Defense Industrial Supply Center (DISC) involving the review and comparison of most national and selected international fastener test methods published by standards organizations. The goal of this study was to make recommendations, without bias, for the replacement of all or parts of military fastener test method standard MIL-STD-1312 with existing American fastener test method standards, and to point out any deficiencies that presently exist in the military standard. This is particularly timely with the efforts now underway by DoD to replace military test standards with existing American standards published by consensus standards organizations. This effort culminated in a NIST Interagency Report titled, "Review and Upgrading of Military Fastener Test Standard MIL-STD-1312."

National Hardness Standardization Program
John H. Smith

Hardness test machines are regularly checked by using hardness calibration blocks supplied by the hardness machine manufacturers. The hardness calibration blocks are a de-facto "transfer standard". At the present time, in the United States, the hardness value assigned to the hardness calibration blocks by each manufacturer is based only on "past performance" of similar hardness calibration blocks and is not traceable to any fundamental units of measurement. As a result, there are no established "Standard Hardness Reference Scales" in the United States and the hardness calibration blocks from different manufacturers are not interchangeable.

To develop recognized National "Standard Hardness Reference Scales" in the United States, a hardness standardization facility has been constructed at NIST consisting of a precision dead-weight hardness test machine and a hardness indentor characterization machine. The precision hardness calibration machines is used (1) to maintain Standard Hardness Reference Scales that are stable over time and (2) to calibrate hardness reference test blocks to transfer the "Standard Hardness Reference Scales" to hardness machines used in testing laboratories.

The emphasis has been on developing a standard for the Rockwell hardness test because it is the most widely used indentation hardness test in the United States. Although extensive research on the metrology of hardness testing has been done on the Rockwell test, this test has proven to be the most difficult of any of the indentation hardness tests to establish "Standard Hardness References Scales" that are universally accepted.

With the special NIST hardness test machine, the indentor velocity and each part of the load-time cycle can be controlled independently, specified, and changed easily with the computer control software during the hardness test. This makes it possible to study the load-time cycle in detail by independently varying each part of the cycle to determine the effect on the final hardness value. In addition, the continuous measurement of the indentor position and the force throughout the entire test permits the exact behavior of the indentor and force to be studied during the test. It is now possible, for the first time, to completely control the load-time cycle of the hardness calibration test and to follow the displacement of the indentor during the entire hardness test. as part of the studies to evaluate the uncertainty in the Rockwell hardness test, studies have been carried out on the Rockwell 'C' scale (HRC) to determine the significance of some of the test variables that may influence the hardness values. The HRC values are significantly affected by changes in the load-time cycle, the indentor velocity, and the geometry of the indentor. The results of these tests are being used to define the uncertainty in the NIST hardness SRM.

The improved control and data acquisition system on the NIST standardizing hardness machine make it now possible to study, in detail, the test parameters that control the hardness test and that define the "Standard Hardness Reference Scales". This should make it possible to define more accurate "Standard Hardness Reference Scales" than has been possible in the past.

The present ISO, ASTM, and other National standards for hardness testing and for the calibration of hardness test blocks define the hardness tests only in terms of very broad limits on the force- time cycle and/or the indentor velocity. Studies at NIST have shown that the actual behavior of the force and indentor differs significantly from the behavior assumed in setting the present standards.

If more accurate "Standard Hardness Reference Scales" to be established, precision hardness tests must first be carried out to determine the effect of all aspects of the hardness test loading cycle on the measured hardness values. The standards for calibrating hardness tests blocks may need to be more precisely defined and narrow limits on all of the controlling test parameters may will have to be specified to obtain more accurate and uniform "Standard Hardness Reference Scales".

Standard Reference Material (SRM) hardness calibration blocks have been produced for al ranges of the Rockwell 'C' scale. These SRM's have been calibrated using the NIST precision dead-weight hardness test machine.

METALLURGICAL PROCESSING

John R. Manning

The properties of metals and alloys are affected strongly by their processing history. The emphasis in the Metallurgical Processing Group is on developing measurements, process models and understanding concerning these processing effects. The goal is to aid metals producers and manufacturers in controlling alloy properties and performance. Methods are developed to predict and control alloy compositions, distributions, and microstructures formed within a material during processing and to provide understanding of how these features influence properties. To maintain a focus on important industrial problems, the development of cooperative projects with U.S. industry is an important aspect of the work.

During 1994, the Metallurgical Processing Group has worked on four consortium-based projects with groups of industrial companies and three cooperative research and development projects (CRADA's) with individual companies. The consortia are (1) the Consortium on Casting of Aerospace Alloys with six industrial members, (2) a consortium on automated control of powder atomization with five industrial members, (3) an NCMS-led consortium on Development of Alternatives to Lead-Based Solders with nine industrial members, and (4) the NIST-based Solder Interconnect Engineering Working Group which provides broad collaborations between universities and microelectronic companies. Individual CRADA cooperative projects are formally underway on nitrogenated steels, concentration of magnetic fields for induction melting, and solder jet printing for microelectronics applications. Other mission-oriented work has included modeling of microstructure evolution and of interface stability during solidification, measurement of high temperature properties important for processing technologically important alloys, thin film studies, mechanical alloying measurements, and measurements on special materials, such as intermetallics, composites, and lead-tin solders. Projects also were pursued in cooperation with other U.S. agencies, including Advanced Research Projects (ARPA), National Aeronautics & Space Administration (NASA), Office of Naval Research (ONR), Naval Air Warfare Center, and the Smithsonian Institution.

FY94 Significant Accomplishments

- The Consortium on Casting of Aerospace Alloys was expanded by the addition of United Technologies - Pratt & Whitney as its sixth industrial member, and the Consortium published its first annual report. Consortium work has emphasized studies of processing models suitable for incorporation in industrial software.

- Crystallographic characteristics of grain defects in single crystal turbine blades were identified, in collaboration with scientists at Howmet Corporation. A model was developed to describe dendrite growth in complex containers, identifying some of the conditions leading to formation of these defects.

- A procedure and a preliminary thermodynamic data base were developed to compute the solidification path (temperature vs. fraction solid) for superalloys with nine components.

- Simulations of dendritic growth and resulting microsegregation patterns during cooling of a binary alloy were obtained using a phase-field approach.

- NIST researchers performed measurements of unsurpassed accuracy of selected thermophysical properties of Inconel 718 and Ti-6Al-4V alloys at high temperatures in both solid and liquid phases up to about 300K above their melting region.

- The US Industry/NIST consortium on in-situ particle size measurement and control during gas atomization completed a study of Inconel 625 alloy atomization using expert system control and is now focused on the transfer of expert system and control software to an industrial gas atomizer.

- A new metal flow rate sensor was developed for the Metallurgical Processing Group's supersonic inert gas metal atomizer (SiGMA). This sensor uses a thermocouple to measure the temperature of the gas and powder mixture in the process plumbing. Response time is approximately 0.25 s.

- Methods have been developed and implemented in our mechanical alloying program which broaden the processing capabilities of the technique, reducing contamination of reactive materials by oxygen and nitrogen, resulting in alloys which are far cleaner than materials produced by standard practice.

- By means of transmission electron microscopy, it was found that the Al-Cu alloy used in the crankcase of the engine of the world's first powered flight, the Wright Brothers' First Flight of December 17, 1903, was precipitation hardened, leading to revisions in the history of technology and the history of flight.

- Dynamic measurements of Pb-Sn solder meniscus shapes on metallic substrates were performed to aid in wetting balance analyses of solderability.

- NIST researchers collaborating with US industry in an NCMS-led consortium project provided measurements that helped consortium scientists select the most promising lead-free solder alloys from 65 possible candidates. Multicomponent phase diagrams and other data from NIST also are being used to identify additional candidate systems.

- In collaboration with ATP Awardee MicroFab Technologies, of Plano, Texas, and a consortium including Delco, AMP, Universal Instruments, Texas Instruments, and Motorola, means have been identified to overcome technical barriers to good mechanical and electrical contacts in solder joints fabricated by solder jet technology.

Modeling of Casting and Solidification

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Solidification research covers a wide spectrum of modeling activities that focus on microscale phenomena such as interface motion and dendritic growth. In several areas, these activities bridge between the microscale and the macroscale through involvement with industrial projects on the modeling of casting.

Casting of Aerospace Alloys - Modeling of casting on both macroscopic and microscopic scales is being advanced through the work of a "Consortium on Casting of Aerospace Alloys" which links NIST to approximately 20 other consortium members, including industrial companies, universities, and government agencies. The consortium's work emphasizes aircraft engine components made from nickel-based superalloys or titanium, which are the primary concern of the consortium's industrial members. The consortium functions as a distributed research effort in that actual casting experiments are carried out in the facilities of the industrial members but much of the analysis and modeling is carried out at NIST or by university members. The majority of the NIST effort is carried out by members of the Metallurgical Processing Group of the Metallurgy Division.

The goals of modeling this type of casting include prediction of the microstructure and defects generated by the casting process. Such predictions can greatly shorten the time required to develop an acceptable casting design, and can reduce the number of costly prototype test castings. However, the modeling of aerospace castings is more difficult than traditional laboratory studies of alloy solidification because it must deal with multicomponent alloys, reactions between the metal and the mold, and complex casting geometries. Listed below are individual projects which attack some of these problems. In each project, the aim is to obtain sufficient understanding so that models suitable for incorporation in commercial software can be produced for use by industrial designers. For example, such applications are being investigated by industrial consortium members in connection with ProCAST software.

1. Prediction of Solidification Path for Multicomponent Alloys - One of the basic requirements for heat flow modeling of castings is a knowledge of the fraction solid versus temperature relation during dendritic solidification in the mushy zone. This relation describes how the latent heat is evolved over the freezing range of the alloy. Results for an eight component alloy (Inconel 718) have been obtained by use of a Scheil analysis, which assumes that the liquid composition is uniform at each temperature and that diffusion in the solid is absent. A preliminary thermodynamic model for the liquid-solid equilibrium concentrations at each temperature in the freezing range was utilized as a subroutine for this analysis. The solidification of the fcc Ni solid solution (gamma) is predicted to begin at 1336°C followed by a gamma+Laves eutectic reaction that begins at 1160°C, in close agreement with DTA measurements and metallographic examination. Predictions also are made for how the individual elemental concentrations change in the mushy zone; these will be used in the future to predict the occurrence of freckle defects. Use of the thermodynamic model is not limited to Inconel 718 and can be employed for other superalloy compositions. Refinement of the database for the thermodynamic model is being conducted in a new activity through an in-depth examination of the Ni-Cr-Fe-Nb quaternary system. The thermodynamic model has also been incorporated into a subroutine of code that is available for a variety of more complex models of the solidification path. Current work involves a multicomponent solid diffusion model that removes the restrictive assumption of no solid diffusion of the Scheil approach.

2. Modeling of Alpha-case Thickness in Ti Castings - During investment casting of Ti alloys, reaction with the shell mold causes the surface of castings to be contaminated with oxygen to depths ranging from 50 to 2000µm. The high oxygen content causes the formation of a brittle surface layer, referred to as alpha-case, that must be removed by chemical milling. Incorporation of a model for alpha case thickness prediction into commercial solidification software is desired by the investment casting industry.

The oxygen penetration is controlled by the oxygen content at the surface of the alloy and the rate of diffusion into the metal. The oxygen concentration in the metal at the surface is determined by the decomposition of ZrO_2 (the major constituent of the shell mold near the metal surface). Thermodynamic calculations have been used to obtain this value as a function of temperature for Ti liquid, beta, or alpha. Various diffusion based models have been prepared in the previous year and are now subject to experimental verification. Verification of the model will consist of obtaining experimental temperature-time data from the surface of a casting and using these data to compute the oxygen penetration distance for comparison to measured penetration. In collaboration with Howmet Corporation, Whitehall, MI, two instrumented Ti-6wt%Al-4wt%V castings have be poured. In the first attempt, thermocouple data were unreliable. In a second casting, completed in November 1994, reliable data from the casting were obtained that should permit assessment of the model accuracy.

3. Generation of Grain Defects Near Mold Corners and Edges - Many superalloy turbine blades are produced as single crystals by a directional solidification process. In such blades the constituents which are normally used to prevent high temperature grain boundary sliding can be omitted from the alloy, thus raising the temperature of incipient melting. This leads to increased operating temperatures and engine efficiencies, but it also means that any blades containing even small regions of misoriented crystal must be rejected. Production experience has shown that these misoriented regions can be classified into several specific types of grain defects, some of which are associated with the problems of propagating the dendritic single crystal into a mold of complex shape. The goal of this project is to identify the conditions which lead to the formation of these defects and, thereby, to identify ways to minimize defect formation.

Crystallographic analysis of one type of defect, known as a "zebra grain," had indicated that it was probably the result of fragmentation of a dendrite which grew into a region of undercooled liquid. Depending on the shape of the isotherms, such regions can easily develop in the vicinity of the platform of a single crystal turbine blade, and this is where the zebra grains occur. Analysis of the crystallography of zebra grains, carried out in collaboration with researchers at Howmet Corporation, revealed that the orientation of the dendrite's crystallographic axes with respect to the platform edges had a strong effect on the tendency to form zebra defects. To provide a better understanding of these effects, an analytical model is being developed describing the spreading of a dendritic growth front across a platform in a moving temperature gradient. Figure 1 shows the development of the shape of the dendrite growth front spreading from a single dendrite at the origin. These calculations are being used to understand the probable direction of growth and the rate of growth, and thus the tendency for defect formation, in different regions of a dendritic single crystal casting.

The growth front calculations indicate that even a small slope of the isotherms has a large effect on the rate at which the dendrites spread across the platform. Modeling of the thermal field during directional solidification in containers with large changes in cross section (similar to the platform of a turbine blade) is being used to evaluate the sensitivity of the isotherm shape in this region to parameters such as the thermophysical properties of the mold material.

Modeling of Solidification Microstructure Using the Phase Field Method - Compared to sharp interface approaches to modeling the microstructural aspects of solidification, the phase field method employs an extra variable to specify whether a particular location is liquid or solid. The burden of this additional variable and its associated governing equation is offset by the avoidance of the mathematically difficult free boundary problem. Simple finite difference calculations can then provide realistic simulations of two dimensional dendritic growth and Ostwald ripening.

For binary alloys, the method has been used in work supported by ARPA to simulate dendritic growth, with the objective of characterizing the solute patterns that remain in the solid after solidification. Two cases have been studied and compared: growth at a fixed temperature (solution growth) and growth subject to recalescence due to latent heat release. The latter results can be compared to approximate models of dendritic growth in equiaxed regions of alloy castings. During recalescence the concentration at the dendrite tip decreases and the formation of secondary arms is suppressed.

Ostwald ripening simulations also have been done, in an effort to determine the consequences of volume fraction variations upon the dynamics of the system. The phase-field method allows coalescence of drops, a phenomenon often unaccounted for in other theoretical treatments. Comparisons can be made between the classical (LSW) theory of Ostwald ripening and this more complete description.

Solidification Interface Stability - The directional solidification of a binary alloy during the initial transient period, in which the interface velocity, concentration, and temperature gradients are changing with time, has been modeled numerically. If a directional solidification experiment is carried out under conditions for which the steady-state base state is unstable, then morphological instability will occur during this transient period. The time evolution of sinusoidal perturbations of the planar crystal-melt interface is calculated by solving a large set of ordinary differential equations. The results for morphological instability are in good agreement with the Mullins and Sekerka analysis of the time-independent base state if the instantaneous values of the temperature gradient and solidification velocity are used in the analysis; the agreement increases with decreasing degree of instability. The results are being compared with experiments by J. J. Favier and colleagues on the directional solidification of tin-bismuth alloys. This effort is supported by NASA as part of their investigations of materials processing in microgravity environments.

Subsecond Thermophysics

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Thermophysical Properties Data for Casting of Alloys - Development of successful casting processing models for alloys depends on, among other factors, the use of reliable thermophysical and related properties data for the specific materials involved in the process. At present, such data for most of the required properties are not available. The goal of this project is to obtain accurate thermophysical and related properties data on selected aerospace materials in both solid and liquid phases utilizing millisecond- and microsecond- resolution pulse heating techniques. This activity is an integral part of the Consortium on Casting of Aerospace Alloys. The materials of interest are selected nickel alloys (such as Inconel 718), titanium alloys (such as Ti-6Al-4V), and their key constituent elements. The properties of interest are enthalphy, specific heat, heat of fusion, electrical resistivity, and normal spectral emissivity. The experiments on specific aerospace alloys will be supplemented by measurements on well-characterized binary and ternary alloys with the objective of developing methods to predict thermophysical properties of alloys from the knowledge of the properties of the constituent elements.

During 1994, measurements on Inconel 718 were completed that yielded properties data up to 1900 K (about 300 K above the liquidus temperature). Measurements also were performed on Ti-6Al-4V alloy up to 2400 K (about 400K above its liquidus temperature). The results (shown in Figure 2) indicate that above the melting region enthalpy increases linearly with temperature. The linearity suggests a constant specific heat capacity for the alloy at least up to 2400 K. The results for the electrical resistivity above the liquidus temperature show a decrease with increasing temperature in contrast to the trend at temperatures below the liquidus. Similar measurements of a preliminary nature were made on the binary alloy 53 Nb-47 Ti (in mass percent) up to 2500 K (about 300 K above the melting region).

Optical Properties for High Temperature Materials Research - The objective of this project is to obtain definitive values for the normal spectral emissivity of selected high-melting-point metals by two independent techniques in order to provide a foundation for reliable radiometric temperature measurements in materials research at high temperatures. The research involves accurate measurements of the normal spectral emissivity of selected metals near and at melting points in a series of subsecond duration pulse-heating experiments in which the emissivity is determined at two laser wavelengths in the range of 0.5 and 0.9 μm by two techniques involving high-speed pyrometry and laser polarimetry. The results of this research will enable the reliable measurement of the true temperature of a material at high temperatures without the requirement of having a blackbody configuration or a prior knowledge of its emissivity. During 1994 construction of the optical and electronic components was completed and the laser polarimeter was integrated into the millisecond-resolution pulse heating system. Operation of the entire system was tested by performing preliminary experiments on molybdenum. This research is being undertaken in cooperation with scientists at Containerless Research Inc. and is sponsored by NASA.

Thermal Diffusivity of Multilayered Thin Films - A new project was initiated during the second half of 1994 to develop a technique for the measurement of thermal diffusivity of multilayered thin films at high temperatures (above about 1000 °C). The technique utilizes a modified version of the laser-pulse method. An apparatus based on this method is available in our laboratory for measurements on thick (1-3 mm) specimens. The required modifications include Q-switching the laser to enable generation of very short (<50 ns) pulses, design and construction of the relevant fast electronic components, and design and construction of a new specimen holder assembly. During 1994, significant progress has been made in all the above modifications.

Advanced Metals Processing Methods

S. D. Ridder, F. S. Biancaniello, F. W. Gayle, R. D. Jiggetts, R. J. Schaefer

Processing activities have continued to focus on the application of intelligent processing techniques using real-time measurements to control production and consolidation of metal powders. The Metallurgical Processing Group's gas atomization program completed a three year consortium managed effort to apply intelligent processing to particle size control. This second phase activity was a cooperative effort with three other NIST divisions and several US companies. Studies of melt-spun materials have continued, and mechanical alloying studies have been expanded.

Atomization - The NIST/Industrial consortium on powder processing concluded a three year multi-disciplinary study on automation utilizing the SiGMA system. NIST research groups include the Machine Intelligence Group of the Factory Automation Systems Division (824.04), the Surface and Particle Metrology Group of the Precision Engineering Division (821.06), the Fluid Flow Group of the Process Measurements Division (836.01), and the Metallurgical Processing Group of the Metallurgy Division. The NIST scientists collaborated in this work with representatives from Ampal/Metallurg, Crucible Materials Corp., General Electric Co., Martin Marietta Energy Systems, Inc., Office of Industrial Processes of DoE, and Pratt & Whitney Aircraft.

A metal flow rate sensor has been developed for the atomizer that uses a thermocouple to measure the temperature of the gas and powder mixture in the atomizer's exhaust plumbing. This technique has several advantages over the previously developed method that employed a bubbler tube to monitor the static head of metal in the crucible. The thermocouple in the exhaust plumbing is far more reliable than the ceramic tube used for the bubbler, the temperature data from this thermocouple is less noisy than the bubbler tube pressure data, and the calculation of the ratio of gas mass flow ($\dot{m}_g$) to metal mass flow ($\dot{m}_m$) is less complicated than with the bubbler tube. This "Gas to Metal Ratio" (GMR) is an important quantity for controlling particle size and evaluating the efficiency of gas atomizers. This new technique is based on the following assumptions: 1) there is no net accumulation of gas in the atomizing chamber ($\dot{m}_g|_{in} = \dot{m}_g|_{out}$), 2) negligible heat is transferred to the chamber walls, etc., 3) the powder and gas temperatures have equilibrated as they exit the atomizing chamber, and 4) the difference in the constant pressure specific heat (C_{pm}) for the liquid and solid is insignificant. A simple energy balance results in the following expression:

$$\dot{m}_m[H_{fm}+C_{pm}T_{DT}+(v_{DT}^2/2)] + \dot{m}_g\,[C_{pg}T_e+(v_e^2/2)] = \dot{m}_m\,[C_{pm}T_{exh}+(v_{exh}^2/2)] + \dot{m}_g\,[C_{pg}T_{exh}+(v_{exh}^2/2)]$$

where v_{DT} = metal velocity as it leaves the delivery tube (m/s)
v_e = gas velocity as it leaves the die (m/s)
T_{DT} = the temperature of the metal as it leaves the delivery tube (K)
T_e = temperature of the gas as it exits the die (K)
T_{exh} = temperature of the gas as it exits the chamber (K)
v_{exh} = gas velocity as it exits the chamber (m/s)
C_{pg} = the constant pressure specific heat of the gas
H_{fm} = the metal latent heat of fusion

Solving for the GMR ($= \dot{m}_g/\dot{m}_m$) results in the following expression:

$$GMR = [H_{fm} + C_{pm}(T_{DT} - T_{exh}) + ((v_{DT}^2 - v_{exh}^2)/2)] \,/\, [C_{pg}(T_{exh} - T_e)+((v_{exh}^2 - v_e^2)/2)]$$

For the delivery tubes and flow rates used in atomizers $(v_{DT}^2-v_{exh}^2)/2$ is insignificant and the "v_{exh}^2" term is insignificant compared to the "v_e^2" term. It is also convenient to group the terms that are associated with the alloy and the gas separately:

$$GMR \approx (H_m^* - C_{pm}T_{exh}) \,/\, (C_{pg}T_{exh} - H_g^*)$$

where H_m^* and H_g^* are defined as follows:

$$H_m^* \approx H_{fm} + C_{pm}T_{DT}$$

$$H_g^* \approx C_{pg}T_e + v_e^2/2$$

Substituting known values or estimated values of "unknown" thermodynamic data leads to the following relationships for some of the common atomization setups:

When using Ar gas to atomize Ni-Cr alloys:GMR $\approx (2000-T_{exh})/(T_{exh}-280)$
When using N_2 gas to atomize Fe-Cr alloys:GMR $\approx (2000-T_{exh})/2(T_{exh}-290)$
When using air to atomize Al alloys:GMR $\approx 7(1340-T_{exh})/8(T_{exh}-280)$

Recent experiments where bubbler tube and exhaust gas temperature data were both available have shown excellent correlation with significant improvement in the reduction of noise for the exhaust gas temperature data compared to the bubbler tube. The use of this new GMR data has provided a better correlation of "steady state" GMR to the average particle size calculated from powder sampled during the "steady state" period than was possible using an overall average of the GMR and powder size calculated from the entire batch.

Current atomization process control activities are focused on the transfer of the Expert System Control Shell (ECSS) technology to a commercial atomizer at Crucible Research near Pittsburgh. This work will involve software and hardware conversions to move the control system from its current Macintosh environment to a PC computer running Labview for Windows under DOS. This change of software and operating platforms is being done in an effort to simplify the hardware requirements and relinquish software maintenance to a third party vendor. The current system uses three computers: the data acquisition DOS PC, the DOS PC for the particle sizer, and the Macintosh with the ECSS communicating with the other two via RS-232. This setup was required when the project started because Macintosh was the only graphical platform capable of running a sophisticated controller and the DOS PC was required for the particle sizer. Now that Windows and Labview have evolved into a sufficiently mature and user friendly status, a single DOS PC can be configured with the data acquisition, the particle sizer, the process controller, and the user interface. The resulting Labview control system will be easily portable to other computer systems (Labview is cross-platform compatible with UNIX, Macs, Windows/DOS, and Windows NT.), other atomizers, and other industrial processes.

Mechanical Alloying: Mechanical alloying, or ball milling, is a means to achieve nanoscale structures in a wide variety of materials. Such nanocrystalline structures can be single or multi-phase and often exhibit unusual properties due to the high density of grain boundaries and other defects. This year a number of systems have been investigated at NIST by mechanical alloying. Our work on Cu-Co and Cu-Fe alloys has pointed out how planar faults in mechanically alloyed materials led to erroneously small calculated grain sizes when standard methods of x-ray characterization are used. (An accurate assessment of grain size is needed in nano- materials since various properties are correlated with grain size). A full characterization of stacking fault density and grain size (with accounting for stacking fault effects) can be carried out through analysis of hkl-dependent peak broadening and peak shifts using the theory of Warren and Wagner. See Figure 3.

Another finding is that phase transformations into metastable structures can be effected purely by energy stored during deformation, rather than being due to chemical disorder or grain refinement. In this work, pure cobalt powder was ball milled resulting in transformation from the stable hcp structure to a metastable fcc structure. These systems are also being characterized for magnetic properties, including apparent superparamagnetic behavior, in cooperation with the Magnetic Materials Group. Other systems currently under investigation by ball milling include AlFeNiGd metallic glasses, Ti-Al-Nb alloys, and nitrogenated stainless steels.

As a part of this program, we have developed techniques which broaden processing capabilities. Modifications of standard equipment and procedures have allowed us to maintain specimen containers close to room temperature and reduce contamination of reactive materials by oxygen and nitrogen to levels far below reported values. A collaborative study with the University of Idaho has shown that our methods allow production of Ti-Al-Nb structures which are far cleaner than materials produced by standard practice.

Melt-Spinning to Produce Superior Magnetic Materials - Magnetic flux concentrators are used in the induction heating industry to increase heating rates, sharpen temperature gradients, and/or reduce power consumption in the thermal processing of materials. In the induction melting industry, this technology is used to reduce melting times and/or reduce the power requirements needed to melt a variety of metal alloys. In collaboration with L. Swartzendruber of the Magnetic Materials Group, melt-spinning was used to produce two new alloys with superior soft magnetic properties compared to currently available commercial alloys. These properties include high permeability, low coercivity and high resistivity. This material can not be produced by the conventional ingot metallurgy route. This work is in support of a CRADA between NIST and Fluxtrol Manufacturing Co. Inc. The goal was to design a new composite material for flux concentrators having both superior magnetic properties and a higher temperature (>500 °C) binder system.

Special Materials

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Nitrogenated Stainless Steel - NIST researchers are collaborating with ARPA and Sandia National Laboratories to develop alloys that could be used in the design of armor materials. Studies are concentrating on thermodynamics, kinetics, microstrutures, and processing of gas atomized and hot isostatic pressing (HIP) consolidated nitrogenated stainless steel powders. Nitrogenated stainless steels were selected because they can simultaneously have very high strength (1030 MPa UTS, 670 MPa YS) and elongation (50%) and up to 0.7 wt% N_2. Work is in progress to produce thin plates, 1.5 to 2.5 mm thick by hot rolling. Additional work is underway under a CRADA agreement with Crucible Materials Corporation to investigate highly corrosion resistant nitrogenated stainless steels and to determine the effect on these properties of the rapid solidification that occurs during powder atomization.

Electrodeposition of Intermetallics - The excellent high temperature properties, low density, and corrosion resistance of aluminum-titanium intermetallic alloys have led to consideration of these alloys for structural applications, both monolithic and for reinforced composites. Electrodeposition is an attractive method for fabrication of such alloys since undesirable compositional inhomogeneities are very limited in scale, grain sizes are typically very small, and a variety of shapes is readily formed. Fundamental aspects of the theory of electrodeposition of alloys are being investigated in this joint project with the NIST Metallurgy Division's Electrodeposition Group. As a general approach the relationships between non-equilibrium phenomena of rapid solidification processing and electrodeposition are under study. In addition, the role of the electroactive complex ions and their contribution to the composition and crystallographic structure of the electrodeposited alloy are being considered. Understanding of microstructural development of the metastable deposits at high temperature has been greatly enhanced by high resolution transmission electron microscopy augmented by image manipulation techniques, which have been used to show that the electrodeposited Al_3Ti contains a high anti-phase boundary density, with $L1_2$ domains on the order of 5-10 nm in size.

The Mechanical Properties and Microstructure of O+B8$_2$ Titanium Aluminides - In collaboration with the Naval Air Warfare Center and R. G. Rowe of General Electric Company, ordered orthorhombic "O" phase-based alloys have been modified by the precipitation of a $B8_2$ phase to determine effects on room and high temperature mechanical properties in an attempt to develop alloys for high temperature applications. Attractive mechanical properties (>2000 MPa room temperature strength coupled with non-zero bending ductility and extremely low creep at 650 °C) were achieved. The creep resistance of these alloys is significantly greater than most creep resistant Ti_3Al-based alloys.

Study of Microstructural Evolution in Ni$_3$A1-Ni$_3$V Alloys Involving Ordering and Phase Separation - Transmission electron microscopy and powder x-ray diffraction methods have been used to investigate the evolution of two-phase ($L1_2$ + $D0_{22}$) microstructures from a quenched fcc phase of $Ni_3\ A1_xV_{(1-x)}$ alloys (x=0.1, 0.2, 0.3, 0.4, 0.5, and 0.6). The most rapid quenching was obtained with melt-spun specimens. This work is part of a general study of ordering processes and microstructural evolution supported by ARPA. Development of the microstructure in the temperature range between 650 to 900 °C has been found to be controlled by the fast kinetics of ordering in the fcc $\rightarrow L1_2$ and fcc $\rightarrow D0_{22}$ phase transitions. The morphology of the two-phase coherent structure depends on the volume fraction of phases and is controlled by a balance of interfacial and elastic energy. Different stages in the microstructural evolution were studied for coherent states. In addition, a final stage of discontinuous coarsening characterized by the growth of lamellar grains assisted by primary grain boundary migration was investigated. This last process is accompanied by formation of fcc-type twins of the two-phase structure.

Coarsening Behavior of Lamellar Structure in Ti-(40-47)Al (at %) Alloy - The continuous and discontinuous coarsening of α_2-Ti_3Al/γ-TiAl lamellae is under investigation for Ti-Al alloys containing 40, 44 and 47 at% Al, at temperatures ranging from 900 to 1050 °C.

Discontinuous coarsening is a critical mechanism that controls the stability of lamellar microstructures in these alloys. Understanding the mechanism can contribute significantly to the design of γ-TiAl alloys for higher temperature performance. Based on the present experimental results, the mechanism of initiation of discontinuously coarsened grains was identified. The kinetics of coarsening were analyzed using thermodynamic consideration of the chemical and interface driving forces. Special attention was paid to the effects of volume fraction of each phase on the growth mechanism of discontinuous as well as continuous coarsening and to the interaction between the two types of coarsening.

Aluminum-Lithium Alloys for Space Shuttle. - NASA and Martin Marietta Corporation are presently developing the Super-Lightweight External Tank which uses new design and new ultra-high strength aluminum alloys to reduce vehicle weight, thereby increasing payload capacity by approximately 3600 kg. In collaboration with Martin Marietta Laboratories, the most promising of the candidate alloys have been examined by transmission electron microscopy and assistance was provided in the evaluation of these alloys for critical properties.

Microstructural Study of the Wright Flyer Crankcase - In collaboration with the Smithsonian Institution (Martha Goodway), we have found that the Al-Cu alloy used in the crankcase of the engine of the world's first powered flight, the Wright Brothers' First Flight of December 17, 1903, was precipitation hardened. Using transmission electron microscopy, we identified a duplex distribution of Guinier-Preston (GP) zones in the alloy, larger zones (10-22 nanometers) which originated in the casting practice, and finer zones (3 nanometers) resulting from ambient aging over the last 90 years. See Figure 4. Castings were re-created in our labotatory which suggest that the original crankcase was cast into a preheated mold that allowed precipitation to occur during the extended cooling of the casting. This application of a precipitation hardened alloy occurred six years before Alfred Wilm first developed a precipitation-hardened alloy ("duralumin"), and predates the accepted first aerospace application of precipitation-hardened aluminum in 1910.

Solder Measurements and Interface Reactions

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Wetting Balance Studies - The wetting balance is widely used to assess the solderability of electronic components. The instrument records the force on a sample during immersion into a solder bath. The force-time data is related to the rate at which the solder meniscus rises along the surface of the component. Although the test is required to meet specific federal standards, its relationship to solderability in the manufacturing environment is questioned by industry. In order to gain insight into the test and to provide a vehicle to test theoretical models for reactive wetting that are under development, detailed studies of the wetting balance are being performed. Video images of the rising meniscus against a metal plate have been obtained. Meniscus shapes have been digitized and compared to calculated shapes obtained using the principle of minimum surface energy. When combined with the measured force data, the obtained values of solder surface energy, meniscus rise, and contact angle are inconsistent. Similar experiments performed with the wetting of silicone oil on a glass surface at room temperature produce consistent values. The reasons for the discrepancy for solder are being explored in relationship to the validity of the wetting balance test.

Solderability Aging Tests - In collaboration with statisticians in the NIST Computing and Applied Mathematics Laboratory, scientists from the Metallurgy Division are examining the robustness of an accelerated aging test designed at NIST for components and printed wiring boards. The new aging test allows for the independent control of temperature and humidity, thereby creating a reproducibility in surface reactions not possible with the current aging test. The aging test is designed to amplify minor defects in the surfaces which lead to solderability defects at the parts-per-million level and to simulate component solderability after storage in air. The effects of changes in the aging test conditions on solderability as measured by the wetting balance were determined using statistical analyses and design-of-experiments techniques for both surfaces with Pb-Sn surface finishes on copper and with bare copper. The results of this study are being used as a basis for comparisons between current test practices and the new aging test conditions.

Alternatives to Lead-based Solders - In response to possible legislation requiring the removal of Pb from solder alloys or the imposition of a use tax on Pb, a national consortium has been organized through the auspices of the National Center for Manufacturing Sciences (NCMS) to develop new Pb-free solder alloy systems that meet a wide range of manufacturing, performance, and environmental standards. This consortium was formed with representatives from industry, university, and government laboratories. NIST and NCMS have a multi-year CRADA describing NIST participation in this $8M 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, Rockwell International, Texas Instruments, Ford, GM-Hughes, GM-Delco, Motorola, MicroFab Technologies, United Technologies-Hamilton Standard, Rensselaer Polytechnic Institute, and Sandia National Laboratories.

As part of this program, extensive analyses of the compositions of Sn-based multicomponent phase diagrams have been performed to determine Pb-free alloys that have melting ranges required for commercial manufacturing. These analyses, requiring thermodynamic calculations, differential thermal analysis, and solidification experiments, predict the equilibrium and non-equilibrium phases which will occur for any temperature proposed for soldering. These NIST calculations and measurements were used by consortium members to select the most promising lead-free solders from 65 suggested alloys and are being used to identify additional candidate systems.

This program for developing alternatives to Pb-based solders may have a profound impact on the whole electronics industry, as well as on other manufacturers of equipment or products that use soldered assemblies. The development of reliable alternatives through this program would allow industry to manufacture solder interconnections in a more environmentally conscious manner, consistent with government restrictions. At the same time, these solders must also meet or exceed the performance and reliability currently realized with Pb-based solders in order to maintain U.S. competitiveness.

Physical Metallurgy of Sn-Pb and Pb-free solders - The ultimate physical properties of solder joints will be strongly affected by the phases formed during solidification and cooling to room temperature. These phases include both the intermetallic phases that form at the solder/substrate interface and the small metal and intermetallic particles that precipitate in the solder. The precipitation hardening and microstructure of various proposed Pb-free solders are under examination using optical microscopy, SEM, and TEM. Our initial focus is on binary and ternary solders of the Sn-Ag-Bi system. TEM cross section studies of conventional Sn-Pb solder joints also are being used to determine the role of intermetallic phase formation in solder joint development. We have found that at an early stage of joint development non-equilibrium structures may exist. In particular, in Cu joints made with Sn-Pb eutectic solder, the equilibrium ϵ-Cu_3Sn intermetallic phase does not appear and a metastable equilibrium between η-Cu_6Sn_5 and Cu is established.

Solder Interconnect Engineering - During the last year, materials scientists from the NIST Metallurgy Division have begun working with scientists and engineers from industry and academia to develop an integrated design system for solder interconnects. Collaborating with NIST are: Digital Equipment Corporation, Marquette University, University of Colorado - Boulder, State University of New York - Binghamton, Massachusetts Institute of Technology, University of Technology - Loughborough, and Sandia National Laboratories. The goal of this Solder Interconnect Engineering Working Group is to provide modeling tools to component and printed wiring board designers that will allow them to design solder interconnect geometries with high manufacturing yields and good reliability without the need for extensive manufacturing trials. The decreasing size scale of electronic components places increasing demands on the soldering process itself and on the mechanical strength of resulting solder joints. The small size and the geometry of surface mount components limit visual inspection of the solder joint and make rework of improperly soldered connections virtually impossible. Good first-pass solderability is, therefore, an important industrial goal. The design system must be able to evaluate an interconnect design for its susceptibility to defect formation during soldering and for its reliability under conditions of thermo-mechanical fatigue.

Representatives from these organizations established the collaborative program at a workshop held in May sponsored by the NIST Center for Theoretical and Computational Materials Science (CTCMS) and the National Science Foundation's Geometry Center in Minneapolis MN. The CTCMS program is examining how a general purpose computer program called "Surface Evolver" can be used to determine interface shapes for complex solder joint geometries and how the resulting shapes can be incorporated into finite element analyses for joint strength and into heat flow programs for assessment of thermal management.

Solder Jet Printing for Microelectronics Applications - 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 ($< 100\ \mu m$). These capabilities are needed for the next generation of microelectronic packaging.

The NIST Metallurgy Division is working with ATP Awardee MicroFab Technologies Inc., of Plano, Texas, and a consortium including Delco, AMP, Universal Instruments, Texas Instruments, and Motorola, to bring ink jet technology closer to commercial reality. NIST scientists are focusing on (1) materials compatibility issues involving the liquid solder and the jetting apparatus and (2) reactions between the jetted solder and the various substrate materials used in microelectronic interconnects. Working closely with MicroFab and the consortium members, we have identified means to overcome technical barriers to good mechanical and electrical contacts in these solder joints.

Formation of In-Situ Composite Materials - The formation of composites by in-situ techniques provides a major advantage over conventionally fabricated composites: all of the initial processing, including powder processing and production of the unsintered shape, is greatly simplified by having a material with uniform characteristics. The reinforcing phase is then formed by phase transformation or grain growth during fabrication, with the resulting microstructure depending on the system and on processing parameters.

Research was conducted on in-situ formation techniques for producing alumina-chromia-chromium composites by the partial reduction of mixed alumina-chromia oxides. In this work, funded by ONR, oxide solid solution powders are sintered to high density as oxides. The dense compacts are then heated in a reducing atmosphere to precipitate chromium metal particles in the grains adjacent to the surface, and a precipitation front moves into the material by a combination of oxygen grain boundary and lattice diffusion. The final composite microstructure is composed of ceramic and metal grains near the surface, with the depth of partial reduction and the fraction of metal particles depending on the temperature, the oxygen partial pressure, the starting composition, and the initial microstructure.

Several different processes occurring at different size scales were identified by a combination of light microscopy, SEM, and TEM. The microstructures contain Cr grains at several size scales: small scale Cr particles form inside strained oxide grains, and large scale Cr particles form in an oxide of lower strain by a discontinuous coarsening reaction. In discontinuous coarsening, grain boundaries migrate into regions containing small particles. The small particles dissolve and reprecipitate as larger particles along the grain boundary. Grain boundary migration continues into the oxide matrix containing small particles and leaves behind an oxide matrix with significantly lower strain than the original matrix. The fracture toughness is reduced in the regions with small, strained particles; after discontinuous precipitation, the fracture toughness of the regions with the larger chromium particles increases.

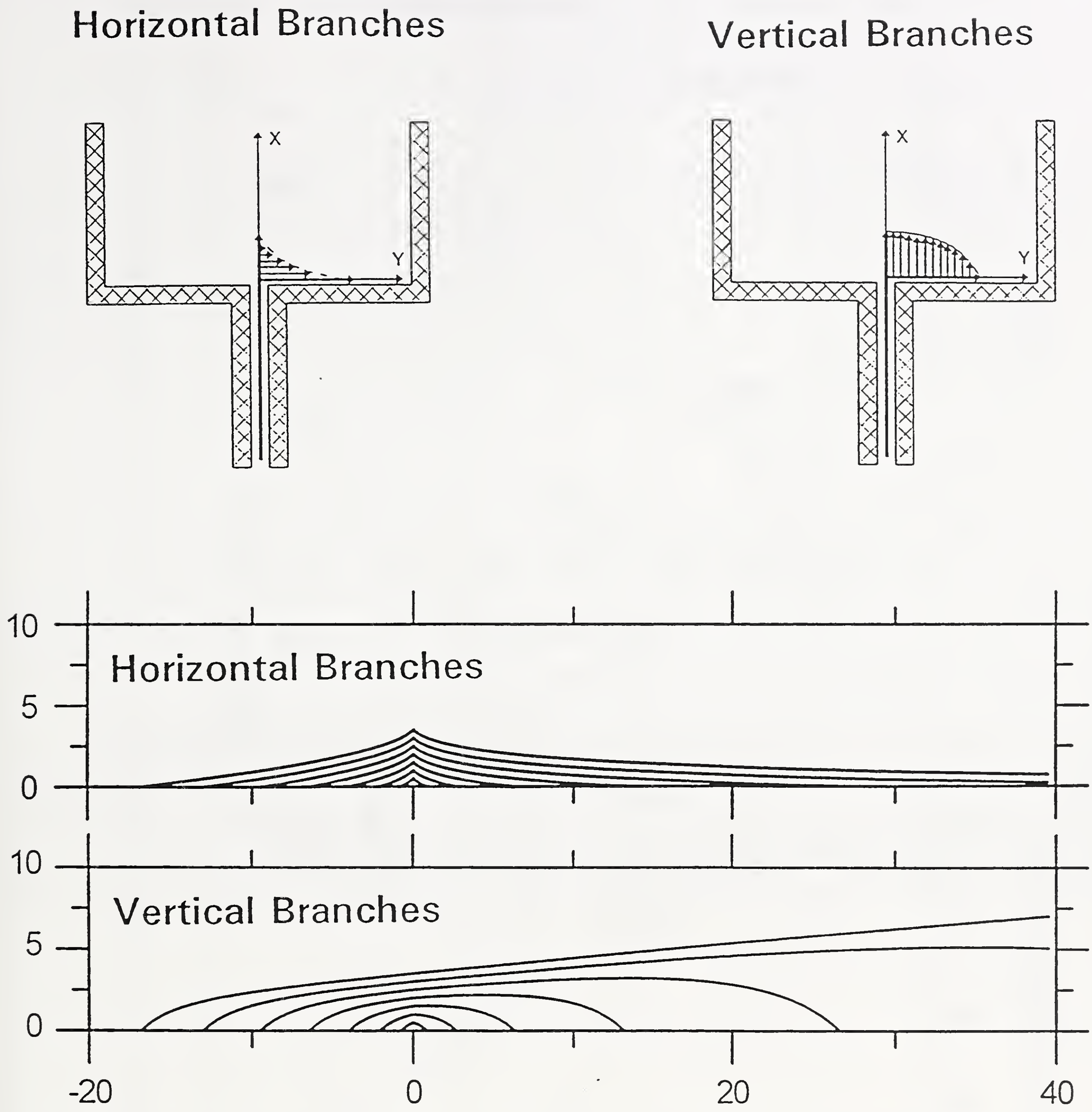
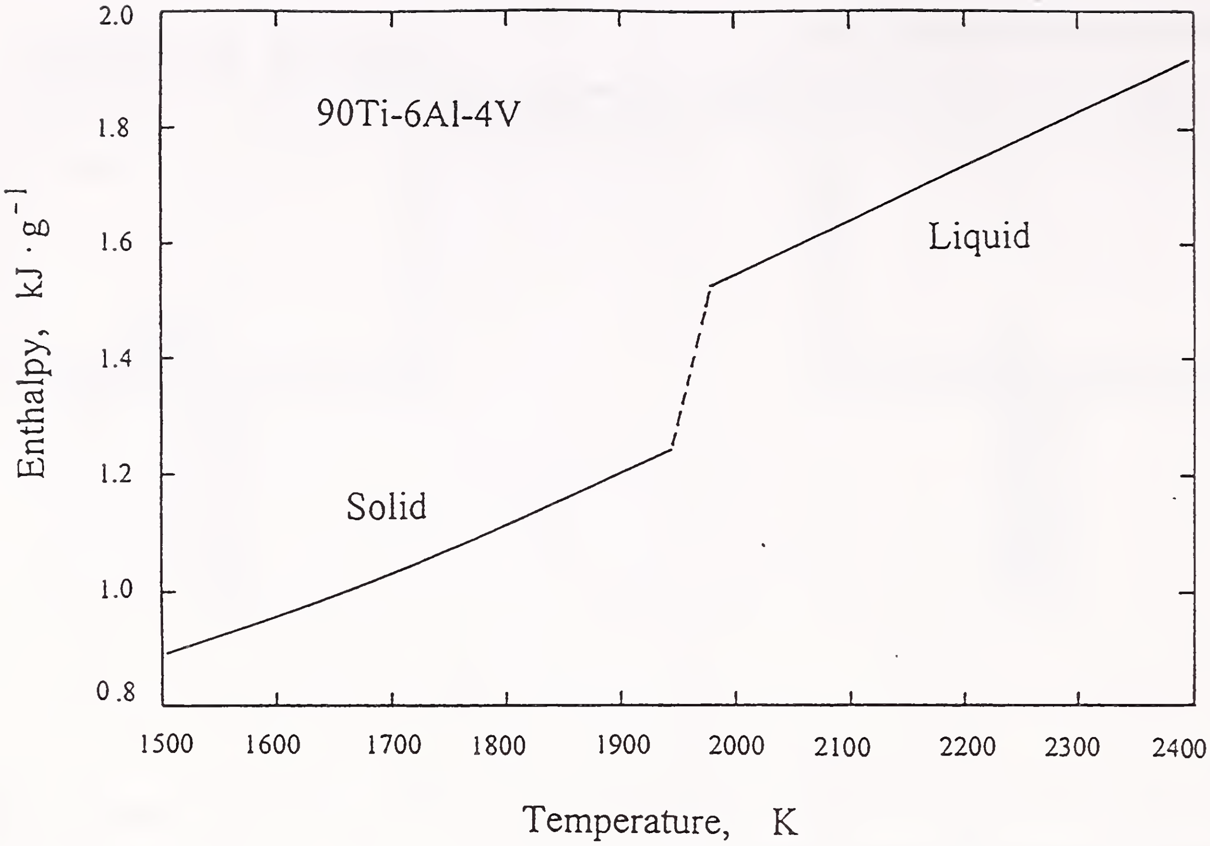


Figure 1. Shape of the advancing dendritic solidification front, at intervals of approximately 10 seconds, for horizontal branches spreading outward from a single upward-growing stem and vertical branches growing upward from horizontal stems. In this example the isotherms are assumed to have a slope of 0.1. The normalized distance units used correspond, in the case of superalloy, to approximately 1.6 mm.



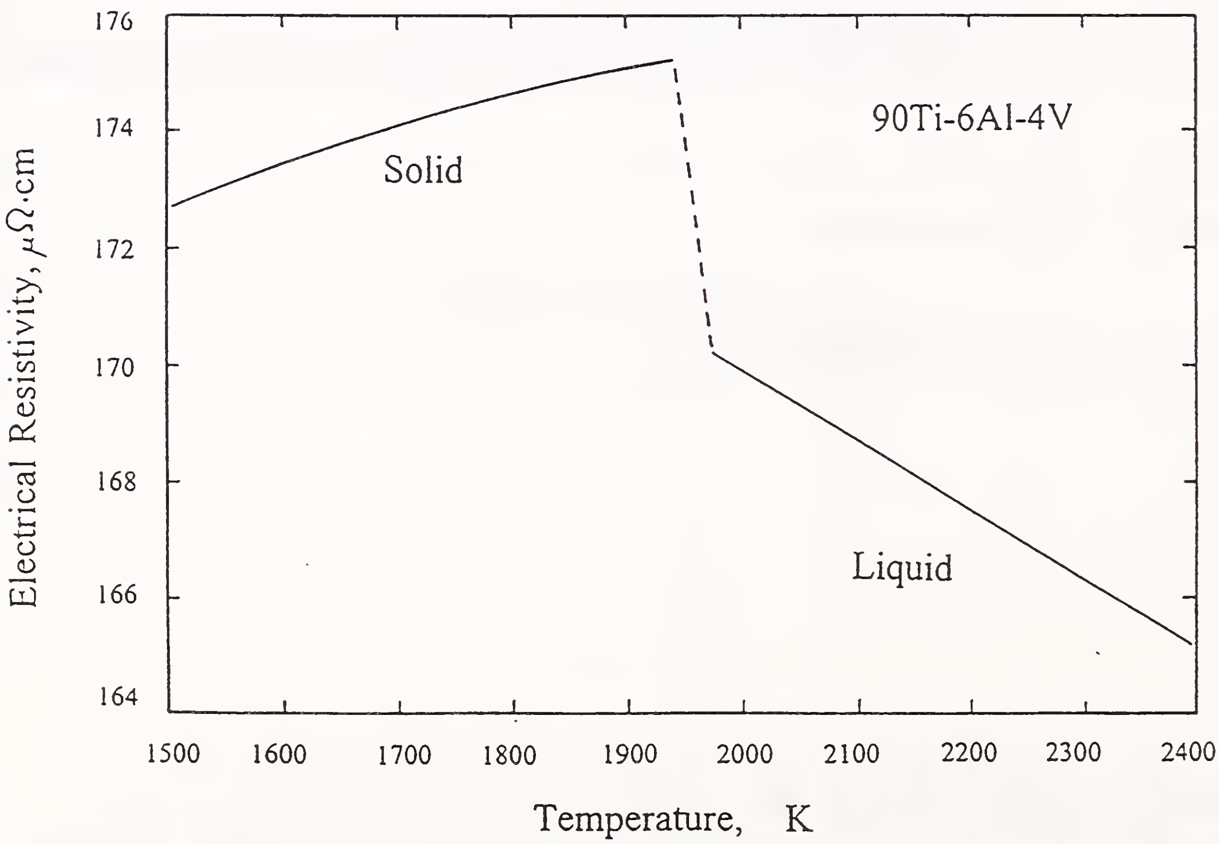


Figure 2. Enthalpy and Electrical Resistivity of Solid and Liquid 90Ti-6Al-4V.

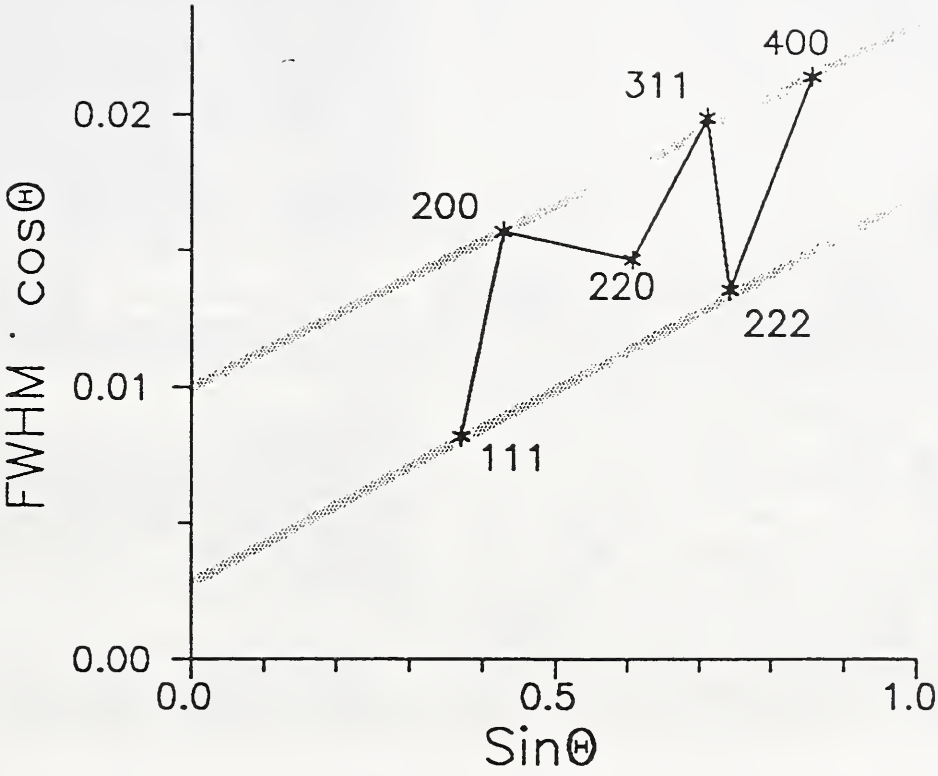


Figure 3. Williamson-Hall plot of X-ray diffraction peak breadths (FWHM) for single phase, FCC, mechanically alloyed Cu-50%Co. In this method for determining grain size and microstrain, all data points should lie on a single line for isotropic grain shape and strain (e), where the slope = 4e and y-intercept = 1.39/D, where D is grain size. A high density of stacking faults on {111} planes (approximately one fault per 75 atomic planes in the present case) leads to greatly enhanced peak broadening of the 200, 311, and 400 peaks compared with the 111 and 222 peaks. Thus the presence of stacking faults leads to a falsely refined estimate of grain size, which can be in error by as much as a factor of 10. The present example gives a calculated grain size of 35 nm, whereas the true grain size is > 100 nm.

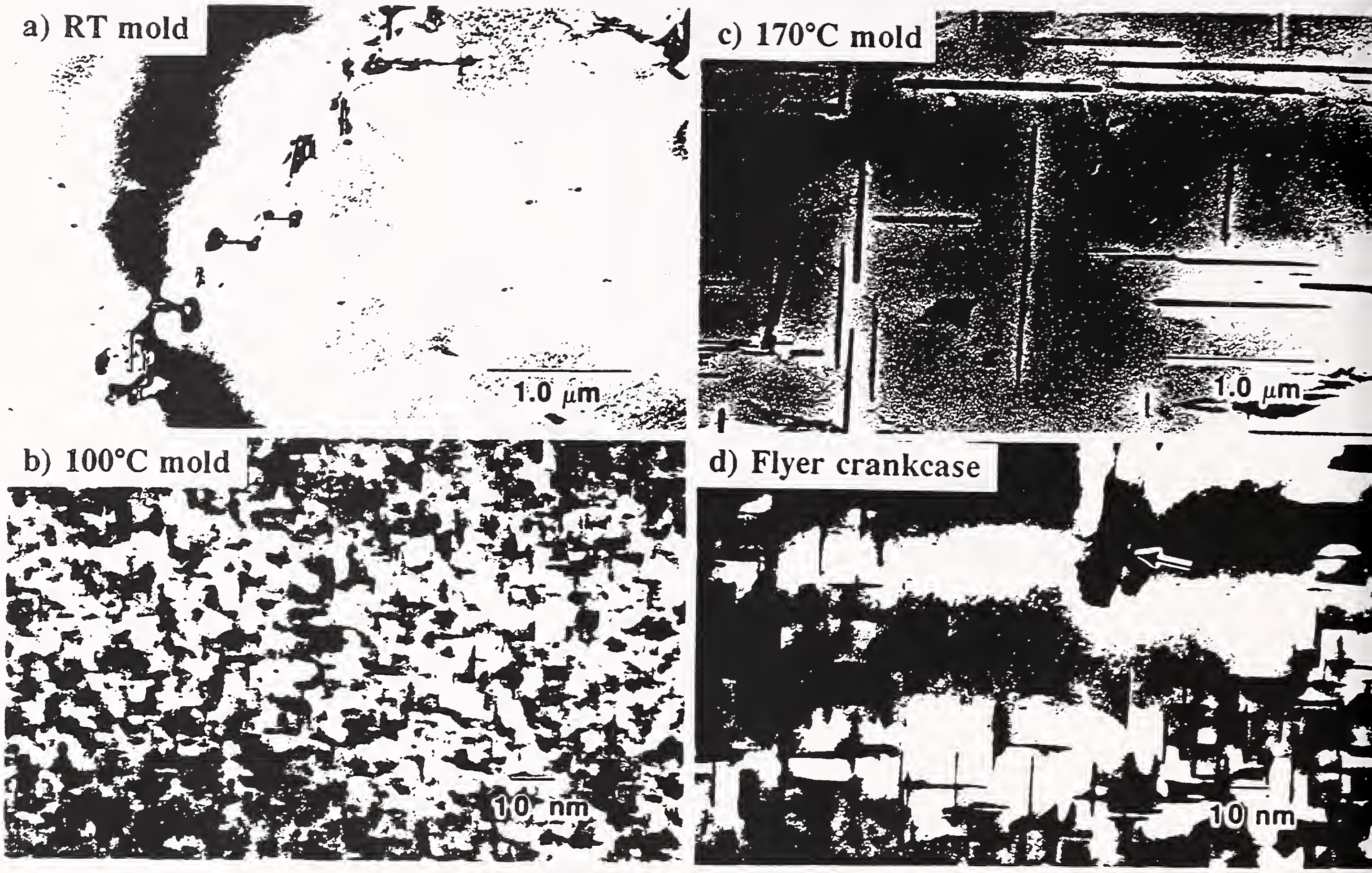


Figure 4. Transmission electron microscopy of the Wright Flyer crankcase and castings of an Al-8%Cu-1%Fe-0.4%Si alloy produced in the Metallurgy Division to simulate the original casting. We found that the alloy in the engine of the Wright Brothers' First Flight of December 17, 1903, was precipitation hardened by GP zones, leading to revision of the history of the use of precipitation hardening in aerospace applications. This view of the crankcase (d) shows GP zones near an infrequent precipitate of θ'. The simulation alloys were cast into sand molds at a) room temperature, b) 100 °C, and c) 170 °C. The resulting microstructures are a) no matrix precipitation, b) GP zones, and c) θ' precipitates with no GP zones. The simulations suggest that the original crankcase may have been cast using mold preheat somewhat greater than 100 °C.

METALLURGICAL SENSING AND MODELING

G. A. Alers

The focus of the Metallurgical Sensing and Modeling Group is to support the Metallurgy Division's activities in the processing of materials. Specifically, the objective of the group is not only to investigate new sensor concepts but, also, to insure that the sensor device measures quantities that are closely related to the properties that are desired in the final product. Hence, there is considerable emphasis on developing mathematical models that provide quantitative relationships between the sensor output and the desired properties. For example, modeling of the response of an eddy current coil to moving sheet metal at an elevated temperature has led to a system for monitoring the temperature of aluminum alloy sheet as it passes through the final stage of rolling in an operating rolling mill. Also, recent theoretical models that describe sound wave propagation in polycrystalline aggregates are being combined with noncontacting ultrasonic transducers in a way that will produce a system for monitoring the development of textures and the growth of grains during the rolling process. In the area of sensor development, emphasis is being placed on ultrasonic devices that detect and measure the resonant modes of vibration of the object under test. If that object has a regular shape such as a flat plate, a sphere or a cylinder, the mathematical analysis is greatly simplified and very accurate measurements of the elastic properties can be made. These shapes are actually commonplace in manufacturing as they are found in sheet metal, ball bearings and drive shafts.

FY 1994 Significant Accomplishments

- A noncontact thermometer to monitor the temperature of sheet aluminum at the output of a commercial rolling mill has been demonstrated successfully at the Alumax Mill in Lancaster, PA. (Jointly sponsored by The Aluminum Association).

- Noncontact ultrasonic transducers that excite particular Lamb wave modes in thin sheet metal are being developed for monitoring texture development and measuring grain size during the manufacture of copper and brass sheet and during the spin casting of metallic glass ribbon.

- Precision measurements of certain vibrational resonant frequencies of a cylinder have been used to demonstrate the feasibility of instruments for measuring the case depth in drive shafts, the stress in cylindrical load cells, the pressure inside piping and the recrystallization process in aluminum alloys.

Applications of Vibrational Resonance Measurements in Cylinders and Spheres

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Resonance techniques involving unique electromagnetic-acoustic transducers (EMATs) are being applied to a variety of nondestructive sensing applications on metallic cylinders. Since EMATs operate without mechanical coupling, they provide highly reproducible and accurate measurements of elastic constants, and, therefore, can be used to detect small changes in a sample's microstructure, dimensions, or environment. In addition, they provide a high degree of spatial filtering, so that only selected vibrational modes are excited and the interpretation of resonance spectra is simplified.

One application of such techniques is the nondestructive determination of case depth in induction-hardened steel. In 63 shafts with case depths (distances from the surface where the hardness drops to Rockwell-C 50) ranging from 3.0 mm to 5.6 mm, the values for the case depth obtained from the ultrasonic resonance measurements were found to have an uncertainty (standard deviation) of only 0.13 mm with respect to the values obtained from destructive indentation measurements.

Another application being explored in collaboration with Sonometrics, Inc. is the measurement of applied axial stress in solid cylinders. For this application, the EMATs are similar in design to those described in Refs. 1 and 2 but have only two magnets around the circumference. Two EMAT coils with different symmetries are used simultaneously, one to couple to torsional modes and the other to couple to axial-shear (flexural) modes. Figure 2 shows measurements of a torsional mode near 251 kHz and an axial-shear mode near 417 kHz in a 10.26-mm-diameter solid rod of aluminum subjected to a varying axially-compressive load. Since the elastic constants and diameter are dependent on the drifting sample temperature, the data are nonlinear and not reproducible between the application and release of the force. The reason for measuring two modes is to eliminate this problem. Since the torsional and axial-shear modes are dependent on approximately the same elastic constant (exactly the same constant in perfectly isotropic material), they vary in almost the same way with temperature and the ratio of the two resonant frequencies is almost independent of temperature. Figure 3 shows this ratio for the same data as in Figure 2.

Similar stress measurements have been performed on a zirconium alloy tube with an outer diameter of 9.1 mm and a wall thickness of 0.7 mm. The ratio of torsional and axial-shear resonant frequencies was recorded as the gas pressure in the tube was increased and decreased through the 0 to 1 MPa range. The ultrasonic data reflected the changes in pressure with an uncertainty of approximately 0.05 MPa. This work was pursued in collaboration with Siemens Corporation.

A vacuum furnace has been constructed for measuring ultrasonic properties of metals from 100 °C to about 1200 °C using electromagnetic-acoustic transduction. The purpose of this system is to provide background data necessary for the development of sensors for monitoring material properties during industrial processing. Currently, reliable data on elastic constants and damping at high temperature is rare because of problems associated with mechanically bonding transducers to samples. The new vacuum furnace incorporates noncontacting EMAT transduction to excite ultrasonic resonances in spherical samples, providing simultaneous measurements of longitudinal and shear velocities and damping. Figure 4 shows data on an aluminum alloy sphere (Aluminum Association alloy designation 2024) obtained during an initial test of the system. The irreversible drop in damping observed on heating through the 230 °C to 270 °C range corresponds to the velocity changes previously observed in several aluminum alloys and associated with recrystallization.

Modeling of Microstructure Evolution in Intermetallic Alloys

J. W. Cahn, J. A. Simmons, W. J. Boettinger and L. Bendersky

The relationships between processing parameters and the material microstructures they produce are not understood, and quantitative prediction of novel microstructures is currently impossible. Many of today's new processes must be described by many-dimensioned nonlinear evolution equations. Computational techniques for treating such systems are very advanced in the mathematics community; however, such techniques are not known in the materials science community. This program links materials science capabilities at NIST with mathematical expertise at Rutgers, Georgia Institute of Technology and elsewhere to develop an interdisciplinary approach to understanding and computing solutions to the field equations governing microstructural evolution, including solidification, in metal alloy systems. Effects such as the influence of stress, discrete crystal structure, and multiparticle potentials are being incorporated into the field equations, and surface energy anisotropy is being incorporated into new, more physically accurate, algorithms describing dendritic solidification. Comparison of computer simulations and controlled quantitative experiments also are underway.

During FY94 the phase field program developed a formulation for eutectic growth where two solid phases freeze from a liquid at the same temperature. The eutectic interface shape in a temperature gradient was computed. This provides the last step necessary to compute the growth of a eutectic. Experiments are being conducted to compare theoretical predictions with real material behavior. In the case of solidification, quantitative metallography methods are utilized for comparison with microsegregation predictions in nickel based alloys; in addition, the extensive literature on dendrite tip velocity, tip radius and arm spacings will be compared with computations.

Two dimensional dendritic growth microsegregation patterns were obtained from the alloy phase-field model. They were found to closely resemble those observed experimentally in real alloys. Solutions to a one-dimensional binary phase field model in the rapid solidification regime were calculated, showing that the solidification velocity where solute trapping occurs depends on the value of the equilibrium partition coefficient. This nonequilibrium effect has been observed experimentally. Simulations of isothermal Ostwald ripening (coarsening) of a collection of spherical alloy particles were performed. The simulations show coalescence events not possible with sharp interface simulations. Nonuniform solute distributions were found to persist in particles after coalescence. A matched asymptotic analysis in the sharp interface limit of a phase-field model with anisotropic gradient energy coefficient which has been shown to recover the classical form of the anisotropic Gibbs-Thomson equation has been published.

In the area of solid-solid phase transformations, a theory of surface motion by surface diffusion, which gives the Cahn-Hilliard, viscous Cahn-Hilliard, and the Cahn-Allen equations as special cases of a gradient system for the same Lyapunov function in appropriately normed spaces was carried out. The linking of anisotropic sharp and diffuse surface motion laws via gradient flows will be published later this year, and a computational comparison of shape evolution by surface diffusion and surface attachment limited kinetics on completely faceted surfaces has been submitted for publication. This latter effort represents the first time rigorous continuum calculations have been obtained for highly anisotropic surfaces which evolve by surface diffusion or surface attachment limited kinetics. A video of the results was produced.

Using Onsager type microscopic diffusion equations in which the thermodynamic driving force is linearly proportional to the rate change of the order parameter, a paper entitled "A Computer Simulation Technique for Spinodal Decomposition and Ordering in Ternary Systems" has been published. This represents the first modeling of kinetics in ternary systems, and is, perhaps, the most computationally advanced of all modeling algorithms of solid-solid kinetics. Because of the linear proportionality, this method exploits an Fast Fourier Transform (FFT) algorithm on a square lattice to exhibit spinodal decomposition, phase separation and coarsening. Elastic energy effects also can be incorporated easily into this model. A videotape showing this process has been produced. This approach is now being applied to model the Ni-Al-V system.

The physical disadvantages of the above technique can be overcome by using the Clustered Master Equation method. A paper "The Clustered Master Equation Approach to Diffusional Transformations in Inhomogeneous Systems---Single Site Approximation and Direct Exchange Mechanism" has appeared. This model is physically more basic than a free energy model in lattice based solids, and promises to give more realistic kinetics, including stress effects. A computer simulation based on point probabilities in a square lattice was published. Even using only single site probability distributions and an elementary exchange mechanism (approximations inherent in most free energy models), rather than vacancy controlled diffusion, the simulation carried out on a square lattice system shows theoretical equilibrium states closer to those predicted by 'exact' theories than other techniques. In addition the kinetics obtained from this approach seems to differ significantly from that obtained using free energy formulations. Again, as in the above simulation, spinodal decomposition, simultaneous ordering and phase separation as well as coarsening are all exhibited. Computation for pair probabilities is in progress, and the 3D equations for a vacancy driven second nearest neighbor model have been developed for the body centered cubic (bcc) structure. The only input to this code is the effective interchange energies between atoms, which may be obtained by ab initio methods. A large scale parallel machine such as a CM5E is necessary for their implementation.

A computer code has been developed for modeling microstructure development in Ni-Al-V ternary alloys using microscopic diffusion kinetic equations formulated in reciprocal space. Preliminary results using two-dimensional projections from a real three-dimensional system indicate that the sequence of L12 and DO22 ordering and decomposition kinetics predicted from the code agrees roughly with experimental observations carried out at NIST. Large scale computation is required for 3D comparison. Calculations of the Cahn-Hilliard-Larche equations for stress affected diffusive phase changes have been carried out for a thin plate with one-dimensional composition profiles taking coherency stresses into account and show exponentially rapid coarsening and spontaneous buckling.

Fundamental studies have been undertaken in collaboration with John Willis of Cambridge University and Vinod Tewary at NIST, Boulder to incorporate inhomogeneous stress effects into microstructure modeling. The Hashin-Shtrikman technique, which allows the use of second order rather than third order correlations in the continuum formalism, yields no advantage in the discrete formalism and a new first principles development is in process.

To study ordering, a series of alloys from two alloy systems, nickel--aluminum-vanadium (Ni-Al-V) and a simpler bcc. binary system suitable for monitoring the earliest stages of ordering, are being utilized. Crystallographic and morphological details of phase transformations in the Ni75Al5V20 alloy, in its cast and rapidly solidified form, have already been carried out by analytical transmission electron microscopy and x-ray diffraction, and the work published. Kinetics of phase decomposition were studied for specimens quenched and annealed for different lengths of time. Four morphological stages (as compared to single-stage classical eutectoid growth) have been identified. X-ray diffraction patterns which have been obtained have shown low contrast at early stages of ordering. Neutron scattering techniques are being evaluated. These experiments will be carried out in such a manner as to produce results that can be compared with computational models which are being developed in this program and are currently being made ready for implementation on a high performance, large memory parallel machine.

In order to give young mathematicians direct experience in formulating and solving materials science programs joint postdoctoral exchange programs have been established with Rutgers and Georgia Institute of Technology. Extensive workshops have been organized (the most recent in Telluride, CO, 7/25--8/12/94) to bring together members of the mathematics, materials science and physics communities to address new techniques in modeling materials microstructure evolution. Specific research programs with graduate student support have also been implemented at Pennsylvania State University, Cambridge University and Colorado School of Mines. The next meeting, which will be cosponsored by The Metallurgical Society (TMS), NIST, ARPA and the Society for Industrial and Applied Mathematics (SIAM) will be held at the October 1995 TMS meeting in Cleveland and will have published proceedings.

Eddy Current Temperature Measurement During Hot Rolling of Aluminum Sheet

L. C. Phillips and A. H. Kahn in collaboration with the Aluminum Association, Inc.

The objective of this project was the development of a non-contact method of measuring the temperature of aluminum sheet during the hot rolling process. Maintaining precise temperature control is necessary in order to achieve the desired mechanical properties and metallurgical state. Eddy Current (EC) impedance measurements can determine the electrical resistivity of the material under test by non-contact electromagnetic induction of current in the material. The resistivity, in turn, depends upon the temperature of the product. If the temperature dependence of the resistivity of the alloy of interest is known, then eddy current methods can be used to provide measurements of the temperature during the processing. The eddy current temperature sensor was installed at the exit of the final reducing rolls of the 3-stand hot mill at the Alumax Hot Rolling Mills in Lancaster, Pennsylvania. The sensor data were collected along with other system parameters such as thickness and velocity of the sheet. A graph of the EC sensor output at Alumax operation is shown in Figure 1. The hot-rolling processing time for each billet was approximately 4 minutes. The run is a 3004 aluminum alloy and shows that the temperature at the beginning of the run was 365 °C and decreased to 350°C near the end of the billet due to radiative heat loss. For comparison purposes, the diamonds on the graph represent thermocouple measurements made at the entrance to the hot-mill and on the final wrap-up once the product was coiled. The difference between the final EC temperature and the thermocouple wrap-up temperature was about 45 °C. This qualitatively agrees with the expected temperature difference for these two points in the process.

This eddy current sensor was operated for a four month period, October 1993 to January 1994, at the Alumax Mill Products in Lancaster, Pennsylvania. During this time, the operation and testing of the sensor did not cause any interruption in the normal production schedule. In determining the accuracy of the technique, an error analysis was performed to identify the individual error sources and to quantify their effect. This process was found to yield an overall temperature error of 8.6 °C (3-σ) when individual alloy correction measurements were made, but if an average alloy value was used as the correction factor for each ingot then an error of 12.4 °C was found. Based on the Alumax tests, an expected error limit for the remote eddy current sensor system was formulated and was determined to be 6.5 °C. This estimate assumes that an eddy current sensor for measuring the conductivity of the individual sheets would be positioned at the entry of the mill in order to determine the alloy shift for each ingot.

Application of Scanning Acoustic Microscopy to Residual Stress Analysis

E. Drescher-Krasicka

In previous years a novel technique for imaging residual stress distribution using acoustoelasticity to analyze the signals obtained in a scanning acoustic microscopy experiment was developed. This approach uses interference phenomena between pairs of reflected signals to increase the sensitivity of the experiment to small changes in the acoustic properties of the media introduced by residual stresses. This work relied upon a simple physical model of the shear and longitudinal wave polarizations realigning along the axis of the acting principal stresses. The model is valid for all kinds of ultrasonic transmitters and receivers like acoustic microscope lenses, EMATs, air coupled transducers or laser transmitters and detectors, where the polarized waves will interfere at the water/solid or air/solid interfaces. In the past year two mathematical models were developed as a result of cooperation with R. Kline: 1) An " exact" solution based upon wave propagation in a three dimensional anisotropic medium and 2) An approximate solution based on a first order perturbation of the isotropic solution. Results for both models were presented for some simple stress states (e. g. diametric compression). Results were compared with experimental data. There is a good agreement between the theoretically predicted amplitude change and the experimental results for the stresses which do not exceed the yield strength value of experimentally compressed aluminum and plexiglass disks.

Signal Processing of Acoustic Emission for Materials Processing

R. B. Clough and B. Kedem*
* Guest Scientist - University of Maryland

Statistical signal processing was combined with wave mechanics to retrieve and analyze acoustic emission signals from simulated materials processing environments where noise and complex geometries can invalidate conventional methods. Physically based on a vibratory model, the statistical distribution of acoustic power reverberating in an aluminum plate was examined. A generalized model was developed from which all of the commonly used peak distribution functions could be obtained by simple parameter selection. Also it was found that in many cases the acoustic power could be measured with increased accuracy by only counting the peaks above a threshold voltage.

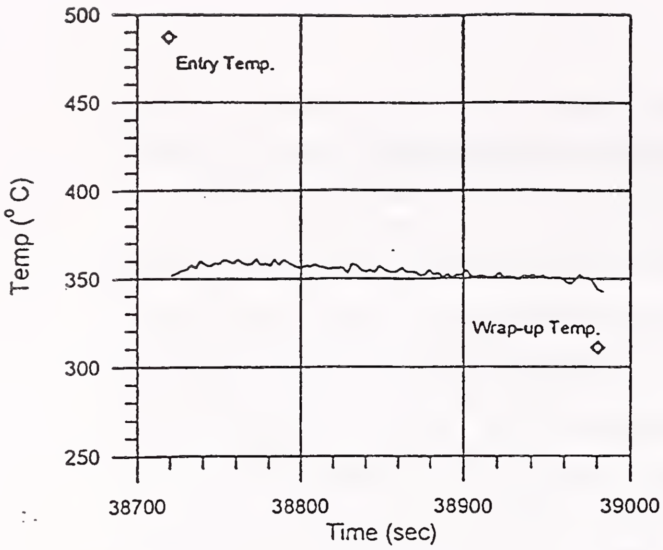
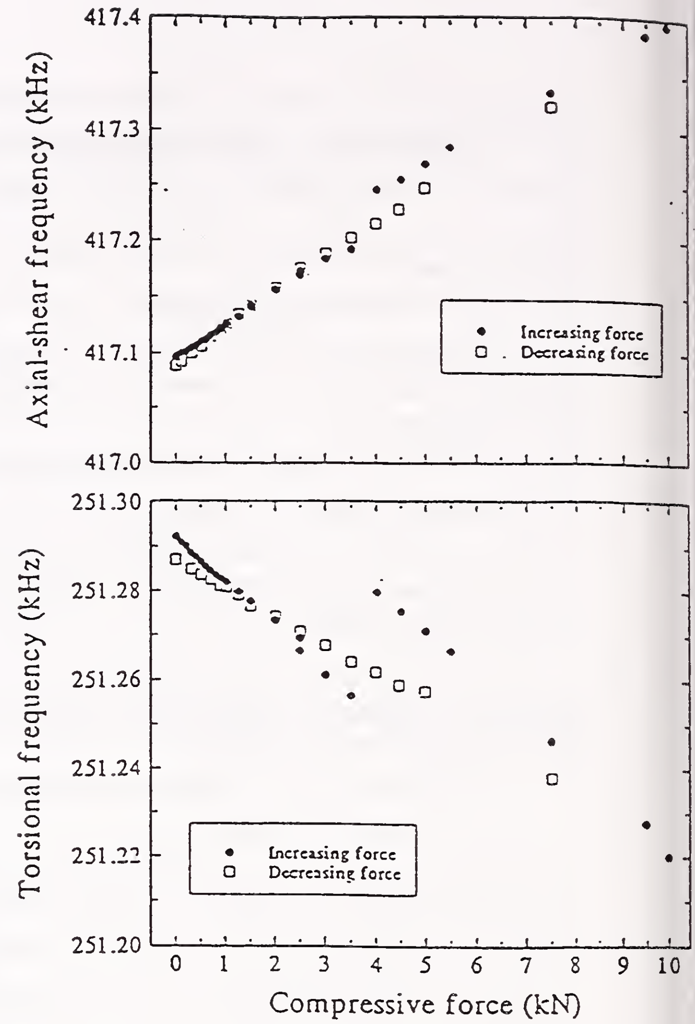


Figure 1 Temperature versus time output from the eddy current sensor during the in-plant Alumax tests.



Figures 2&3 Measurements of a torsional mode near 25 kHz & an axial shear mode near 417 kHz.

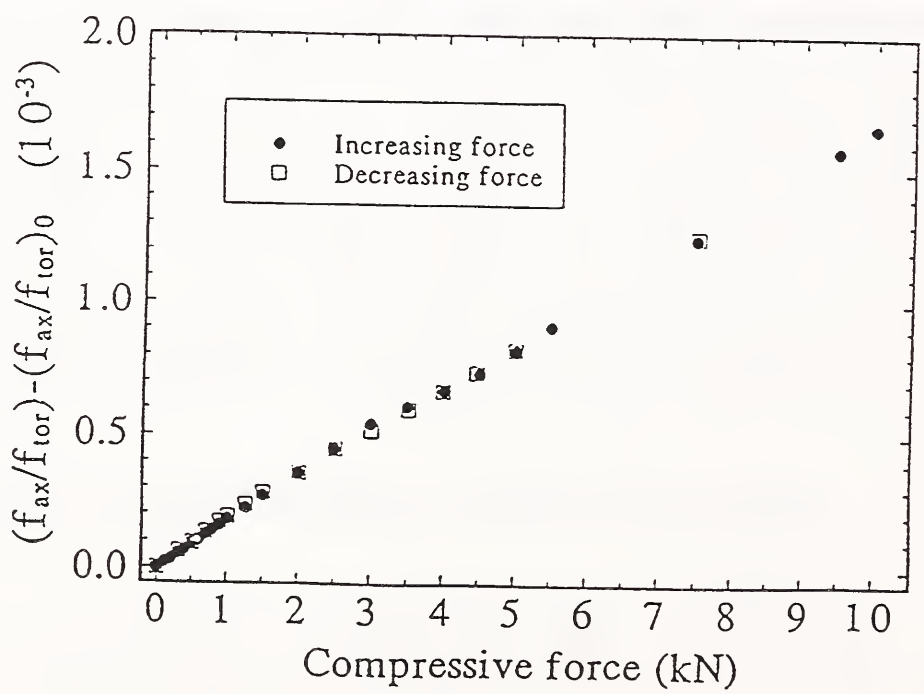


Figure 4 Data on an aluminum alloy sphere obtained during an initial test of the system.

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INDUSTRIAL/ACADEMIC INTERACTIONS

The research programs of the Metallurgy Division are designed and carried out in support of industrial and scientific needs. Specialized facilities within the Division, including metals processing and nondestructive evaluation, attract scientists from both academic and industrial organizations for cooperative research efforts. Interactions with industry, universities, and professional organizations are viewed as an important element of our work. Collaborative programs, consulting and general involvement with outside groups have been a long standing practice of the Division.

In 1994, the Division performed collaborative research with many private and some public organizations through its Research Associate and Guest Scientist programs and other arrangements. Representative examples of such interactions include:

INDUSTRY

1. American Ceramic Society (ACerS)

   P. K. Schenck is copllaboration with ACerS and the industrial sponse of the NIST-ACerS phase diagram optimization program, in the development of a graphical phase diagram database for ceramic and other inorganic systems.

2. Advanced Technology Program

   Several industrial firms have requested High Temperature Materials Chemistry Group support in preparation for participation in the NIST ATP program. Companies include US, Inc. (H. Kott, plasma deposition processes and mixed target materials problems), Jet Process Corp. (B. Halpern and J. Schmitt are considering a novel adaptation of laser/sonic expansion techniques as a materials synthesis route), and Superconducting Components, Inc. (J. R. Gaines, target stability/uniformity).

3. Aluminum Association

   The Aluminum Association represents many U.S. and Canadian companies. The Association has contributed financial support in the form of a Cooperative Research Associate and through its contract with Data Measurement Corporation (DMC). Member companies have supplied materials and have invited NIST researchers to their operating facilities for testing. Efforts to commercialize the sensor and broaden applicability are continuing.

4. American Iron and Steel Institute (AISI)

   G. E. Hicho, L. J. Swartzendruber are currently interacting with AISI under a CRADA (CN-987) to develop on-line methods for the determination of the mechanical properties of sheet steel using magnetic methods

5. Ampal/Metallurg, Crucible Materials Corp., General Electric Co., Martin Marietta Energy Systems, Alcoa, and Pratt & Whitney Aircraft.

   Work continued on the NIST-industrial consortium project on automated processing of rapidly solidified metal powders by high pressure inert gas atomization. The NIST supersonic inert gas metal atomizer (SiGMA) in the Metallurgy Division's metals processing laboratory has been the focal point of this pioneering work in advanced sensor development and artificial intelligence control. Scientists from the participating companies collaborated with NIST scientists, led by S. D. Ridder and F. S. Biancaniello, to develop an in-situ particle size measurement sensor and integrate this device with an automatic control system.

6. Atotech

   C. E. Johnson of the Electrodeposition Group is engaged in a CRADA for joint research on development of trivalent chromium as a replacement for toxic hexavalent chromium electrolytes.

7. Bethlehem Steel

   E. Escalante of the Electrochemical Processing Group visited the zinc plating plant at Sparrows Point, MD to discuss issues associated with on line coating thickness measurments and view the continuous electrogalvanizing of steel sheet for automotive uses.

8. Bureau of Mines, Albany Research Center

   F. W. Gayle and F. S. Biancaniello are working with Cynthia Dogan and James Rawers of the Bureau of Mines on processing of nanostructured ferrous alloys.

9. Children's Television Workshop

   F. W. Gayle and A. J. Shapiro supplied scanning electron microscopy images to Children's Television Workshop for an article on materials in 321-Contact!.

10. Concurrent Technologies Corporation (CTC)

C. E. Johnson made a site visit, presentation, and attended meeting to discuss the scaling up of the trivalent chromium process at CTC as a replacement for toxic hexavalent chromium. Industry would then be invited to use the process at CTC.

11. Containerless Research Inc.

A. Cezairliyan is collaborating with the scientists at Containerless Research, Inc. in Chicago to develop and verify a unique optical technique for measuring normal spectral emissivity of high temperature materials.

12. Containerless Research, Inc.

D. W. Bonnell is collaborating with S. Krishnan regarding levitation of liquid metals, pyrometric, emissivity, and laser ellipsometric measurements at high temperatures, and related studies.

13. Continuous Electron Beam Accelerator Facility (CEBAF)

D. W. Bonnell is collaborating with L. C. Phillips on the development of new technologies for producing superconducting radio frequency (RF) accelerator cavities as part of the goal of a world-wide consortium of government, academic and industrial groups. Dr. Phillips' staff is considered one of the Mid-Atlantic regions's premier sputter research groups. In addition to collaborating on application of process measurement methodology there is also a joint interest in possible adaptation of NIST-developed pulsed laser deposition (PLD) deposition techniques as an attractive alternate route to fabricating niobium alloy-based thin film superconducting RF cavities. Dr. Phillips is supplying HTMC targets, substrates, and surface characterization analysis for HTMC-produced Nb thin films.

14. Copper Development Association (CDA)

R. J. Fields and G. E. Hicho are working with members of the CDA determining the mechanical properties of new lead-free solders used in piping applications.

15. Corning, Incorporated

D. W. Bonnell is consulting with Dr. Frank Woolley of Corning for the purpose of providing model and possible experimental results in order to control the transport of arsenic, used as a glass fining agent.

16. Creswell Scientific Products and Services

L. J. Swartzendruber is working with Creswell Scientific Products and Services to develop test methods whereby the properties of steel samples may be depth profiled using surface magnetic methods.

17. Crucible Compaction Metals

F. S. Biancaniello, S. D. Ridder of the Metallurgical Processing Group and G. Janowski, University of Alabama and Crucible Compaction Metals have signed a Cooperative Research and Development Agreement concerning improved nitrogenated alloys produced by atomization, including investigations of approaches patented by NIST.

18. CTS Corporation

R. J. Fields and R. deWit provided Craig Ernsberger of CTS Corp. with data on Cu/Sn intermetallics and discussed the modeling of diffusion bonding of copper with tin.

19. Defense Industrial Supply Center (DISC)

S. R. Low assisted DISC in upgrading military fastener test method standard MIL-STD-1312 with existing American fastener test method standards, and to point out any deficiencies that presently exist in the military standard.

20. Dentsply

C. E. Johnson of the Electrodeposition Group is collaborating with Dentsply on a joint research of dental restoratives as replacements for silver amalgams.

21. Data Measurement Corporation (DMC)

G. E. Hicho is working with physicists of DMC Corporation at Gaithersburg, MD on the on-line measurement of the mechanical properties of fast-moving sheet steels.

22. DSM Corporation

R. J. Fields provided Bill McCall of DSM Corp. with conversions between Knoop Hardness and Vickers Hardness for an industrial heat treating problem.

23. DuPont (Wilmington, DE)

P. K. Schenck, J. W. Hastie, D. W. Bonnell, and A. J. Paul are collaborating with Drs. D. Kountz, A. Lauder, and other members of the DuPont Superconductivity Group as part of a CRADA to develop process control technology for laser and sputter deposition of complex oxide thin films.

24. Eaton, Corporation, Enthone-OMI Scott Industries and Frederick Gumm Chemical Company

C. E. Johnson attended preliminary meetings to discuss transferring information on trivalent chromium process for in-plant investigation as replacement for hexavalent processes.

25. Electric Power Research Institute (EPRI)

EPRI is an industrial consortia concerned with the generation and distribution of electric power. With EPRI sponsorship, the Corrosion and the NACE research associates in NACE-NIST Corrosion Data Program work with representatives of EPRI member companies and their consultants to develop computer programs which will assist electric utility engineers in avoiding critical equipment failures. This program focuses on selected applications in power plant condensers, steam generators, flue gas desulfurization systems and service waters.

26. Fluxtrol Manufacturing

A Cooperative Research and Development Agreement has been signed for NIST scientists (F. Biancaniello, L. Swartzendruber and S. Ridder) to collaborate with Fluxtrol Manufacturing, Inc. in investigating improved materials for magnetic confinement and energy conservation.

27. FractuREsearch, Inc.

R. deWit and R. J. Fields collaborate with Dr. David Broek on residual strength investigations of thin-sheet structural aluminum alloy panels.

28. General Electric

L. A. Bendersky is collaborating with the General Electric Company, Corporate Research and Development Center (Dr. R. G. Rowe) in studies of the microstructures and properties of new Ti-Al-Nb alloys. This research program is supported by Naval Air Warfare Center, Aircraft Division.

29. General Electric

E. Drescher-Krasicka has a CRADA with General Electric Superabrasives (David Cerutti) on residual stress detection in the abrasive disks.

30. General Electric(GE)-Aircraft Engines

As part of the activities of the Consortium on Casting of Aerospace Alloys, A. Cezairliyan is collaborating with GE Aircraft Engines on generation and compilation of thermophysical property data for several titanium and nickel based alloys. This data will be used in process models describing the casting of these alloys.

31. General Motors (GM)

R. D. Shull and R. D. McMichael of the Magnetic Materials Group have teamed up with Jan Herbst and Carl Fuerst of GM in a collaborative effort (CRADA CN-695) to study the magenetocaloric properties of rare earth transition metal alloys.

32. General Motors, Olin Corp. & Siemens

Cooperative research and development agreements (CRADAs) were established and maintained in order to facilitate transfer of laboratory measurement techniques to process control and nondestructive testing applications in industrial environments.

33. GMW Associates

L. J. Swartzendruber and L. H. Bennett are collaborating with GMW (CRADA CN-701) in the development and testing of a new laboratory electromagnet capable of very rapid changes in magnetic field.

34. Howmet Corporation

As part of the activities of the Consortium on Casting of Aerospace Alloys, NIST scientists are collaborating with Howmet on several projects. These include studies by W. J. Boettinger of the formation of alpha-case on the surface of titanium castings, studies by R. J. Schaefer on the formation of grain defects in the vicinity of mold corners and edges, and studies by L. C. Phillips of eddy-current sensors for monitoring the growth of directionally-solidified cast components.

35. Industrial Materials Institute (IMI) of Canada

L. J. Swartzendruber, G. E. Hicho are cooperating with the IMI in the development of methods for on-line determination of the mechanical properties of sheet steel. IMI is using laser ultrasonics and NIST is using magnetic measurements sharing a common set of test materials and data.

36. International Copper Association (ICA)

ICA is a consortium comprised of copper suppliers and alloy producers concerned with the distribution and use of these materials. With ICA sponsorhsip, the Corrosion Group and NACE research associates are working with ICA representatives and their consultants to develop an expert system for diagnosing failures in copper and copper alloy plumbing systems.

37. Lanxide Electronic Components

C. E. Johnson provided research and development for metallizing SiC/Al alloy composite thermal management devices to promote solderability through the use of thermally fired noble metal resinate films and electrodeposited coatings.

38. Luke Engineering & Manufacturing Co.

A. C. Fraker is working with C. Jurey of Luke Engineering & Manufacturing Co. to evaluate the effectiveness in reducing corrosion of a German patented Magoxid Coat® on magnesium alloys.

39. Martin Marietta Laboratories (Baltimore), Martin-Marietta Astronautics Group (Denver)

F. W. Gayle, NIST, is working with J. R. Pickens of Martin Marietta Laboratories on the evaluation of ultra-high strength aluminum alloys for the Space Shuttle Superlightweight External Tank Program.

40. Materials Innovation

C. E. Johnson is working with Materials Innovation in the development of process technology to coat metal and other inorganic powders with metal coatings for consolidation to final shapes with engineered coefficient thermal expansion (CTE) and thermal diffusivity values.

41. Materials Technology Institute of the Chemical Process Industries, Inc. (MTI)

MTI is an industrial consortia concerned with materials used in plants which produce chemicals. With MTI sponsorship, the Corrosion Group and the NACE research associates in the NACE-NIST Corrosion Data Program work with representatives of MTI member companies and their consultants to develop expert systems for selection of materials for the storage and handling of hazardous chemicals.

42. MicroFab Corporation

R. J. Fields interacted with scientists at MicroFab Corp. and developed for them a computer program that predicts the bulk modulus of molten Pb/Sn solders as a function of temperature and composition. They need this information as part of an ATP award to extend inkjet technology to solder application on printed circuit boards.

43. MicroFab Technologies

F. W. Gayle and C. A. Handwerker are working with MicroFab Technologies in their development of solder-jet printer devices.

44. Massachusetts Insitute of Technology Plasma Fusion Lab, Lawrence Livermore National Lab, DOE Office of Fusion Energy, Supercon, Teledyne Wah Chang, Oxford Superconducting Technologies, and Intermagnetic General Corporation

C. E. Johnson of the Electrochemical Processing Group provided tutorials on Technology of Chromium Plating and Quality Assurance in the Plating Process. This association was developed due to chromium plating problems in the U.S. production of low temperature Nb_3Sn superconducting wires for magnet coils of the International Tokamak Experimental Reactor (ITER) and Tokamak Physics Experiment (TPX) Programs.

45. National Association of Corrosion Engineers (NACE) International

NACE is a professional society whose membership is concerned with the avoidance of corrosion failures and the distribution of information on corrosion prevention. NACE and the Corrosion Group agreed to work together to achieve these common objectives and formed the NACE-NIST Corrosion Data Program in 1982. The objective of this program is to use the latest advances in information science to provide industry with convenient and reliable information on corrosion and corrosion prevention. For this program, NACE provides full time Research Associates who work with the NIST Corrosion Group to collect, evaluate, and develop computer databases, expert systems and hybrid systems for the dissemination of information on materials performance and corrosion failure avoidance. NACE distributes the computer software developed by this program to industry.

46. National Aero-Space Plane Joint Program (NASP) Office

A. C. Fraker is participating in a consortium set up by NASP, as part of their technology transfer program, to characterize and establish a data base on an alloy, Ti21SRx, a modification of the Ti21S alloy that was developed for the aero-space plane. The Ti21SRx alloy is being tested for its suitability for use in surgical implants, and it will be available to implant producing companies.

47. National Center for Manufacturing Sciences

R. J. Fields participated in two meetings with the National Center for Manufacturing Sciences' Pb-free solder consortium for electronics. His contributions were mainly in the area of solder joint reliability.

48. National Center for Manufacturing Sciences (NCMS)

A broad-based collaboration has been established between the National Center for Manufacturing Sciences (NCMS) and NIST (C. A. Handwerker, R. J. Fields, and U. R. Kattner) to evaluate environmentally safe alternatives for lead-based solder alloys used for electrical/electronic assembly interconnections. In addition to NIST, members include IBM, AT&T, Rockwell, Texas Instruments, Ford, GM-Hughes, GM-Delco, Motorola, United Technologies Corporation, RPI, and Sandia National Laboratories.

49. Naval Research Laboratory (NRL)

C. A. Handwerker has been collaborating with Dr. Steven Hues of NRL on the oxidation of Cu-Sn intermetallic compounds. Dr. Hues performs scanning Auger electron spectroscopy experiments on the oxidation of bulk Cu-Sn intermetallic materials prepared at NIST by rapid solidification and HIP'ing.

50. Naval Research Laboratory (NRL)

A. C. Fraker collaborated with M. A. Imam of the NRL in a study to compare and evaluate mechanical and electrochemical properties of titanium alloys for use as surgical implant materials.

51. National Storage Industry Consortium (NSIC)

R. D. McMichael and W. F. Egelhoff (CSTL) are cooperating with the NSIC heads group to improve spin valve materials for magnetoresistive high density recording heads. NIST is using ferromagnetic resonance, magnetoresistance and superconducting quantum interference device (SQUID) magnetometry to evaluate magnetic behavior and thermal stability of films produced by NSIC companies and films produced by NIST.

52. NERAC

R. J. Fields interacted with Luis Santos of NERAC and his client, Bill Avid, in correlating the compressive strength of 1055 steel with its Rockwell C-scale hardness.

53. Nanophase Technologies Corporation

R. D. Shull is collaborating with Dr. John Parker at Nanophase Technologies on the preparation of composite materials with nanometer-scale dimensions. Magnetic methods are being used to characterize the material, including the determination of whether true composite morphologies are achieved.

54. Oak Ridge National Laboratory (ORNL)

R. deWit, L. Mordfin, R. J. Fields, S. R. Low, and D. E. Harne collaborated with ORNL to develop data on the fracture toughness of nuclear pressure vessels by testing full thickness bend bars extracted from an unused vessel.

55. Office of Naval Research (ONR)

R. J. Fields, L. Mordfin, and R. J. Schaefer collaborated with the NIST Reactor Division and ORNL to provide ONR with validated models that predict residual stress fields during and after welding.

56. Polaroid Corporation

P. K. Schenck is collaborating with Dr. Kwang Sup Kim of Polaroid to study the mechanism of laser ablation transfer being utilized in a state of the art printer.

57. Rotorex, Inc.

R. J. Fields assisted Colin Walker of Frederick, MD in identifying appropriate substitute steel for a valve backer on a rotary air compressor.

58. Sandia National Laboratories

Sandia National Laboratories (F. Yost, P. Vianco) and NIST (W. J. Boettinger and C. A. Handwerker) are jointly investigating fundamental reaction mechanisms that influence solderability mechanisms and solderability tests. NIST has supplied Sandia with bulk samples of the intermetallic compounds Cu_6Sn_5 and Cu_3Sn that form in solder interconnects. NIST is the only available source of these alloys, which play key roles in the wettability and mechanical properties of these interconnects. Sandia plans to use these samples in its mechanical measurements and other solder interconnect studies. NIST also has supplied Sandia with thermo-dynamic data for phase stability in solder-substrate systems and with data on the wettability of these intermetallic compounds and their oxides by solders.

59. Sandusky International, Inc.

M. R. Stoudt is collaborating with J. Rogers (Sandusky International) to characterize and evaluate corrosion fatigue related failures in duplex stainless steels used in pulp paper industry.

60. Science Applications International Corporation (SAIC)

A. C. Fraker and E. Escalante collaborated with Dr. Richard Wulleart in two areas (1) a database that provides information on corrosion of materials and effects of environments on corrosion in high-level waste storage tanks, and (2) materials for conductive ceramic electrodes for use in water electrolysis.

61. Sonix, Inc.

E. Drescher-Krasicka has a CRADA with Sonix, Inc., Springfield, VA on residual stress detection on electronic packaging.

62. U. S. Council for Automotive Research (USCAR)

R. J. Fields and R. B. Clough participated in meetings with the Advanced Materials Division of USCAR (which represents the Big Three and their suppliers) to develop low cost powder processing technologies for particle reinforced aluminum components for cars.

63. U.S. Hardness Testing Community

S. R. Low is acting as liaison between the National Voluntary Laboratory Accreditation Program (NVLAP) at NIST and the primary U.S. companies that sell and/or manufacture hardness calibration test blocks. NVLAP is seeking assistance from the hardness testing community in the development of the requirements for accrediting laboratories that conduct calibrations of hardness test blocks, indenters, and hardness test machines.

64. UES, Inc.

As part of the activities of the Consortium on Casting of Aerospace Alloys, W. J. Boettinger is working with UES, Inc. on the enhancement and application of their software for modeling the metal casting process. Dr. Boettinger is helping UES develop microstructure models for inclusion in their software, and UES is using their software to analyze heat flow in a differential thermal analysis system which is used in Dr. Boettinger's laboratory.

65. Weirton and LTV Steel Companies

G. E. Hicho is working with Weirton and LTV Steel research metallurgists at Weirton, WV and Cleveland, OH, respectively, on the on-line measurement of the mechanical properties of fast moving sheet metals.

66. Westinghouse Hanford Company

E. Escalante met with personnel in regard to waterline corrosion of nuclear waste tanks.

67. Westinghouse Science and Technology Center

S. R. Coriell is collaborating with N. B. Singh and colleagues on the modelling of convection and interface stability during the directional solidification of lead bromide doped with silver bromide; this material has nonlinear optical applications.

68. Wright Patterson Air Force Base (WPAFB)

The NIST Corrosion Group was funded by WPAFB to determine materials compatibility between certain alloys and replacement candidates for halon 1301. J. F. Dante developed a three electrode electrochemical technique to make electrochemical measurements in these candidates. This technique was used in one phase of the agent/alloy screening tests.

69. Xerox Corporation

R. D. Shull is collaborating with R. F. Ziolo, Xerox (CRADA CN 784) to evaluate the polymeric method for creation of magnetic nanocomposites useful in magnetic refrigeration and magnetic fluids.

INDUSTRY/UNIVERSITY

1. NIST Metals Processing Laboratory

   Facilities and personnel in the NIST Metals Processing Laboratory (F. S. Biancaniello, R. D. Jiggetts, S. D. Ridder, R. J. Schaefer) aid in preparation of special samples for various materials characterization studies by the scientific and technological community. University and industry scientists can assist in sample processing for independent or collaborative research projects involving alloy development, rapid solidification and particulate consolidation. During the past year, investigators from Crucible Materials Corp., Fluxtrol Manufacturing, Ford, General Electric Co., GM-Delco, Norfolk and Western, Rennselaer Polytechnic Institute, Stratonics, Inc, and the University of Idaho have interacted in this program.

2. Georgia Institute of Technology, Rutgers University, Penn. State University, Colorado School of Mines

   The NIST/ARPA project, which has John Simmons as its technical organizer, aims at i) Modeling dendritic growth using phase field and geometric measure methods, ii) Developing and solving realistic modeling equations for solid-solid phase transformations, iii) Utilizing breakthroughs in materials science measurement and microscopy techniques to establish a methodology for in situ monitoring of microstructure evolution in a form which can be directly compared with computational models, and iv) Establishing extensive dialogue between the materials science community and centers of excellence in the mathematics community.

UNIVERSITIES

1. ACCESS e. V., Aachen, Germany

   Cellular growth during the directional solidification of transparent materials is being studied by Klaus Leonartz of ACCESS. S. R. Coriell and colleagues are carrying out linear stability calculations and modelling of the directional solidification process.

2. Auburn University

   As part of the activities of the Consortium on Casting of Aerospace Alloys, A. Cezairliyan is collaborating with T. Overfelt at Auburn University's Space Power Institute on measurement of thermophysical properties of aerospace alloys at high temperatures.

3. California Institute of Technology

   R. D. Shull is collaborating with B. Fultz to magnetically probe and characterize ball-milled nanocomposite ferromagnets for soft ferromagnetic applications.

4. Centre d'Etudes Nucleaires de Grenoble

   Collaborative research between J. J. Favier and S. R. Coriell is investigating the initial transient during the directional solidification of tin alloys; the Seebeck voltage is used to determine the interface temperature which is being compared with theoretical predictions.

5. Chonnam University

   A collaborative effort is underway between C. A. Handwerker of NIST and Prof. D. J. Lee of Chonnam University, Kwangju, Korea to study interface properties of Al-based metal matrix composites under an NSF-KOSEF joint program.

6. Cornell University

   R. D. Shull and R. D. McMichael of NIST are collaborating with E. P. Giannelis to magnetically characterize polymeric magnetic nanocomposites prepared by ion exchange (CRADA pending)

7. Darmstadt University

R. D. Shull is collaborating with H. Hahn to investigate the possibilities for preparing magnetic nanocomposites via vapor-condensation routes.

8. Florida State University

A collaborative study between Florida State University (J. Schwartz) and NIST (D. Kaiser, F. W. Gayle) is underway to correlate microstructure with microscopic magnetic flux flow of Li-doped and neutron irradiated $Bi_2Sr_2CaCu_2O_{8+x}$ superconducting tapes by means of a magneto-optical imaging technique.

9. Free University of Brussels

J. W. Hastie and D. W. Bonnell are collaborating with J. Drowart (Brussels) on a survey of ionization cross section usage in high temperature mass spectrometry.

10. George Washington University

Collaborative work (R. D. McMichael and L. H. Bennett) with the Institute of Magnetics Research at George Washington University (CRADA CN 802) on modeling of magnetic domain wall motion and pinning is in progress. This work is in support of an ATP project awarded to the National Storage Industry Consortium which includes Applied Magnetics Corporation, Digital Equipment Company, Eastman Kodak Company, Hewlett-Packard Corporation, IBM, Quantum Corporation, and Storage Technology Corporation.

11. George Washington University

W. J. Boettinger serves as a Professorial Lecturer in Engineering Science at George Washington University, where he teaches the graduate course "Transformations in Materials".

12. George Washington University

G. E. Hicho is Associate Professorial Lecturer in Engineering in the Civil, Mechanical, and Environmental Engineering Department.

13. Georgia Institute of Technology

R. deWit and R. J. Fields collaborate with Professor Satya Atluri to further the understanding of fracture behavior of thin-sheet structural aluminum alloy panels.

14. Howard University - Dental School

A. C. Fraker is working with Dr. A. A. Chohayeb, Dental School, Howard University, to study effects of coupled dissimilar metals on corrosion behavior in dental implants and restorations.

15. Indira Gandhi Institute (IGI) Kalpakkam, India

A collaborative activity is underway between Dr. Hastie and Dr. Mathews of IGI for the mass spectrometric investigation of materials at very high temperatures, generated by laser heating.

16. Indian Institute of Technology, Kanpur, India

J. W. Hastie and P. Ghosh (IIT) are collaborating on a study of ion-molecule reactions in rf plasmas.

17. Italian Metrology Institute

A. Cezairliyan is a participant to the US-Italy Joint Project on Metrological Research and is collaborating with the scientists at the Italian Metrology Institute on a project related to thermophysical properties of high-temperature materials.

18. Johns Hopkins University

M. R. Stoudt is working with Professor R. C. Cammarata to characterize how the presence of layered, epitaxial copper-nickel thin film composites influence the initiation behavior of fatigue cracks.

19. Katholieke Universiteit Leuven, Belgium (KUL), Metalogic, Materials Technology Institute (MTI)

C. P. Sturrock and researchers at KUL/Metalogic are collaborating to develop an expert system that predicts the performance of stainless steels in aqueous environments commonly found in industry. Advanced information technologies such as Bayesian inference networks, fuzzy logic and case-based reasoning are being combined with mathematical models of corrosion phenomena to provide an assessment of the overall suitability of candidate alloys and the likelihood and severity of various corrosion morphologies. This research is being sponsored by MTI.

20. Katholieke Universiteit Leuven, Belgium

C. P. Sturrock is collaborating with W. F. Bogaerts to advance the state-of-the-art in applications of artificial intelligence to problems in corrosion science and engineering.

21. Korea Advanced Institute of Science and Technology

S. R. Coriell collaborated with Professor Z. H. Lee on the effect of solutal convection and macrosegregation during the directional soldification of aluminum alloys containing magnesium.

22. Massachusetts Institute of Technology (MIT)

As part of the activities of the Consortium on Casting of Aerospace Alloys, R. J. Schaefer is collaborating with Professor Julian Szekely of MIT on modeling of fluid flow and dendritic growth during directional solidification of aerospace alloys.

23. National Research Laboratory of Metrology (Japan)

A. Cezairliyan is a participant in the cooperative research in thermophysics between NIST and NRLM of Japan.

24. Norfolk State University

A. C. Fraker worked with J. A. Jacobs, School of Technology, Norfolk State University, to produce a NIST hosted workshop that included experiments for use in the classroom, for college and university science and engineering teachers. Mini-workshops were provided in 16 different NIST laboratories.

25. Northwestern University

T. J. Foecke collaborated with Professor Scott Barnett and Meenam Shinn of the Department of Materials Science and Engineering examining dislocation structures produced during microhardness indentation of ceramic nanoscale laminated materials.

26. Osaka Prefecture University

R. D. Shull is collaborating with T. Yamamoto to prepare and magnetically characterize vapor condensed magnetic nanocomposites for applications as recording heads and magnetic refrigerants.

27. Paris VI University, School of Chemistry

L. A. Bendersky is collaborating with Prof. R. Portier of the CECM/CNRS and University of Paris VI in a cooperative study of phase transformations and structures of the Zr-Pd-Ru and quasicrystalline Al-Fe-Cu systems using methods of high-resolution transmission electron microscopy.

28. Pennsylvania State University

Pennsylvania State University (Prof. G. Messing) and NIST (C. A. Handwerker and J. E. Blendell) are collaborating on a study of the effects of rare-dopants on growth rate anisotropy of sapphire whiskers. The lack of suitably oriented whiskers has been a major obstacle to the commercialization of a low cost manufacturing process for sapphire fibers for use in metal matrix and ceramic matrix composites.

29. Purdue University

A. Cezairliyan is a consultant to the Thermophysical Properties Research Center -CINDAS at Purdue University.

30. Rice University

D. W. Bonnell is collaborating with the High Temperature Group in the Chemistry Department on levitation and thermophysical properties of liquid metals.

31. Russian Academy of Sciences

A cooperative program with Professor Dr. V. I. Nikitenko of the Russian Academy of Sciences and F. W. Gayle and D. Kaiser of NIST is underway to examine the dynamics of twin boundary migration in high temperature superconductors.

32. Smithsonian Institution

F. W. Gayle is collaborating with Martha Goodway of the Smithsonian Institution to study the metallurgy of the first aluminum aerospace alloy, the crankcase of the 1903 Wright Flyer.

33. The Ohio State University

T. J. Foecke collaborated with Professor Peter Anderson of the Department of Materials Science in simulating observed dislocation activity and fracture processes during in situ TEM deformation experiments on nanolaminated metallic materials. It was found that there was a good agreement between the predicted line shape of glissile dislocations spanning several layers in the structure assuming an interfacial stress retarding glide and experimental observations. Work is in progress to simulate the distribution of dislocations ahead of an interfacial crack.

34. University of Bristol (UK)

W. J. Boettinger is collaborating with Dr. Adam Wheeler, Mathematics Department, University of Bristol on phase-field methods to treat solidification problems. The alloy theory developed previously was extended to treat eutectic solidification.

35. University of California - Santa Barbara

T. J. Foecke collaborated with Professor David Clarke of the Department of Materials Science and Engineering on the design of an in situ TEM technique to study the physics of fracture of metal-ceramic interfaces.

36. University of Cambridge

E. Drescher-Krasicka is collaborating with Professor John Willis, Department of Applied Mathematics & Theoretical Physics at the University of Cambridge on developing the amplitude approach to acoustic elasticity for stress imaging.

37. University of Florida

A collaborative effort between Professor Abbaschian (University of Florida) and S. R. Coriell on the in-situ monitoring of crystal growth processes using the MEPHISTO furnace has continued. Bismuth alloys have been solidified; the microstructures and in-situ measurements will be compared with numerical calculations.

38. University of Idaho

F. S. Biancaniello and F. W. Gayle are collaborating with F. Froes and C. Suryanarayana of the University of Idaho in the development of processing techniques to minimize contamination during mechanical alloying.

39. Universite Libre de Bruxelles

S. R. Coriell and colleagues are collaborating with Dr. S. Van Vaerenbergh and Professor J. C. Legros on the effect of Soret diffusion on various alloy soldification processes. The effect of Soret diffusion on the onset of morphological instability during the directional soldification of a binary alloy has been calculated.

40. University of Maryland

A collaborative study between the University of Maryland (A. Roitburd) and NIST (D. Kaiser, F. W. Gayle) involves theoretical aspects of the effect of twin boundary and grain boundary defects on flux flow during magnetization of high temperature superconductors.

41. University of Maryland, Mathematics Department and Institute for Systems Research

R. B. Clough, of the Metallurgical Sensing and Modeling Group, is collaborating with Prof. Benjamin Kedem of the Mathematics Department at the University of Maryland. They are using advanced signal processing methods in the development of smart acoustic emission sensors for industrial and aerospace applications. Prof. Kedem was previously at NIST on sabbatical leave.

42. University of Notre Dame, Notre Dame, IN

The Corrosion Group is collaborating with the University of Notre Dame to study oxide film growth, its growth, its measurement, control and use to fabricate nanostructures.

43. University of Southampton/UK AEC

D. W. Bonnell and J. W. Hastie have been working with Professor Ian R. Beattie to adapt the technology of Transpiration Mass Spectrometry to the quantatitive determination of volatiles from spent reactor fuel pins. This association has developed into a detailed interaction to refine details of system design and instrument selection for Project Osprey.

44. University of Virginia

A collaborative study between the University of Virginia and NIST (N. S. Wheeler-Guest Scientist in the Electrodeposition Group) involves microstructural characterization of Co-W coated graphite fibers.

45. University of Washington

A collaborative effort with Professor Lucien Brush of the University of Washington on the laser melting of silicon is underway. The effect of anisotropy of surface tension on cellular interfaces is being investigated.

46. University of Wisconsin at Madison

Cooperative programs with J. Perepezko and A. Chang of the University of Wisconsin have focussed on studies of microstructure development and phase diagram relationships in the Ti-Al-Nb system.

47. Vanderbilt University

R. D. Shull is collaborating with C. Lukehart to prepare and characterize magnetic nanocomposites prepared by sol-gel routes for magnetic recording applications.

TECHNICAL/PROFESSIONAL COMMITTEE LEADERSHIP ACTIVITIES

Aluminum Association
S. D. Ridder, Standards Committee

American Academy of Mechanics
R. deWit
R. J. Fields

American Ceramic Society
C. A. Handwerker, Sosman Award Committee
Basic Science Division, Vice-Chair

American Electroplaters and Surface Finishers Society
C. E. Johnson, Hard Chromium Committee
Alloy Deposition Committee
Aerospace and Light Metals Committee

American Institute of Mining, Metallurgical and Petroleum Engineers
The Metallurgical Society
W. J. Boettinger, Solidification Committee
C. A. Handwerker, Electronic Packaging Committee
R. E. Ricker, Vice Chairman, Committee on Corrosion and Environmental Effects
S. D. Ridder, Solidification Committee
Powder Metallurgy Committee
R. J. Schaefer, Solidification Committee
R. D. Shull, The Chemistry and Physics of Materials Committee
R. D. Shull, The Titanium Committee

American Physical Society
R. deWit
A. Cezairliyan

American Society of Mechanical Engineers
R. deWit
A. Cezairliyan, Thermophysical Properties Committee
R. B. Clough, Materials Characterization Committee

American Welding Society
J. H. Smith, Committee B-4 on Mechanical Testing of Welds

ASM International

Corrosion and Environmental Effects Committee
R. E. Ricker, Vice Chairman

Government Public Affairs Committee
E. N. Pugh

Journal of Phase Equilibria Commission
W. J. Boettinger
F. W. Gayle

Journal of Phase Equilibria, Editorial Committee
F. W. Gayle
U. Kattner

Residual Stress Committee
L. Mordfin

Technical Divisions Board
E. N. Pugh

Technology Transfer Committee
E. N. Pugh, Chairman

Washington, DC Chapter
R. E. Ricker
M. R. Stoudt, Arrangements Committee Chairman

ASNT

Research Committee
G. A. Alers

E7:04: Acoustic Emission
J. A. Simmons
R. B. Clough

ASTM

Standing Committee on Publications
L. Mordfin, Chairman

A6: Magnetic Properties
L. H. Bennett
L. J. Schwartzendruber

B2:	Nonferrous Metals and Alloys S. D. Ridder
B5:	Copper and Copper Alloys L. J. Swartzendruber
B7:	Light Metals R. D. Shull W. J. Boettinger
B8:	Metallic and Inorganic Coatings D. R. Kelley E. Escalante C. E. Johnson
B8.01:	Ancillary Matters E. Escalante, Vice-Chairman
B8.10:	General Test Methods C. E. Johnson
B8.10.03:	Microhardness Testing C. E. Johnson, Liaison to EO4
B9:	Metal Powders and Metal Powder Products J. R. Manning
D30:	High Modulus Fibers and Their Composites M. R. Stoudt
DS-56D	Metal and Alloys in the Unified Numbering System G. E. Hicho
E4: E4.05:	Metallography Microhardness C. E. Johnson L. J. Schwartzendruber
E7:	Nondestructive Testing L. Mordfin, Executive Subcommittee L. J. Swartzendruber L. H. Bennett

E7:04:	Acoustic Emission J. A. Simmons R. B. Clough
E7.10:04:	Infrared NDT Methods L. Mordfin, Chairman
E7.91:	USA Committee for ISO TC 135 L. Mordfin, Chairman
E8:	Fatigue and Fracture R. deWit R. J. Fields G. E. Hicho S. R. Low, III J. H. Smith J. A. Simmons
E8.02:	Fractography & Associated Microstructure R. J. Fields G. E. Hicho
E8.08:	Elastic-Plastic G. E. Hicho
E24.04:	Environmental Cracking R. E. Ricker
E28:	Mechanical Testing L. Mordfin, Executive Subcommittee S. R. Low, III
E28:04:	Uniaxial Testing S. R. Low, III
E28.06	Hardness R. J. Fields S. R. Low, III J. H. Smith
E28.06.03:	Macro-Rockwell Hardness S. R. Low, III

E28.06.07:	Traceable Hardness Standards S. R. Low, III, Chairman J. H. Smith
E28.12:	Accreditation of Mechanical Testing Labs S. R. Low, III
E28.13:	Residual Stress Measurement L. Mordfin, Chairman
E28.90.02:	Proficiency Test Program S. R. Low, III, Chairman
E28.94:	USA Committee for ISO TC 164 L. Mordfin
E28.94.06:	Terminology and Symbols L. Mordfin, Chairman
E37:	Thermal Measurements A. Cezairliyan
E49:	Fourth International Symposium on the Computerization and Use of Material Property Data C. P. Sturrock, Chairman
F4:	Medical and Surgical Materials and Devices A. C. Fraker
F16:	Fasteners S. R. Low, III
G1:	Corrosion of Metals E. Escalante R. E. Ricker M. R. Stoudt
G1.06:	SCC and Corrosion Fatigue R. E. Ricker
G1.10:	Corrosion of Metals in Soil E. Escalante

G1.10.01: Measurement of pH of Soil
E. Escalante

G1.10.02: Measurement of Soil Resistivity
E. Escalante

G1.11: Electrochemical Measurements in Corrosion
R. E. Ricker

G1.14: Corrosion of Steel in Concrete
E. Escalante

Compressed Gas Association
J. H. Smith, Cylinder Specification Committee
J. H. Smith, Technical and Safety Standards Council
(TASS)

Electrochemical Society
T. P. Moffat, Vice-Chairman-elect of Washington Local Section
Treasurer of Washington Local Section
Member at Large of the Electrodeposition Division

Corrosion Division
R. E. Ricker

Electronics Division
R. E. Ricker

High Temperature Science Journal
J. W. Hastie, Editorial Board Member
A. Cezairliyan, Editorial Board Member

IEEE Committee on Metric Police
L. H. Bennett, Magnetic Society Representative

IEEE Ultrasonics, Ferroelectrics and Frequency Control
G. A. Alers

IPC Subcommittee on Solderability
Steam Aging Task Group
C. A. Handwerker

International Advisory Committee for International Conference on Rapidly Quenched Metals

W. J. Boettinger, Member

International Advistory Committee and Program Committee for the International Conference on Nanostructured Materials

R. D. Shull, Recording Secretary/Treasurer

International Advisory Committee of the 14th World Conference on NDT

R. B. Clough

International Commission on Standardizing Thermophysical Properties Measurement Methods

A. Cezairliyan, Member

International Conference on Solid-Solid Phase Transformations in Inorganic Materials

C. A. Handwerker, Organizing Committee

International Conference Series on High Temperature Materials Chemistry, Organizing Committee

J. W. Hastie, Member

International Journal of Thermophysics

A. Cezairliyan, Founding Editor-in-Chief

International Organizing Committee for International Workshop on Magnetic Properties of Fine Particles and their Relevance to Materials Science

R. D. Shull, Member

International Organizing Committee of the Subsecond Thermophysics Workshops

A. Cezairliyan, Member

International Organizing Committee of the European Thermophysical Properties Conferences

A. Cezairliyan

International Organization for Standardization

TC58.SC-3: Cylinder Design
J. H. Smith, Delegate

TC107: Metallic and Other Non-Organic Coatings
C. E. Johnson, Delegate

TC107.02: Methods of Inspection and Co-Ordination of Test Methods
C. E. Johnson, Delegate

TC107.03: Electrodeposited Coatings and Related Finishes
C. E. Johnson, Delegate

TC135: Nondestructive Testing
L. Mordfin, Delegate

International Thermal Expansion Conferences
A. Cezairliyan, Governing Board

International Thermophysics Congress
A. Cezairliyan, Chairman

International Union of Pure and Applied Chemistry Commission II-3
High Temperature and Solid State Chemistry
J. W. Hastie, Titular Member

Journal of the American Ceramic Society
C. A. Handwerker, Associate Editor

Journal of High Temperatures - High Pressures
A. Cezairliyan, Editorial Board Member

Journal of Crystal Growth
S. R. Coriell, Assoc. Editor

Journal of Nanostructured Materials
R. D. Shull, Associate Editor

Journal of Phys. Chem. Reference Data
D. W. Bonnell, Editorial Board Member

Maryland Institute of Metals
R. deWit

Materials Research Society
R. E. Ricker
T. P. Moffat

Materials Science and Engineering
L. H. Bennett, Associate Editor

NACE Awards Committee
E. N. Pugh

NACE International

	T.3K:	Corrosion and Other Deterioration Phenomenon Associated with Concrete E. Escalante
	T.3U2:	Artificial Intelligence Applications in Corrosion C. P. Sturrock

NACE-NIST Corrosion Data Program
Joint Coordination Committee
R. E. Ricker
C. P. Sturrock

NACE Research Committee
E. N. Pugh, Past Chairman and Chairman of Research in Progress Symposium Sub-Committee

National Aeronautics and Space Administration
Materials Science Discipline Working Group
R. J. Schaefer

National Research Council
Transportation Research Board
E. Escalante, Panel Member

NSF Institute for Mechanics and Materials Young Investigator Advisory Committee
T. Foecke

Office of Energy-Related Inventions, National Institute of Standards and Technology
L. H. Bennett, Reviewer of Invention Disclosures

Sigma Xi
R. deWit
T. P. Moffat
R. J. Fields

Society for Experimental Mechanics
R. deWit

Society for Natural Philosophy
R. deWit

Society of Automotive Engineers
R. E. Ricker

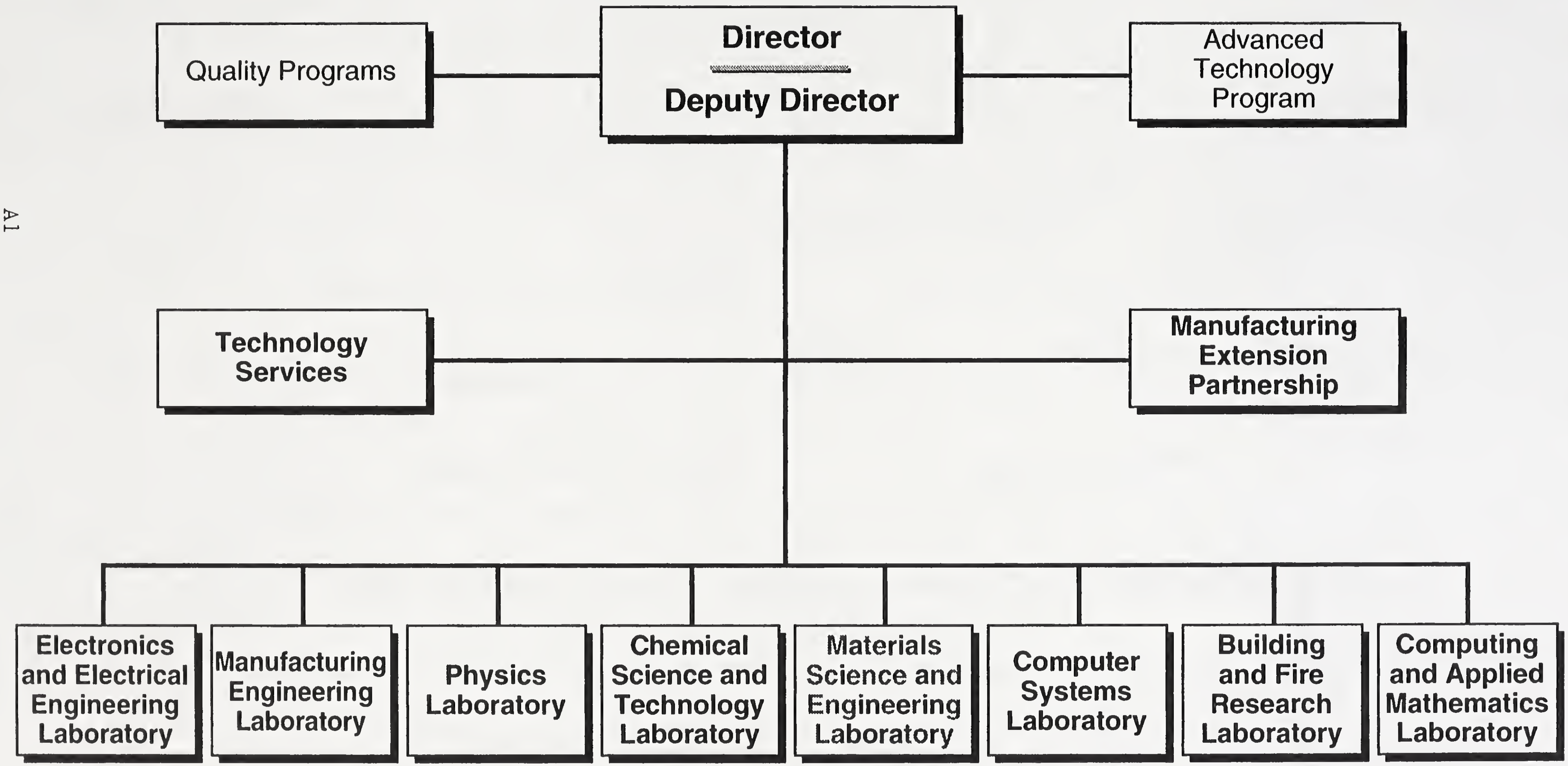
Society of Automotive Engineers/ASTM
Unified Numbering System for Metals and Alloys
L. H. Bennett, NIST Representative

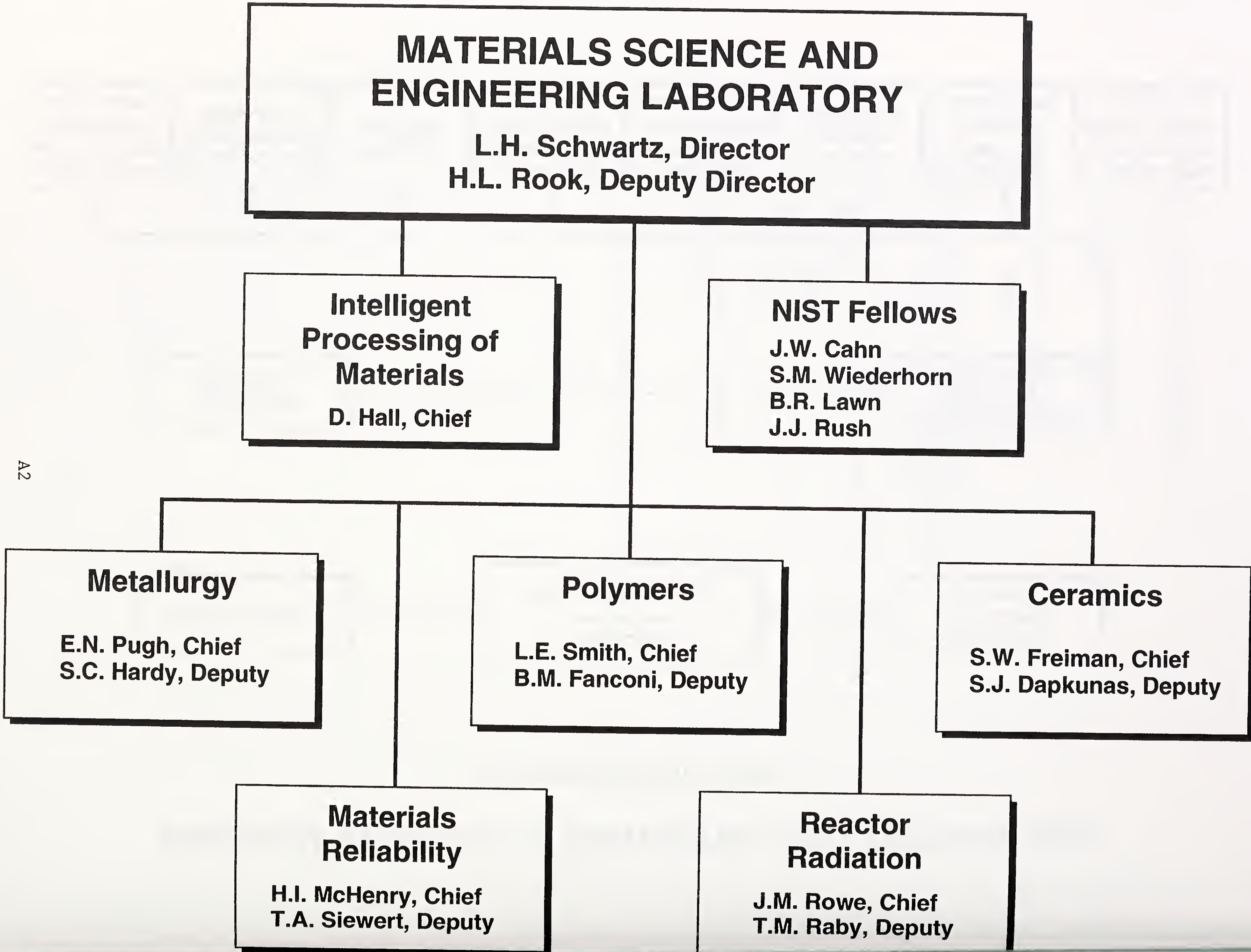
The Minerals, Metals & Materials Society (TMS) of the AIME
R. deWit
T. P. Moffat
R. E. Ricker
M. R. Stoudt

Washington Academy of Sciences
R. deWit

National Institute of Standards and Technology

Organizational Chart




MATERIALS SCIENCE AND ENGINEERING LABORATORY
L.H. Schwartz, Director
H.L. Rook, Deputy Director
Intelligent Processing of Materials
D. Hall, Chief
NIST Fellows
J.W. Cahn
S.M. Wiederhorn
B.R. Lawn
J.J. Rush
Metallurgy
E.N. Pugh, Chief
S.C. Hardy, Deputy
Polymers
L.E. Smith, Chief
B.M. Fanconi, Deputy
Ceramics
S.W. Freiman, Chief
S.J. Dapkunas, Deputy
Materials Reliability
H.I. McHenry, Chief
T.A. Siewert, Deputy
Reactor Radiation
J.M. Rowe, Chief
T.M. Raby, Deputy