METALLURGY DIVISION

FY 2000 PROGRAMS AND ACCOMPLISHMENTS

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

NISTIR 6597

NIST CENTENNIAL 1901-2001

Cover Caption

State-of-the-art electron microscopy allows materials characterization with atomic scale structural and compositional resolution. These measurements can reveal the nanoscale crystallographic and defect structures which impart unique properties to modern materials. For observations on this scale, special sample preparation techniques are needed to avoid the production of artifacts and reveal the true structure. The MSEL Electron Microscopy Facility serves the Metallurgy, Ceramics, and Polymers Divisions as well as other NIST staff and outside collaborative efforts.

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MATERIALS SCIENCE AND ENGINEERING LABORATORY

METALLURGY DIVISION

FY 2000 PROGRAMS AND ACCOMPLISHMENTS

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NISTIR 6597

January 2001

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Executive Summary

This report describes major programs and accomplishments of the Metallurgy Division of the NIST Materials Science and Engineering Laboratory (MSEL) in FY2000.

The mission of the NIST Metallurgy Division is to provide critical leadership in the development of measurement methods, standards, and fundamental understanding of metals behavior needed by U.S. materials producers and users. As a fundamental part of this mission we are responsible not only for developing new measurement methods with broad applicability across materials classes and industries, but also for working with individual industry groups to develop and integrate measurements, standards, and evaluated data for specific, technologically important applications.

With that mission in mind we have established our research priorities through extensive consultation and collaboration with our customers in U.S. industry and with our counterparts in the international metrology community. Our priorities are established by the Division's technical leaders through formal and informal means: industrial roadmapping activities, workshops, consortia, technical meetings, standards committee participation, and individual visits with our customers. Most times when we undertake a new program or begin a project within an existing program we can see a clear path to success. For these projects, the commitment of the industrial or metrology community and NIST expertise and resources must be sufficient to accomplish the technical goals. In addition, there must be a clear path for use of NIST results, whether these are in the form of fundamental understanding of materials behavior, measurement techniques, standard reference materials, evaluated data, software, or sensors for on-line process control. In other cases, we undertake projects with a high degree of scientific and technical risk: (1) a new materials phenomenon has been discovered but as yet has no established industrial application or market; (2) the special materials property is sensitive to materials microstructure, composition, and processing, and is the subject of intense study by the research community; (3) there are possibilities that this behavior, if controlled, could be exploited in new markets, new applications; and (4) we see a NIST role in establishing the needed control and understanding.

Within the context of these requirements for current or future industrial relevance and effectiveness, several factors influence the technical directions addressed by Metallurgy Division projects. We strongly prefer to work in rapidly evolving technologies, where advances in measurement science are needed to understand the limitations on system behavior. In our Magnetic Materials and Materials for Microelectronics activities, many projects deal with phenomena on a nanometer scale, such as the effect of pinholes in the nano-oxide layers of giant magnetoresistance devices. Our studies of electrodeposited copper for chip interconnection technology demonstrated that hysteresis in current-potential curves is a good indicator of the ability to fill deep and narrow trenches. This simple macroscopic measurement may eliminate the need for resource-intensive evaluations of various electrolytes with patterned nanostructures.

We take advantage of advances in theory, modeling and computation power by applying them to problems important to U. S. industry and by promoting their wider dissemination. We have been instrumental in helping the electronics industry use the freeware computer code Surface Evolver to analyze the forces on solder joints. This year, we extended the use of Surface Evolver to predict the forces on misaligned solder joints during wafer-level underfill, and demonstrated that the predictions were in good agreement with forces measured by a new technique which we developed. We have been aggressive in our efforts to extend the powerful phase field method for analysis of phase transformations, applying it this year to prediction of the shape of three-dimensional alloy dendrites and to electrodeposition processes.

We help U.S. industry to improve responsiveness and competitiveness by accelerating the design of manufacturing processes. Several of our projects provide the tools needed for this purpose. The reaction path analysis of multicomponent alloys helps foundries analyze the solidification of castings on the computer and eliminate the time and expense of multiple test castings. Sensors and diagnostic tools help thermal sprayers determine the processing parameters for reliable coatings. We are developing tools to evaluate combinatorial arrays intended to rapidly screen multiple chemistries of advanced materials.

Several of our projects help U.S. industry develop the alternative technologies mandated by environmental considerations. These technologies include lead-free solders, which acquired additional urgency in FY2000 due to impending restrictions in Japan and the European Union. We worked with the US microelectronics industry to evaluate the performance of lead-free solders and to refine the thermodynamic description of the Sn-rich part of the Sn-Ag-Cu system, critical for their alloy selection. Our major activity in the Forming of Lightweight Materials is the development of test methods and deformation models which will help the U.S. auto industry accelerate the design of forming operations for lightweight materials such as aluminum, to improve the fuel economy of its products.

At the core of NIST's mission, standardization activities are a continuing responsibility. We provide national and international leadership in the standardization of Rockwell hardness, the primary test measurement used to determine and specify the mechanical properties of metal products. We are providing a growing range of Standard Reference Materials for magnetic measurements, and have replenished the inventory of electrodeposited coating thickness standards used to evaluate all types of non-magnetic coatings on steels.

The Metallurgy Division is organized into groups that correspond to our core expertise in Metallurgical Processing, Electrochemical Processing, Magnetic Materials, Materials Structure and Characterization, and Materials Performance. However, by virtue of the interdisciplinary nature of materials problems in the industrial and metrology sectors that we serve, the Program teams are assembled across group, division and laboratory boundaries in order to best meet the goals of the projects.

In FY2000 we carried out major programs that focused on fulfilling specific, high priority metrology needs of importance to the automotive, magnetic recording, microelectronics, aerospace, and metal producing industries. The research accomplishments and industrial impact of our programs in the following sections provide an indication of the scope and quality of programs in the Metallurgy Division.

Of equal importance to the program areas which have already had strong industrial impact are the new program areas started in FY2000. Two new projects in high throughput/combinatorial methods for materials research were started in the areas of metal interconnects to GaN and phase transformations in library fabrication for magnetic, dielectric, and optoelectronic materials. These two projects are part of the new MSEL-wide program in Combinatorial Methods. The project on Lightweight Materials for Automotive Applications was expanded into a major program on Forming of Lightweight Materials with four separate projects, including development of standard test methods, analysis of surface roughness during deformation, fundamental measurements of plastic deformation, and development of process models for particle reinforced composites. The significance of this expansion is a recognition of the importance to the auto industry of improved metrology and prediction of the final shape and the willingness of that industry to collaborate with us to address these issues. Other projects started in response to specific industrial needs are in the areas of the electrodeposition of lead-free alloys, bond pad design for wire bonding, and characterization of tailored metallic powders.

In FY2000, Metallurgy Division staff members were recognized for their outstanding contributions to measurement science and technology transfer in the areas of solidification, magnetism, lead-free solders, and solderability measurements for microelectronics. Sam Coriell was named as a fellow of the American Physical Society for his pioneering work in crystal growth and solidification. A symposium in Sam Coriell's honor titled "S. R. Coriell Symposium on Alloy Solidification and Crystal Growth" was held at the Materials Solutions 1999 Conference of ASM International in Cincinnati. In the fall of 1999, the Metallurgy Division received three awards from IPC, the electronic packaging standards and trade association representing over 2,600 microelectronics companies. The Metallurgy Division received the US award for Lead-Free Solder Research, the Distinguished Committee Service Award for outstanding contributions to ANSI J-STD-003A, Solderability Standards for Components and Leads, and the Best US Paper Award on Lead-Free Solders, presented to Carol Handwerker for her paper at IPC Works, '99, the International Summit on Lead-Free Electronics Assemblies.

In this report we have tried to provide insight into how our research programs meet the needs of our customers, how the capabilities of the Metallurgy Division are being used to solve problems important to the national economy and the materials metrology infrastructure, and how we interact with our customers to establish new priorities and programs. We welcome feedback and suggestions from our customers on how we can better serve their needs and encourage increasing collaboration with them to this end.

Carol Handwerker
Chief, Metallurgy Division

Technical Highlights

The following Technical Highlights section includes expanded descriptions of research projects that have broad applicability and impact. These projects generally continue for several years. The results are the product of the efforts of several individuals.

New X-ray Imaging Techniques Shed Light on Fundamentals of Metal Forming

Increased use of lightweight aluminum alloys and high strength steels in automobiles has the potential to greatly increase fuel efficiency. Unfortunately, these materials are not fully utilized because the forming response of sheet metal parts is difficult to predict, making design an enormously expensive trial and error process. Accurate deformation models would remove this limitation, but in spite of efforts over the past 65 years this problem remains unsolved. Recent advances in computer simulations, the development of statistical physics models of deformation, and new experimental techniques developed at NIST have generated widespread hope that a solution may at last be achievable. During FY 2000, NIST organized and ran Dislocations 2000, *the largest international conference on this topic ever held. At this conference, NIST researchers introduced a revolutionary new X-ray imaging technique, USAXS imaging, that has great potential to shed light on the fundamental microscopic behavior during deformation of metals.*

During metal forming operations, metals deform plastically through the production and motion of defects known as dislocations. After a modest level of metal deformation, dislocations form complicated, immobile, three-dimensional structures that impede the motion of other mobile dislocations. In this manner, a metal *work hardens* during deformation. Within a single crystal, this work hardening depends strongly upon the strain, temperature, alloy composition, and deformation history.

This complexity makes it difficult to predict how the mechanical properties of a metal will change during a forming operation, such as stamping a car door panel, and what the resulting shape of the metal sheet will be. Although finite element analysis (FEA) is widely used for design of stamping dies, more than eight die redesigns are typically needed before an acceptable auto part is produced from commonly used steels. The problem is much worse for aluminum alloys and high strength steels, requiring even more trials. The use of these newer alloys in automobiles would boost fuel efficiency, but the large number of die redesigns inhibits the widespread introduction of these alloys. The situation could be greatly improved if quantitative, accurate models for the changes in mechanical properties during deformation of these new alloys were available as input to FEA.

During the 1950's and 1960's, the international scientific community attempted to lay the foundations for a fundamental, dislocations-based understanding of plastic deformation and strain hardening. This effort lagged, however, because the existing theoretical, computational and experimental techniques were not sufficient for the task. For most of the 1970's and 1980's, research in this area plateaued.

Since the mid-1990's, U.S. research into the fundamentals of plastic deformation began to recover, with NIST taking a leading role. NIST researchers developed several new synchrotron X-ray techniques for studying the evolution of dislocation structures *in situ*. NIST researchers also developed a new statistical-physics model of plastic deformation, called "strain percolation theory," that relates the changing mechanical properties to the statistical behavior of the interacting dislocations. Work in both of these areas is continuing.

Building upon NIST's strong experimental and theoretical research program, the NIST team helped develop national and international research in the field by organizing conference workshops and symposia. Over the past few years, research into the fundamentals of plastic deformation has surged. As a result of this renewed international activity, NIST held the International Conference *Dislocations 2000*, the largest dedicated dislocations conference ever held.

Dislocations 2000 was held at NIST on June 19 through 22, 2000. The focused topics covered were "Experimental Techniques and Observations," "Atomic Scale," "Mesoscopic and Multiscale," "Nonlinear and Statistical Approaches," "Size Effects and Strain Gradients," "Dislocation-Interface Interactions," and "Non-Crystalline Dislocations." Nine plenary talks, 30 additional oral presentations and 119 posters were presented. There were 154 registered attendees from 18 countries on 4 continents. The conference proceedings will be published in a special issue of the journal Materials Science and Engineering: A. A total of 107 papers were accepted for publication in this volume. As a result of this success, *Dislocations 2000* will become a conference series, held every three years. The next conference, *Dislocations 2003*, will be held in Europe.

The topics covered at *Dislocations 2000* demonstrate that the current researchers in the field are borrowing extensively from approaches proven effective in other fields of research. Mesoscopic, three-dimensional, many-dislocation computer simulations, numerically intensive atomistic simulations, the application of modern statistical physics, and the introduction of new experimental techniques and methods were recurring themes at the conference. Ambitious attempts are also underway to develop multi-scale models that bridge the length and time scales between atomistics and continuum plasticity. Many of these approaches show great promise for tackling a wide range of many-dislocation problems. In the past, however, little coordination has existed between research efforts. It is hoped that *Dislocations 2000* has provided the needed focus. Additional NIST research has produced major advances in the strain percolation theory of deformation and in developing a completely new X-ray imaging technique, ultra-small-angle X-ray scattering (USAXS) imaging. Although not specifically aimed at dislocations, this new imaging technique is applicable to a broad range of problems, including the deformation of metals.

USAXS imaging is based upon a widely used experimental technique, small-angle X-ray scattering (SAXS), which can provide quantitative, volume-averaged, micro-structural information from bulk specimens. In SAXS, X-rays are scattered at small angles by density variations within the sample. The intensity of the scattering as a function of angle provides information on the size, shape and number distribution of the scattering objects. Our USAXS instrument is located on the UNICAT Sector 33 insertion device beam line at the Advanced Photon Source (the first and only 3rd generation synchrotron in the U.S.). The instrument uses a pair of silicon {111}analyzer crystals that, through multiple Bragg reflection, selects specific scattering angles. Only X-rays scattering from the sample at the selected angle can pass through the analyzer crystals. Very small scattering angles (down to 0.0014°) can be reached using this technique, prompting the use of the name USAXS. USAXS data typically begins 2 to 6 decades below the peak intensity of the transmitted beam and often extends over 8 decades of intensity.

In USAXS imaging, the selected X-rays are used to form an image of the sample. Since the *only* X-rays that contribute to the image are those produced by small-angle scattering, the image is a direct map of where the USAXS beam originates within the sample. Information on the size and shapes of the scattering objects can be obtained by comparing images produced at different scattering angles. Such information can be determined even when the scattering objects are smaller than the spatial resolution of the imaging process! The image contrast does not change during sample rotation about the scattering vector (vertical axis in the lab) and stereo USAXS images have been produced by combining images from two such rotations. In principle, a full 3D tomographic reconstruction should also be feasible.

USAXS imaging was first demonstrated in June, 2000 on polycrystalline copper that was very slightly deformed under tension at 600 °C to produce creep cavities on the grain boundaries. The total volume fraction of cavities was about 0.045 %. Figure 1 shows a view of a cluster of spherical creep cavities obtained at a scattering angle of 0.0019(2)°. Images obtained at a scattering angle of 0.0099(2)° show large collections of much smaller cavities that are not visible in the lower-angle images. The distribution of these voids within the sample cannot be measured using any other existing experimental technique. Analysis of several such images taken with a range of exposure times and scattering angles demonstrates that these smaller voids are disk shaped whereas the larger voids are all roughly spherical.

USAXS imaging is a completely new class of X-ray imaging technique that is remarkably sensitive to the microstructures within a scattering volume. USAXS imaging

Figure 1: USAXS image of creep cavities in copper.

microstructures within a scattering volume. USAXS imaging should prove useful both as an independent imaging technique, and as an important adjunct to SAXS generally. It is likely to find application to a broad range of materials problems in metal, ceramic, polymer and biological systems.

" I am certain that (Dislocations 2000) will have a major impact on developments around dislocation science and its connection to metals engineering. I am certain that it will be seen as a major feather in NIST's cap."

Owen Richmond
Research Director (until 1998)
ALCOA Technical Center

"The work you are doing to develop measurement techniques to study dislocation structures in situ during deformation, use statistical physics methods to develop a microstructure-based model for deformation, understand and quantify friction, and organize the scientific community to work in these and related areas is most relevant to the needs of the sheet metal stamping industry. The industry is just now going through a major advancement in applied physics in that most new die designs are now checked by finite element analysis of how the sheet metal will form. ... As better mathematical representations of these [plastic deformation] behaviors, such as you are developing, become available, they can be put into practice."

Edmund A. Herman
Senior Advisor
Metal Fabricating Division
General Motors Corporation

For More Information On This Topic

Information on the *Dislocations 2000* conference can be obtained from the conference proceedings, to be published by Mat. Sci. & Eng. A, Editors: L. E. Levine, L. P. Kubin and R. Becker (2001).

For information on USAXS imaging, please contact L. E. Levine, G. G. Long or R. J. Fields.

Improving Giant Magnetoresistance Materials by Controlling Interface Growth Processes

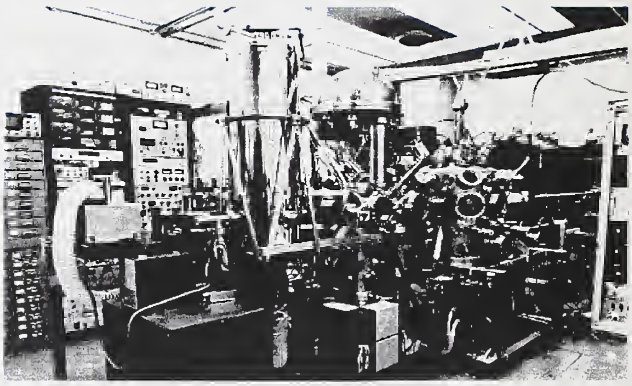
Giant magnetoresistance (GMR) materials already play a key role in computer hard disks and will be incorporated into a variety of consumer products over the next few years. The race to produce the best GMR materials is intensely competitive, and at present it is unclear whether the U.S. or Japan will dominate in this technology in the years to come. As part of a NIST program to improve manufacturing methods of GMR materials, a NIST scientist discovered that GMR materials can be improved significantly if oxygen is used as a surfactant to keep growing interfaces flat during fabrication. This discovery demonstrated the role of specular electron scattering at interfaces on the magnitude of the GMR effect and was quickly used by head manufacturers worldwide to improve GMR. Furthermore, Veeco/CVC, the U.S. company which has 80% of the world market in manufacturing equipment for GMR materials, has adopted control of oxygen during deposition. This NIST discovery is helping to keep U.S. industry in the lead in the field of GMR materials.

GMR spin valves are technological marvels, quickly finding their way into a variety of consumer products. These materials operate by changing their electrical resistance in response to the presence of a magnetic field. This property makes them useful as detectors of magnetic fields. Many other types magnetic-field detectors exist, but they do not have the highly attractive features of GMR materials. GMR magnetic field detectors can be designed to be highly sensitive, microscopically small, and ultrafast. In addition, they are cheap, rugged, and highly reliable. As a result, in many applications no other present technology is as promising as GMR materials.

Some of the most immediate applications are in computer hard-disk drives and random access memory, magnetic sensors for automation of factory production lines with position-sensing robots, antilock braking systems for cars, "smart" shock absorbers, vehicle-counting systems, and currency sorting and counting based on magnetic inks. A much longer list of applications is likely to develop over the next few years.

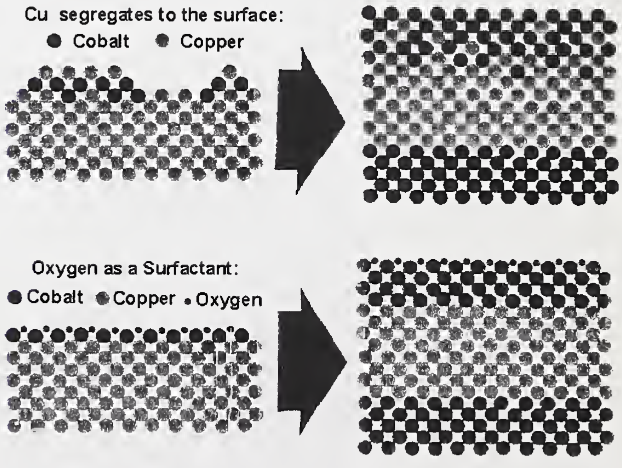
The many applications and high performance of GMR materials make them a matter of great economic significance. A race is now underway to develop the best GMR materials. Although there are small efforts elsewhere, the U.S. and Japan currently lead the competition. At this point it is not clear which country will dominate this technology. The rapid rate of change is forcing U.S. companies to rush GMR materials into products and onto the market, and to devote relatively little effort to scientific research on how to improve GMR materials. Japanese companies, however, do not follow this pattern, and most of the long-range research in GMR materials is presently being done in Japan. This situation puts the current U.S. lead in GMR products in jeopardy.

To assist U.S. industry, NIST set up a major new research program specifically aimed at providing the scientific understanding and measurement capability needed to allow U.S. industry to make the best GMR materials in the world. This program was centered on a new facility, known as the Magnetic Engineering Research Facility (MERF), which is the most elaborately instrumented magnetic thin-film production facility ever constructed.



Magnetic Engineering Research Facility

Research at the MERF has identified an important new approach to manufacturing GMR materials in which oxygen is used as a surfactant to improve the crystallinity and smoothness of GMR thin films. The figure below illustrates how oxygen acts as a surfactant.

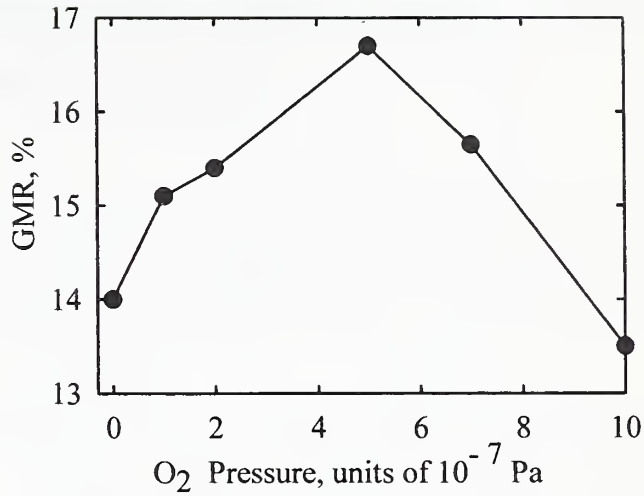


Effect of oxygen on the deposition of cobalt on copper.

The active region of a GMR film is a layered structure of Co and Cu. When such a structure is made without a surfactant, the copper atoms tend to segregate to the surface when a Co layer is deposited on a Cu layer due to the lower surface free energy of Cu. These Cu atoms gradually get left behind in the growing Co film to leave an intermixed region which degrades the GMR performance of the system. However, this intermixed region is suppressed when the structure is prepared with a layer of oxygen atoms present on the surface. This effect occurs because oxygen atoms bond more strongly to Co than to Cu. As Co is deposited it is energetically favorable for the Co atoms to remain at the surface to form the maximum number of strong Co-oxygen bonds, and this effect suppresses the segregation of Cu atoms to the surface. Fortunately, the oxygen atoms are mobile and float to the growing surface as more Co is deposited, leaving behind an atomically sharp Co\Cu interface with almost no oxygen impurities. The sharp interface gives a larger value of the GMR since the intermixed region tends to scatter electrons diffusely. The plot to the right shows how the GMR varies with the pressure of oxygen present during the GMR film deposition. The best result occurs for an oxygen pressure of $5x10^{-7}$ Pa. Too much oxygen reduces the GMR by forming Co oxide. The optimum effect occurs only over a narrow range of oxygen pressure.

Last year, the results of this work were presented to the staff at Veeco/CVC in Fremont, CA, which is the world's largest manufacturer of GMR production equipment. The staff expressed much interest in this work.

This year we learned that Veeco/CVC was able to reproduce these NIST results and has incorporated this process in their line of GMR manufacturing systems. Since Veeco/CVC has 80 % of the world market in GMR manufacturing systems, this NIST advance is helping to keep the U.S. in a leading role in GMR technology.



Improved performance of a GMR device results from use of a carefully selected oxygen pressure.

"In 1996 Bill Egelhoff conducted and published a set of experiments in which he capped the spin valve with a thin oxide layer. This layer acted to reflect strongly the incident electrons sending then back through the spin valve and making it act like a four-magnetic-layer system rather than a two-layer system, with a resulting increase in magnetoresistive sensitivity. That particular effect has now been incorporated into the latest generation of spin valves by virtually all the major read head manufacturers. ... all this improvement in spin valve sensors is directly traceable to Bill Egelhoff's original investigations. A $100B hard disk drive industry has been impacted in a major way by Bill Egelhoff's seminal experiments."

Robert L. White, Director
Center for Research on Information Storage Materials

Stanford University

For More Information On This Topic

"Oxygen as a Surfactant in the Growth of GMR Spin Valves," W. F. Egelhoff, Jr., P. J. Chen, C. J. Powell, M. D. Stiles, R. D. McMichael, J. H. Judy, K. Takano, and A. E. Berkowitz, J. Appl. Phys., 82, 6142 (1998)

William F. Egelhoff, Jr.

Large Uniaxial Anisotropy for Thin Film Magnetization Pinning

The industry wide trend of 60% per year increase in bit density for hard disks creates increasing demands on the materials used in these products. In particular, the increased demand for sensitivity in read heads has led to higher current densities and hotter operating temperatures. Additionally, as read heads become smaller to accommodate narrower recorded tracks, stronger pinning schemes are required to control the magnetization in the thin film multilayer structures. In the course of studying exchange biasing, a common method for magnetization pinning that involves coupling to an antiferromagnetic film, we discovered that very large anisotropy fields can be produced in a magnetic film by obliquely depositing a tantalum underlayer.

The materials that are used in the recording heads of modern computer hard drives must satisfy an ever more demanding set of requirements. As areal density grows at an industry – wide rate of 60% per year, the magnetic signal from each recorded bit becomes smaller and smaller. Modern read heads use the giant magnetoresistance effect which can produce resistance changes of up to nearly 20% in special structures called spin valves.

The working part of a spin valve consists of two magnetic thin films, typically cobalt or Permalloy, each a few nanometers thick, separated by a 2.4 nm nonmagnetic film, typically copper. When the magnetization vectors of the two films are parallel, the electrical resistance is low, and when they are antiparallel, the resistance is high. To achieve this high resistance antiparallel state, a pinning scheme is needed to hold the magnetization vector in one film, the "pinned" film, while the other film, the "free" film, responds to applied fields.

A good pinning scheme must be able to prevent reversal of the pinned film in up to 50 mT of applied field, and it must be able to do this continuously at temperatures of 100 °C to 150 °C and up to 300 °C for thermal asperities such as head-disk collisions.

The common method for pinning has been the use of antiferromagnetic exchange bias layers, typically ten's of nanometers thick. A large number of antiferromagnetic materials have been investigated for exchange bias pinning, and the majority of them share the undesirable property that the pinning is too weak and the Neel temperature is too low, meaning that the pinning gets weaker as the head gets warm. A notable exception is NiMn, which has strong pinning and a high Neel temperature, but which requires an annealing step to generate the correct crystal structure.

In the course of studying exchange bias, we discovered that a thin underlayer of tantalum, obliquely deposited, has a very anisotropic roughness (See Figures 1 and 2) that can generate very large uniaxial anisotropy fields in a magnetic layer deposited on top.

The anisotropy produced by obliquely sputtered tantalum underlayers has a number of desirable properties:

- The anisotropy is strong, see Figure 3. For a comparable pinning field, the Ta underlayer is much thinner than a NiMn exchange bias layer.
- The anisotropy is uniform. The dispersion in hard axis directions has been measured less than 2.5°, and the relatively low ferromagnetic resonance linewidth of the Ta-pinned layer indicates good homogeneity. In contrast, exchange bias pinning tends to be very inhomogeneous.
- Good thermal stability. Ta has a very high melting point, and since the anisotropy is produced by magnetostatic effects, its thermal stability is as good as the thermal stability of the magnetization itself.
- Corrosion resistance and chemical compatibility. Normally deposited tantalum is already used as an underlayer to promote {111} texturing. Ta is compatible with current manufacturing processes.
- Layer selectivity of anisotropy. In a spin valve sample, the free layer has an anisotropy field of only 13 mT while in the pinned layer the anisotropy field is 160 mT. See Figure 4.

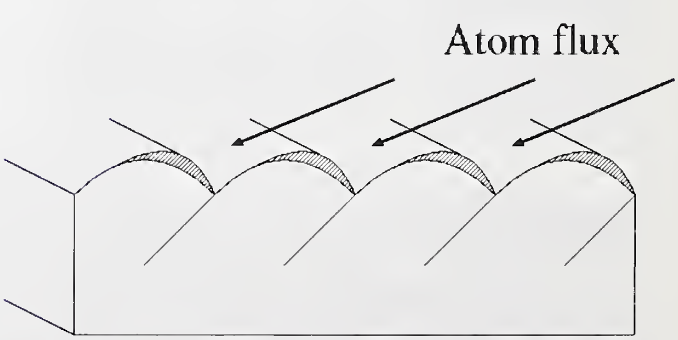


Fig. 1. Grooves are shaded from atoms arriving obliquely, causing ridges perpendicular to the flux direction to be

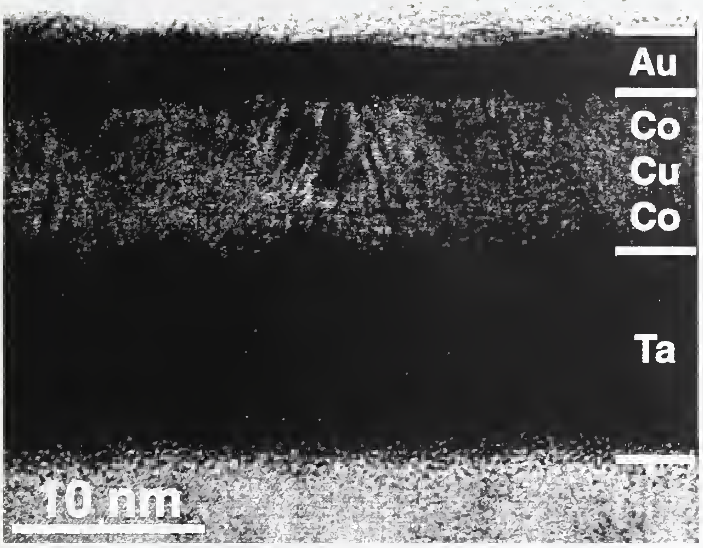


Fig. 2. Microstructure of a Co/Cu/Co spin valve deposited on 7.5 nm of Ta deposited 60° off normal. Note the corrugated interface between the Ta and the Co.

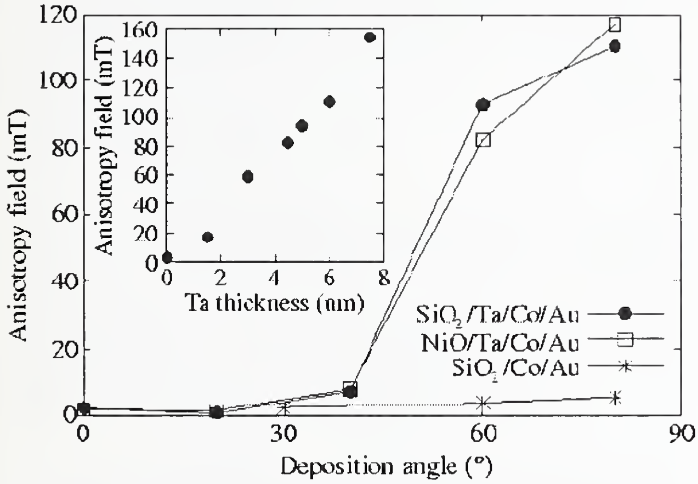


Fig. 3. Anisotropy field for 5 nm Co deposited on 5 nm Ta as a funtion of Ta deposition angle. For the sample labeled SiO_2/Co/Au, the Co was sputtered obliquely. Inset: Anisotropy field for 5 nm Co films as a function of Ta underlayer thickness, the Ta deposited 60° off normal.

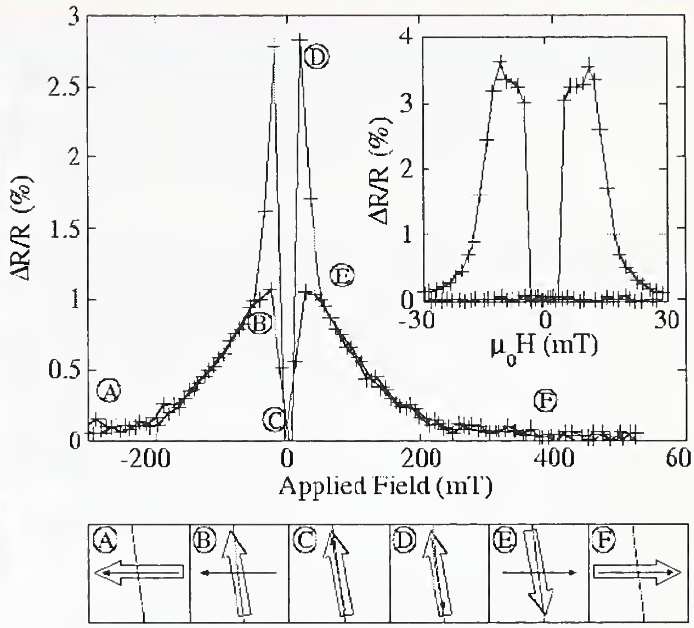


Fig. 4. Magnetoresistance of a spin valve measured with fields applied near the hard axis, and in the inset with fields applied near the easy axis. Below, a series of panels illustrating the magnetization configuration deduced from the hard axis data for the free film (thin solid arrow) and the pinned film (open arrow).

For More Information On This Topic

R. D. McMichael, C. G. Lee, J. E. Bonevich, P. J. Chen, W. Miller, and W. F. Egelhoff, Jr., "Strong anisotropy in thin magnetic films deposited o obliquely sputtered Ta underlayers. J. Appl. Phys, **88**, 5296 (2000).

Bob McMichael, John Bonevich, and Bill Egelhoff

Electrodeposited Copper for On-chip Interconnects: Tools for the Microelectronics Industry

The introduction of copper metallization and low dielectric constant materials into chip manufacture represent the most difficult interconnect challenges of modern microelectronics. Current state-of-the-art chips have interconnects, or on-chip "wiring," as narrow as 180 nm with height:width ratios as great as five to one. The filling of such trenches with copper can currently be accomplished by electrodeposition, but roadmaps for the semiconductor industry state needs for trenches as narrow as 50 nm with a 10:1 aspect ratio. Researchers at NIST are providing the fundamental understanding to enable development of techniques to meet these challenging needs. Measurement tools developed at NIST addressing initial needs of the microelectronics community are already in use by industry.

The semiconductor industry has recently made a major shift in materials used for interconnects, or on-chip "wiring," in integrated circuits. After decades of using aluminum as conductors, a switch to copper has been made to take advantage of an inherently lower resistivity. Electrodeposition has been found to be the best means to deposit copper in the narrow, deep trenches used as circuitry, in that "superconformal" deposition that fills very narrow trenches without porosity can be accomplished.

Streamlining the development of electrodeposition baths. An electrolytic copper linewidth of 180 nm is now the state of technology in IC fabrication. Extension to the much narrower and deeper lines needed in the next generation of IC requires industrial development of new electrolytes and deposition schemes. Development of plating baths able to deposit in trenches with aspect ratios (height/width) as high as 10:1 is limited by the need to do time-consuming, resource-intensive evaluations with actual nano-structures. These experiments typically require microstructural characterization by electron microscopy on an individual basis. The NIST efforts address metrology needed for superconformal deposition while minimizing the most time-consuming experimental work.

Industry has reported performance of baths which allow current chip manufacture, but these are proprietary plating baths with undisclosed compositions. NIST researchers have developed and reported a copper plating bath that produces copper films with recrystallization and superfill behavior identical to that reported by industry. The principal additives in this bath are NaCl, an organic compound known as MPSA, and polyethylene glycol (PEG). The steady-state current-potential (i-E) characteristics for copper deposition from electrolytes containing various combinations of Cl, PEG, and MPSA are shown in Figure 1: the addition of Cl-PEG provides inhibition of the copper deposition reaction while the combination of Cl-MPSA leads to an acceleration of the deposition rate. Note that there is a hysteresis loop in the trace of copper deposition in the electrolyte containing the ternary additions. No hysteresis is exhibited in the additive-free electrolyte or any of the binary mixtures. Experiments at NIST show that such hysteretic behavior by itself indicates an ability to fill narrow trenches, eliminating the need to do more extensive experimental development (Figure 2). The Cl-PEG-MPSA electrolyte (a) yields superconformal copper deposition into trenches between 500 and 90 nm in width with an aspect ratio ranging from 1:1 to ~ 6.6:1. In contrast, similar experiments using either an additive-free electrolyte, or an electrolyte containing the binary combinations Cl-PEG (c) or Cl-MPSA (b) resulted in the formation of a continuous void in the center of the trench.

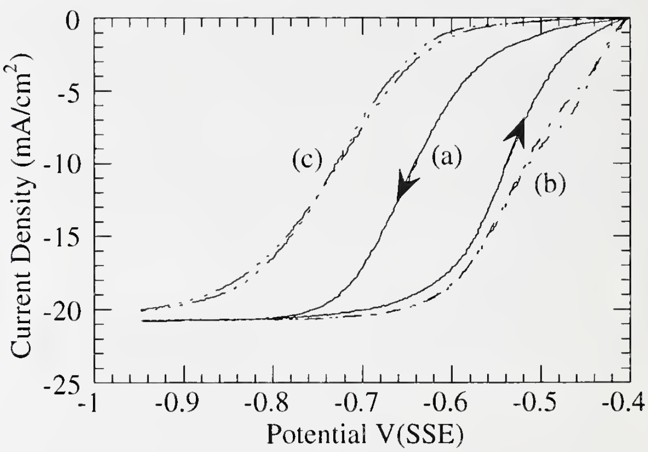


Figure 1. i-E curves for copper deposition on a stationary copper disc electrode in a plating bath containing (a) NaCl + MPSA + PEG, (b) NaCl + MPSA, (c) NaCl + PEG. Note the hysteresis exhibited with three additions in combination. Such hysteresis correlates with ability to fill narrow trenches for interconnects.

Room Temperature Recrystallization of Filling and Non-Filling Electrolytes. The microelectronics industry reports a recrystallization of electrodeposited copper which occurs in the first 24 hours after deposition. This recrystallization is important to device performance since it causes the resistivity to drop approximately 20 %, improving device performance. We have found that copper electrodeposits from the electrolyte containing the ternary Cl-PEG-MPSA additives exhibit recrystallization and an associated decrease of electrical resistivity at room temperature. No room-temperature recrystallization is exhibited by electrodeposits from the additive-free electrolyte or any of the binary mixtures, as seen in Figure 3.

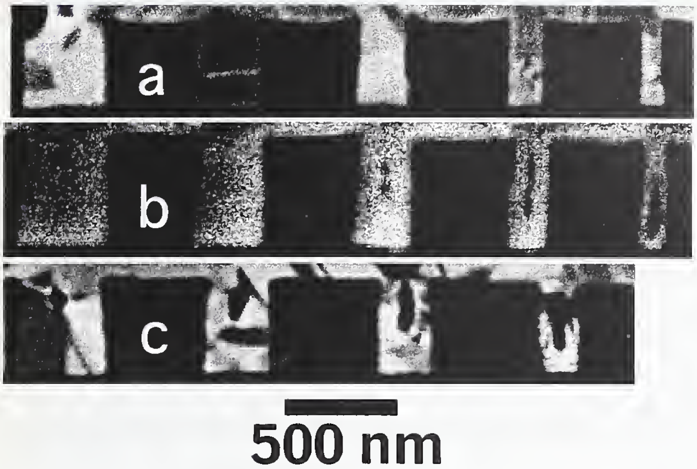


Figure 2. FIB images of copper electrodeposited from an electrolyte containing (a) NaCl + MPSA + PEG, (b) NaCl + MPSA, and (c) NaCl + PEG. The trenches were patterned using electron beam lithography. Note that complete filling of the narrowest trenches, 100 nm, is void-free only with the ternary addition, (a), which also shows hysteresis in Figure 1 and a recrystallization response in Figure 3.

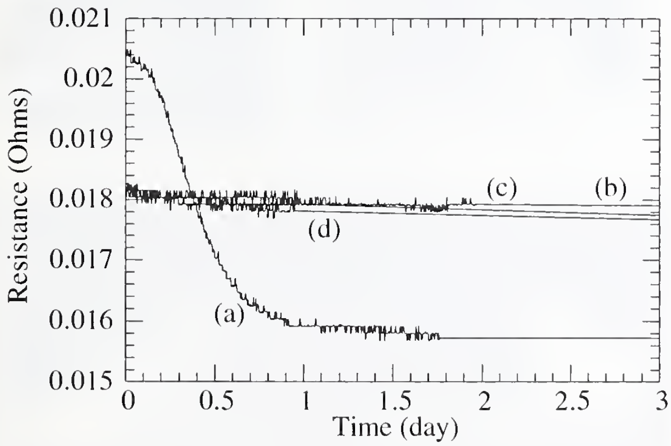


Figure 3. In-situ film resistance as a function of time for 1 μm thick copper films electrodeposited from a solution containing (a) NaCl + MPSA + PEG, (b) NaCl + MPSA, (c) NaCl + PEG and (d) no additives. The desired drop in resistivity occurs only in the case of the ternary additions.

This research has resulted in accomplishments and impacts of consequence to the microelectronics industry. Eight presentations have been given in public forums attended by industry covering the following developments:

- Demonstrated a one-to-one correlation between i-E hysteresis,
  resistance drop and superfill efficacy of electrolytes.
- Organized a cross-laboratory effort which validated this tool.
- Developed the first non-proprietary bath that yields superfill down to dimensions of 90 nm and aspect ratios of 6:1.
- Demonstrated the impact of geometrical leveling in studies using non-vertical sidewalls.
- Demonstrated that inhibition alone is *not* sufficient to ensure superfill, in direct contradiction to current thinking and models.
- Demonstrated and published an electrolyte that exhibits superconformal deposition.

Feedback from the electrochemical bath industry is extremely positive – companies are beginning to supply the NIST-developed measurement technology in commercial software.

In the coming year we will address several short and long term objectives:

- Develop measurement tools to study competitive adsorption on copper using vibrational spectroscopy (with the Chemical Science and Technology Laboratory)
- Develop the mathematics and coding to model electrodeposition using a phase field model.
- Establish a model of the role of adsorbates in superconformal deposition.
- Demonstrate extendibility to smaller dimensions.
- Demonstrate feasibility with simpler bath chemistries
- Pursue further interactions with chemical and bath monitoring industries to incorporate NIST-developed measurement tools.
- Investigate need for standard reference materials in this new area, such as composition standards for electrolytic copper.

Through this work, researchers at NIST are providing the electrodeposition community with a better understanding of the mechanism by which organic addition agents lead to superconformal deposition of sub-micron features. It is anticipated that this will lead to the development of on-line monitoring tools that will allow industry to determine additive efficacy and consumption in commercial copper plating baths.

For More Information On This Topic

T.P. Moffat, J.E. Bonevich, W.H. Huber, A. Stanishevsky, D.R. Kelley, G.R. Stafford, and D. Josell, "Superconformal Electrodeposition of Copper in 500-90 nm Features", J. Electrochem. Soc. 147, p. 4524 (2000).

Gery Stafford, Thomas Moffat, and Daniel Josell

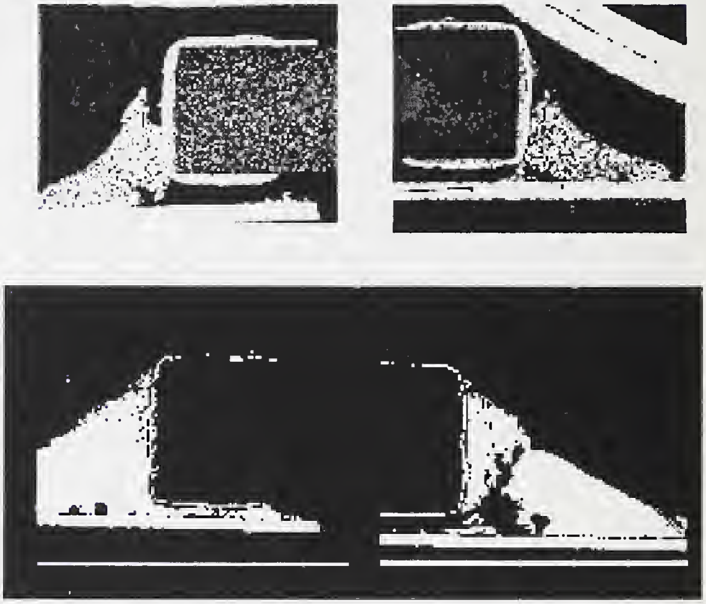
Lead-Free Solders:

Tools for the Microelectronics Industry

Increasing global concern about the environment is bringing regulatory and consumer pressure on the electronics industry in Europe and Japan to reduce or completely eliminate the use of lead in products. As Europe and Japan move toward lead-free electronics, North American electronics manufacturers must prepare to do the same. In 1999, the National Electronics Manufacturing Initiative (NEMI) formed its Lead-Free Task Force with the goal of helping the North American electronics industry develop the capability to produce lead-free products by 2001. NIST has a continuing leadership role in this task force, this year providing definitive, timely materials data and critical analyses needed for evaluating candidate solders, which led to the selection of new Pb-free, industry-standard solders.

The infrastructure for electronics assembly has, from its infancy, been based on tin-lead eutectic solder, a mixture of tin and lead in the ratio of approximately 63/37 (by weight) that melts at 183 °C. Since legislation to eliminate lead from electronics manufacturing was first proposed in the early 1990's, many of the major U.S. electronics manufacturers have been concerned that their ability to produce durable, reliable, safe, and affordable electronic products might be compromised with lead-free alternatives to Sn-Pb solders or other interconnection materials.
To determine the manufacturing and in-use performance of lead-free solders, a U.S. study was carried out from 1993-1997 under the auspices of the National Center for Manufacturing Sciences (NCMS) with project participants including AT&T/Lucent Technologies, Ford Motor Company, General Motors (GM) —Hughes Aircraft, GM—Delco Electronics, Hamilton Standard Division of United Technologies Corporation, National Institute of Standards and Technology (NIST), Electronics Manufacturing Productivity Facility (EMPF), Rensselaer Polytechnic Institute, Rockwell International Corporation, Sandia National Laboratories, and Texas Instruments Incorporated. In the NCMS Lead-Free Solder Project, following down-selection of seven candidate alloys using materials property data, full scale manufacturing and reliability trials were carried out. NIST had a leadership role in formulating the down selection criteria, identifying properties related to manufacturing and reliability performance, and identifying techniques needed to obtain this property data. NIST also coordinated the final analysis of the data, the determination of conclusions and recommendations, and the writing of the NCMS final report. The results of the data evaluation, recommendations, and conclusions were reported by NCMS in 1997, and the full collection of data was released publically on CDROM in 1998.

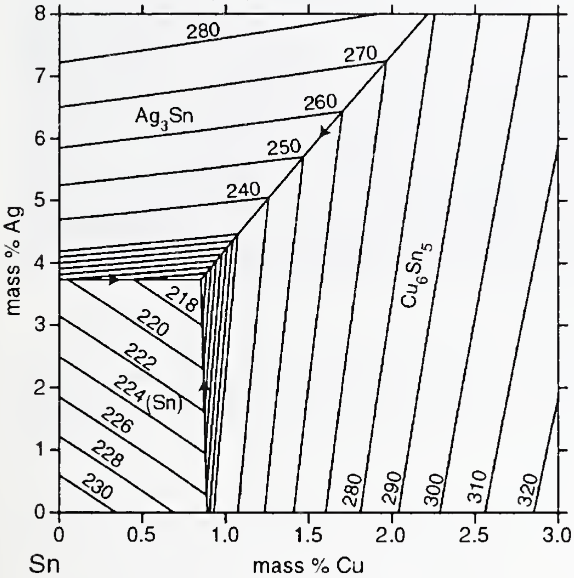
In early 1999, the issue of lead-free soldering re-emerged in Japan and the European Union. From the NCMS project results, analysis, and conclusions, and additional studies in the U.S., E.U., and Japan, our knowledge of the manufacturing, product performance, and reliability of lead-free solders was sufficient for us to understand the major roadblocks in the conversion to lead-free interconnections. In 1999, the National Electronics Manufacturing Initiative (NEMI) formed its Lead-Free Task Force with the goal of helping the North American electronics industry develop the capability to produce lead-free products by 2001. We have had a continuing leadership role in this task force, this year providing definitive, timely materials data and critical analyses needed for evaluating candidate solders which led to the selection of new Pb-free, industry-standard solders.



Cross sections of Sn/Pb (above) and Sn/Ag (below) eutectic solders after thermomechanical fatigue. Failure modes depend on solder alloy and fatigue conditions. (From NCMS study.)

With Solectron, we led the Alloy Selection Subgroup in examining the possible alternatives based on manufacturability and reliability. (This is described in an article in Circuit Assembly, May 2000, coauthored by Solectron, NIST, and Motorola.) NIST measurements of the Sn-Ag-Cu phase diagram were critical to the selection of the new "national standard" solders by the NEMI Lead-Free Task Force. We continue to lead this subgroup with our principal role being the analysis of materials, manufacturing, and reliability data as it is generated by industry, academia, and government labs and coordinating research projects obtaining data important to NEMI.

Of particular note this year is NIST's experimental and evaluation of the Sn-Ag-Cu phase diagram, the system from which NEMI was choosing the standard solder. Major discrepancies in the literature led to disagreements on the composition of the lowest melting alloy in the system, the ternary eutectic (A low melting point is needed to ensure that the alloy melts during assembly reflow.) Based on NIST expertise in phase transformations, NIST scientists designed and performed critical experiments to resolve the discrepancy in a timely manner so that alloy selection could remain on schedule for November 1999. This task also required building an ultra sensitive DTA and modeling the thermodynamics of the phase transformations in this system to identify the sources of inconsistencies in existing data. The results of this study were published in the ASME Journal of Electronic Packaging.



Liquidus projection of the Sn-rich corner of the Sn-Ag-Cu ternary system. The present research has provided the definitive study of this important and controversial system.

NIST has served as a primary advisor to the packaging industry in this activity as a result of NIST's extensive research with the NCMS Lead-Free Solder Project. NIST coordinated the final analysis of the data, the determination of conclusions and recommendations, and the writing of the NCMS final report. It has been widely acknowledged that this provided the first comprehensive analysis of the manufacturing and performance of lead-free solders.

In recognition of NIST's role in making the packaging industry aware of the benchmark manufacturing and reliability data from NCMS and in interpreting that data for the community, IPC, the electronic packaging industry trade association representing over 2,600 companies, awarded NIST a special recognition award for lead-free solder research and for assisting IPC in organizing the IPC International Summit on Lead-Free Assemblies and the IPC Lead-Free Solder Roadmap meeting (October 1999). In addition, the technical paper by NIST presented at the International Summit was voted by the 400+ attendees to be the best technical paper of the Summit.

"NIST personnel brought unique skills and expertise to both NCMS projects [Lead-Free Solder Project, and the follow on project , High Temperature Fatigue Resistant Solders]. Without the support from NIST, both these projects would have extended over a longer period of time and would have been more costly to the project's industrial partners. In the case of the Lead-Free Program, a critical evaluation of the data would not have been done without NIST's leadership."

Duane Napp, NCMS
Program Manager

"As a result of NIST's involvement, I feel NEMI has been successful in responsibly leading the effort to understand the implications of lead-free assembly in a way that is benefiting the entire electronics assembly industry."

Edwin Bradley, Motorola
NEMI Task Force Leader

"We have been extremely pleased with NIST's contributions to the NEMI lead free project, and hope that you can continue to support our efforts in a somewhat sensitive and controversial effort to find reliable alternatives to SnPb solders."

Ronald W. Gedney , NEMI
Vice President, Operations

For More Information On This Topic

NCMS Lead-Free Solder Project Final Report, NCMS, 1998, and CDROM. 1998.

Carol Handwerker and Frank Gayle

The Solder Interconnect Design Team: Helping Industry Solve Failure and Design Challenges

The manufacture of printed circuit boards involves the correct application of thousands of solder interconnects. Failure of any of these joints due to short or open circuits can render the package useless or require expensive reworking. The Solder Interconnect Design Team provides its members, and the entire microelectronics industry, with modeling tools for calculating the shape of solder joints, a fundamental property required for any accurate subsequent modeling of the electronic package. Now at the completion of its work, the Team continues to maintain a WWW site of solved problems, and remains a resource for this community.

Founded in 1994, NIST Solder Interconnect Design Team (SIDT) was the first active working group within the NIST Center for Theoretical and Computational Materials Science (CTCMS). The SIDT was formed to address several pressing issues in the design and fabrication of circuit boards. This multi-billion dollar industry is highly dependent on solder interconnects as the primary method for attaching chips to a circuit board. Over the past six years, in partnership with both academic and industrial researchers, the team has established an agenda for solving modeling problems concerning equilibrium solder joint shapes and the resulting thermal and mechanical properties of the formed joint.

The goal of the SIDT is to provide the industrial community with a suite of useful software tools for solder interconnect design, and to provide a set of standard reference problems. With this in mind, the SIDT actively supports the development of modeling tools based on the public domain program Surface Evolver, which has been shown to be extremely effective for computing equilibrium solder meniscus shapes (see figure). Before the advent of the SIDT, it required significant mathematical expertise to use this software. In order to make the software usable in an industrial environment, the team formulated the representations of the shape and the boundary conditions so they were transparent to the user. They also performed critical tests and validation of the modeling software using precision measurements.

The SIDT has established and fostered an industry-academia - government laboratory working group on solder joint design for the exchange of information and collaboration on topics of special importance. The SIDT acts as a forum for discussion of Evolver calculations and models and, through the CTCMS, provides access to software through the Internet/WWW. Software downloads from the SIDT website number in the thousands per year. In addition, the SIDT also seeks to hold workshops and symposia to promote collaboration and bring the community toward a consensus on the features required for a useful solder modeling system.

The modeling tools promoted by the SIDT enable users to predict the shape of the liquid surface of molten solder in contact with substrates. This shape depends on the surface energy of the molten solder and the contact angle with the substrates. These tools help manufacturers select electronic component geometries and assembly processes that minimize the probability of forming short or open circuits during assembly and predict the reliability of the resulting solder joints. Solder drops are also used for alignment of optical fibers and optical devices, and this software enables manufacturers to compute the forces exerted by solders on the optical devices and to design systems which will establish and preserve critical alignment.

In recognition of its efforts, in 1999 several core members of the SIDT received the Federal Laboratory Consortium Award for Technology Transfer

The SIDT-promoted technology allows electronic devices to be designed to be smaller, lighter, cheaper and more durable, and moreover, failures of assembly processes can be analyzed and corrected far more easily, saving time and money. For example, Motorola needed to solve a particular problem with their two-way radio applications. Namely, "a serious, urgent problem was encountered with electromagnetic shield cans falling off from the PWBs as soon as the oven temperature exceeded the solder melting temperature. In spite of an elaborate, experimental based effort by the product group, the defect rate was still unacceptable (around 2 %). Typically, any modification of the production tooling and pad redesign will take anywhere from 2 to 6 weeks. To investigate the root causes of this fall-off phenomenon, [we simulated] the unbalanced surface tension in the molten solder, which caused the floating/twisting problem... Surface Evolver played a very important role in helping our engineers understand the root causes of the floating/twisting problem. This problem was completely eliminated after a new design, based on the simulation results, was implemented. This effort allowed products to be shipped 2 months earlier than what was scheduled." (X. Wu, Motorola)

Surface Evolver calculation of the geometry of solder wetting a gull-wing lead. The shape of the liquid surface depends on the surface energy and the contact angle with the substrate.

"The introduction of the Surface Evolver software tool into Motorola's electronic packaging applications has proved that it is a very useful tool for eliminating any solder defect for reflow processing. Time and time again, it has reduced design cycle time, cost of tool or PWB modifications, and cost of prototyping and testing. Right now, there are about 10 Evolver users in Motorola,"

-- Dr. Xiaohua Wu
Senior Staff Engineer, Motorola

"Results from the SIDT workshops have provided guidance and root cause analysis (to Ford) to achieve projected manufacturing success,"

-- Dr. Tsung-Yu Pan
Ford Motor Company

Participants over the past few years have included individuals representing a large number of organizations. Organizations represented at the various SIDT workshops include Edison Welding Institute, DEC, Motorola, BOC Gasses, Ford Motor Co., Lucent Technology, AMP, Rockwell, Delphi Automotive Systems (Delco), Texas Instruments (Raytheon), Susquehanna University, University of Colorado, University of Massachusetts, University of Wisconsin, University of Loughborough, Lehigh University, University of Greenwich, Marquette University, RPI, University of Minnesota and Sandia National Laboratory.

For More Information On This Topic

http://www.ctcms.nist.gov

J. Warren and C. Handwerker

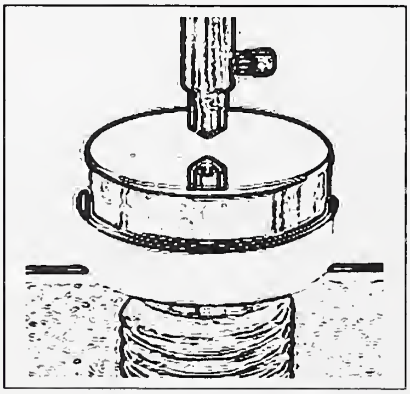
Recommended Practice Guide: Rockwell Hardness Measurement Of Metallic Materials

Throughout industry, the Rockwell hardness test continues to be applied as a tool for assessing the properties of a product while the acceptability tolerances have become tighter and tighter. To achieve meaningful measurement results in these circumstances, it is important that the user make every effort to reduce measurement errors. Adhering to "good practice" procedures when performing Rockwell hardness measurements and calibrations is a critical step to reducing measurement errors. A Recommended Practice Guide has been developed to help users of the Rockwell hardness test reduce their measurement errors and improve their measurements.

Worldwide adoption of the Rockwell hardness test has likely resulted from the many advantages provided by the test method. The test is fast, inexpensive and relatively non-destructive, leaving only a small indentation in the material. The simplicity in the operation of a Rockweil hardness machine has provided the added advantage that Rockwell hardness testing usually does not require a highly skilled operator. By way of correlation with other material properties, the Rockwell hardness test can provide important information about metallic materials, such as the tensile strength, wear resistance, and ductility.

The test is generally useful for material selection, for process and quality control, and for acceptance testing of commercial products. Consequently, in today's manufacturing facilities, Rockwell hardness machines can be found in use in almost every testing environment, from the hot, oily surroundings of some manufacturing facilities, to environmentally controlled metallographic and calibration laboratories.

Since its development, the popularity of the Rockwell hardness test has steadily grown. The test continues to be applied as a tool for assessing the properties of a product while the tolerances on the acceptable material hardness have become tighter and tighter. In many cases, the once thought of manufacturing tool has developed into a metrological instrument. To achieve meaningful measurement results in these circumstances, it is important that the user make every effort to reduce measurement errors. Adhering to "good practice" procedures when performing Rockwell hardness measurements and calibrations is a critical step to reducing measurement errors.



A Recommend Practice Guide has been prepared to assist users of the Rockwell hardness test in achieving better measurement results by reducing errors. The purpose of this Guide is not to specify the requirements for conducting a Rockwell hardness test. Test method standards published by national and international standards writing organizations, such as the American Society for Testing and Materials (ASTM) and the International Standards Organization (ISO), provide specific requirements and procedures for Rockwell hardness testing. The intention of the Guide is to explain the causes of variability in Rockwell hardness test results and to supplement the information given in test method standards with good practice recommendations. Although this Guide is directed more towards the users of Rockwell hardness having the greatest concern for accuracy in their measurements, much of the information given is also applicable for users only requiring test results to be within wide tolerance bands, where high accuracy is not as critical.

The guide also provides recommendations for conducting verifications of Rockwell hardness machines based on the procedures specified by the test method standards. Some procedures recommended by this Guide exceed current requirements of the test methods, however they can be very useful in helping to determine the limit sources of measurement error.

Two extremely important issues covered in the Guide relate to test cycle time and recent changes in the HRC hardness scale. Figure 1 shows the decrease in hardness with increasing force dwell time. Industrial measurements of hardness are often done in the shortest time possible, while calibration laboratories choose longer times in order to achieve the highest possible accuracy. The graph in Figure 1 provides guidance in optimizing the dwell for the desired purpose and alerts the user to potential problems.

TOPICS COVERED IN THE GUIDE

THE ROCKWELL HARDNESS TEST
- Significance of the test
- Rockwell indentation test principle
- Rockwell hardness scales
- Rockwell hardness number
- Test method standards

TEST PROCEDURE
- Choosing the appropriate Rockwell scale
- Test surface preparation
- Rockwell hardness testing machine
- Hardness measurement

REFERENCE TEST BLOCK STANDARDS
- Primary reference test blocks
- Secondary reference test blocks
- Use of reference test block standards

VERIFICATIONS OF ROCKWELL HARDNESS MACHINES
- Direct verification
- Indirect verification
- Correcting measurement biases

MONITORING TEST MACHINE PERFORMANCE
- Reproducibility
- Daily verification

REDUCING MEASUREMENT DIFFERENCES AND ERRORS
- Reduce machine component operating errors
- Verify machine measurement performance
- Measurement locations

TRACEABILITY, ERROR, AND UNCERTAINTY
- Traceability
- Measurement error
- Uncertainty

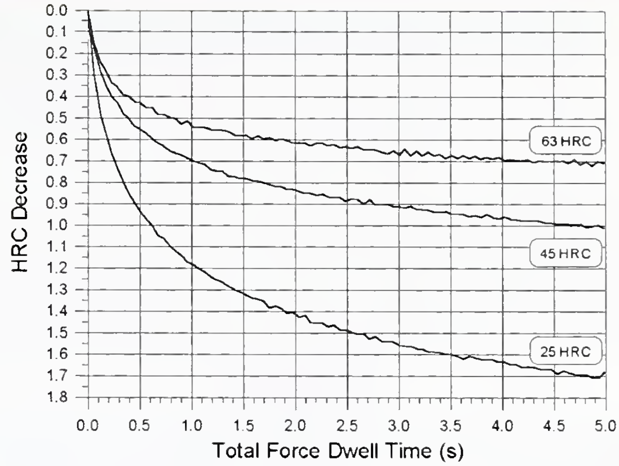


Figure 1. Relationship between the total force dwell time and the HRC measurement value for steel test blocks at three hardness levels.

"NIST involvement in Rockwell hardness has been one of the most significant steps in creating a uniform approach to using the test. This has been achieved through the use of NIST HRC SRMs that commercial testblock manufacturers use as the standard. This national standard has promoted an even playing field in which customers can rely on hardness values from one industry to another on a daily basis.

Industry in the US needs NIST to be its international spokesman for measurements. Recently discussions have been recently held for determining an international hardness standard. While customers in the US often feel comfortable comparing measurements amongst themselves, foreign countries are accustomed to dealing on governmental levels. This is a niche only NIST can fill."

Robert A. Ellis
Quality Manager
David L. Ellis, Inc.
Manufacturer of Secondary Hardness Standards

For More Information On This Topic

S.R. Low, *Recommended Practice Guide: Rockwell Hardness Measurement of Metallic Materials*, NIST Special Publication 960-5, December 2000.

Sam Low, John Song, Walter Liggett

Phase Field Modeling of Solidification and Grain Boundaries: NIST as a World Leader

Phase field modeling allows researchers to develop thermodynamically realistic models of materials and determine the evolution of microstructures within these systems. Avoiding the difficult computational task of tracking interfaces during transformations, phase field methods have provided the research community with a powerful new tool to solve materials science problems in a host of new areas. At NIST, phase field methods have been applied to the areas of solidification and grain growth with great success. Investigations into additional applications such as electrodeposition, stress, sintering, coupling to fluid flow, and crystallization of biological macromolecules are underway, and show great promise for the future.

For the last decade, Materials Science and Engineering Laboratory researchers, in collaboration with scientists from Information Technology Laboratory and universities around the world, have been at the forefront of a new method for modeling solidification microstructures known as the *phase field method*. This technique allows scientists to use the fundamental principles of the thermodynamics of phase transitions to model the development of microstructures within a material undergoing processing. For example the figure below shows the solidification microstructure of a binary alloy. The gray-scale shows the concentration of copper in a nickel matrix. This work was recognized for its potential impact in a Nature magazine News & Views write-up (11 May 1995).

The above example suffers from the obvious limitation that it is only two dimensional. Thus, in collaboration with ITL massively parallel computer calculations were undertaken to extend the model to three dimensions, as is shown in Figure 2.

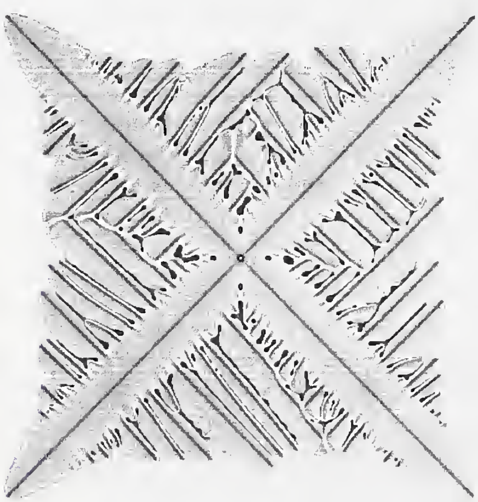


Figure 1: Two dimensional Phase field calculation of a nickel-copper dendrite

Figure 2: 3D phase field calculation of a binary alloy dendrite

These calculations have several advantages over previous methods of simulating solidification pheomena:

- The ease with which complex shapes can be determined.
- The lack of *ad hoc* physical assumptions.
- The ease of implementation on a computer.
- The remarkable variety of physical phenomena which can be modeled with a small set of equations.

In order to intelligently model the processing of materials formed by solidification one must consider the effects of the collision of variously oriented crystals impinging to form grain boundaries. Grain boundaries are of great interest to the materials scientist, as they ultimately control many of the ultimate material properties of a given sample. Modeling of the formation and evolution of grain boundaries has been an area of intense focus in the past few years, and the research is now bearing fruit. The two figures on this page show the microstructures which evolve via solidification and impingement of a group of randomly oriented crystals. In Figure 3 we see a time history of the formation of a microstructure by the collision of several dendrites, while in Figure 4, we see the consequences of the different grain boundary energies for different boundaries (gray levels indicate grain orientation). Figure 4 demonstrates the phenomenon of "grain-boundary wetting," a physical effect where high angle boundaries are wet (black curves) while low-angle boundaries are dry (white curves).

Additional areas where phase field methods are under investigation at NIST include electrodeposition, stress, sintering, coupling to fluid flow, and crystallization of biological macromolecules. The potential application areas are consequently nearly without limit.

NIST researchers have received recognition for their work in phase field modeling in a number of venues. Over the past Three years approximately 40 invited talks on the subject have been presented at professional societies, university colloquia and workshops. The Department of Commerce Gold Medal and TMS Bruce Chalmers Award were both bestowed on W. Boettinger, partly for his work in phase field research. One MSEL phase field paper was awarded the TMS Champion H. Matthewson award for the paper "which represents the most notable contribution to metallurgical science in the award period."

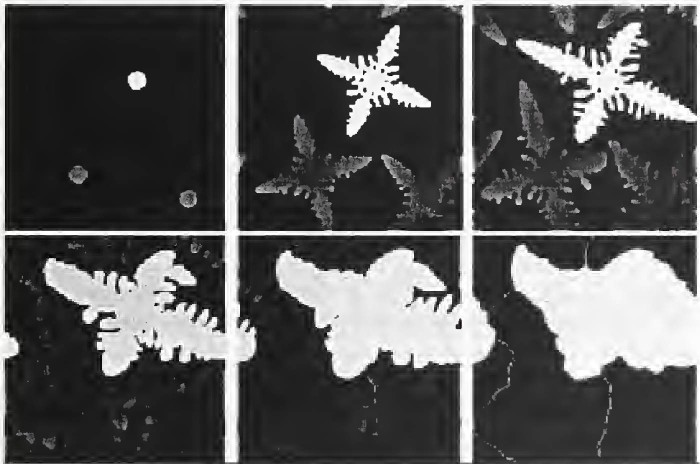


Figure 3: Phase field calculation of a pure material, each color indicates a unique cystallographic orientation. When particles collide they form grain boundaries

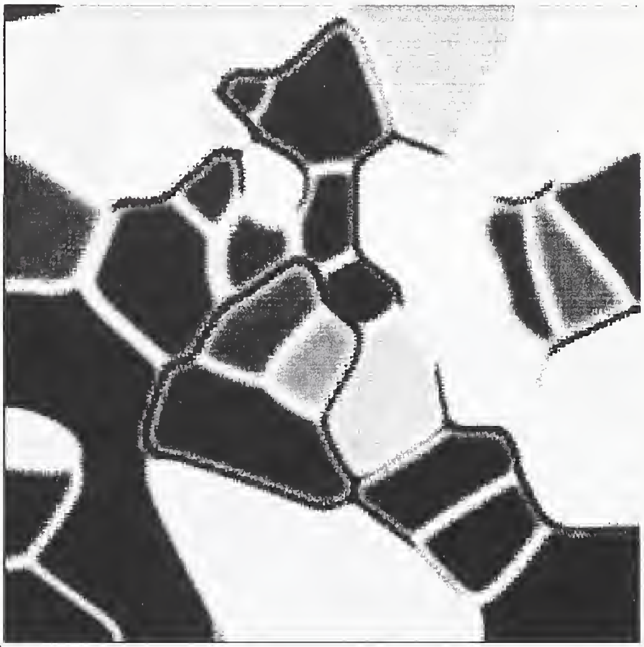


Figure 4: Phase field simulation of the impingement of grains. The black curves indicate wet grain boundaries while the white curves are dry

"...NIST has provided important leadership in the application of phase-field methods to a wide range of pattern-formation problems. Lots of others are now using these methods, largely influenced by the initiatives taken at NIST. The NIST group has set an excellent example by being very careful to understand exactly what their models mean -- and don't mean -- in their various applications. I'm especially impressed by that aspect of their program."

James Langer
Professor, U. California, Santa Barbara
Past President, American Physical Society

For More Information On This Topic

http://www.ctcms.nist.gov/programs/solidification.html

J. Warren and W. Boettinger

COMBINATORIAL METHODS

The Combinatorial Methods Program develops new measurement techniques and experimental strategies needed for rapid acquisition and analysis of physical and chemical data of materials by industrial and research communities. A multi-disciplinary, multi-OU team from the Measurements and Standards Laboratories of NIST participates to address key mission-driven objectives in this new field, including needed measurement infrastructure, expanded capability, standards, and evaluated data.

Measurement tools and techniques are developed to prepare and characterize materials over a controlled range of physical and chemical properties on a miniaturized scale with a high degree of automation and parallelization. Combinatorial approaches are used to validate measurement methods and predictive models when applied to small sample sizes. All aspects of the combinatorial process from sample "library" design and library preparation to high-throughput assay and analysis are integrated through the combinatorial informatics cycle for iterative refinement of measurements. The applicability of combinatorial methods to new materials and research problems is demonstrated to provide scientific credibility for this new R&D paradigm. One anticipated measure of the success of the program would be more efficient output of traditional NIST products of standard reference materials and evaluated data.

Through a set of cross-NIST collaborations in current research areas, we are working to establish the infrastructure that would serve as a basis for a broader effort in combinatorial research. Within MSEL, novel and elegant methods for combinatorial library preparation of polymer coatings have been designed to encompass variations of diverse physical and chemical properties, such as composition, coating thickness, processing temperature, surface texture and patterning. Vast amounts of data are generated in a few hours that help understand how these variables affect material properties, such as a coating's wettability or phase miscibility. Additional focus areas for both organic and inorganic materials include multiphase materials, electronic materials, biomaterials assay, and characterization of materials structure and properties. State-of-the-art on-line data analytical tools, process-control methodology, and data-archival methods are being developed as part of the program.

In order to promote communication with and technology transfer to a wide range of industrial partners, an industry-National laboratories-university combinatorial consortium is being organized by MSEL. The consortium will facilitate direct interactions on combinatorial measurement problems of broad industrial interest and on efficient transfer of the methods developed to U.S. industry.

Contact Information: **Leonid A. Bendersky**

Combinatorial Methods for Industrial Processes

Leonid A. Bendersky

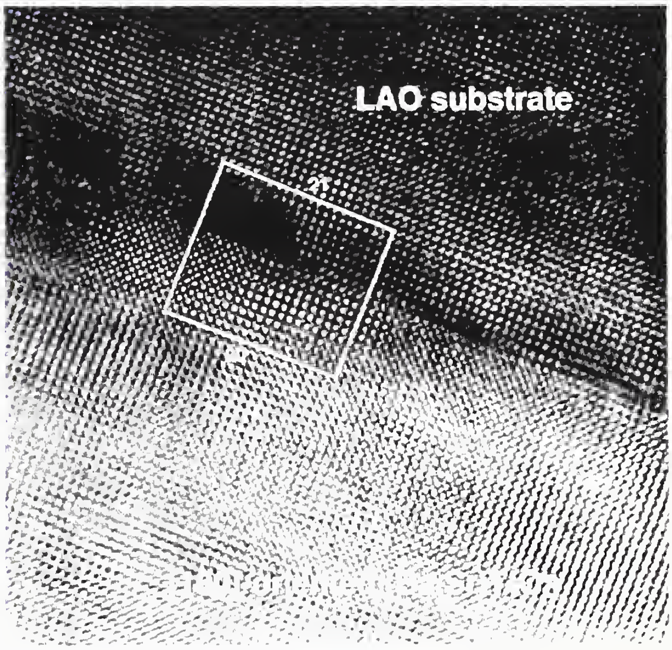
In the search for dielectric material for use in modern microwave communication technology, a variety of complex oxides with different chemistry and structural state are under consideration. With the ability to measure locally the relevant dielectric properties, combinatorial methods can be of significant impact. The method can be used to create the "libraries" designed to either search for a composition with optimal set of dielectric properties or study fundamentals of the relationship between crystallo-chemistry and polarization in complex oxides.

Recently, the effectiveness of applying combinatorial approaches to thin film electronic materials has been demonstrated. This approach facilitates a rapid survey of a large compositional landscape; up to thousands of compositionally varying samples are synthesized, processed, and screened in a single experiment. In particular, novel compositions of $(Ba,Sr)TiO_3$ (BST)-related thin films with improved dielectric properties have identified. Dielectric properties of the cells were measured by using a recently developed scanning tip microwave near-field microscope (MNFM). In these experiments, amorphous precursor layers including fluorides and carbonates were used to create various compositions of BST on spatially addressable combinatorial libraries. It was shown that by carefully controlling the thermal treatments, the amorphous precursor multilayers can be turned into predominantly single-phase epitaxial BST films on lattice-matched substrates. Because this synthesis route is unconventional, it is of great interest to investigate the microstructural details of these films. It is also of great importance to understand the fundamentals of this interdiffusion reaction, since processing occurs at quite low temperatures, in order to apply this combinatorial methodology to other materials.

In FY2000 we established a collaborative effort between NIST and the University of Maryland (Prof. I. Takeuchi) to investigate, using transmission electron microscopy (TEM), the microstructural evolution in $(Ba,Sr)TiO_3$ thin films fabricated from amorphous precursor multilayers consisting of TiO_2, $BaF_2/BaCO_3$, and $SrF_2/SrCO_3$. The films are deposited by pulsed laser deposition (PLD) technique on a single crystal substrate using precursor materials as a target.

We are currently in the process of studying $BaTiO_3$ (BTO) films processed under different conditions (varying temperatures and annealing periods). This will allow systematic investigation of phase formation in BTO made by the present synthesis technique. The study is important for understanding the fundamental growth mechanisms of BTO, as well as for investigating the limitations of this particular synthesis technique for the combinatorial approach.

Our preliminary results with high resolution TEM demonstrated that rather high quality epitaxial perovskite film could be formed by the technique of amorphous precursor multilayer mixing. The figure below shows an example of high-resolution imaging obtained for a BST film.



An example of high-resolution imaging obtained for a BST film. The film was deposited by PLD of TiO_2, BaF_2 and SrF_2 layers on a $LaAlO_3$ substrate and subsequent annealing at 400 < T < 800 °C. The circuit reveals a dislocation in the crystal structure at the interface between the substrate and the film.

Contributors and Collaborators

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Data Evaluation and Delivery

Materials data are critical to the rapid and decentralized design and manufacture of communication, transportation and other devices, which characterize 21st century life. The goal of the Data Evaluation and Delivery Program is to provide the producers and users of ceramic materials with the means of fulfilling their data requirements in the most efficient ways. This goal is accomplished by providing improved access to materials data, development of methods for transferring materials data across the WWW, providing protocols for data evaluation, and enhancing the functionality of existing collections of evaluated data. Much of this research is based on information technology and includes: the development of a materials mark-up language (MatML), the linkage of digitized crystallographic information with full structure analysis in cooperation with the International Center for Diffraction Data and the FIZ Germany, and phase diagrams produced through the NIST/American Ceramic Society Phase Equilibria Program. Other informatics available to the community is contained in the Ceramic WebBook at the Division Website. The Ceramics WebBook provides links to other sources of ceramic data and manufacturer's information, selected evaluated data sets, structural ceramics and high temperature superconductor databases, glossaries, and tools for analysis of ceramic materials.

Contact Information: **Ursula R. Kattner**

Thermodynamic Databases for Industrial Processes

Ursula R. Kattner

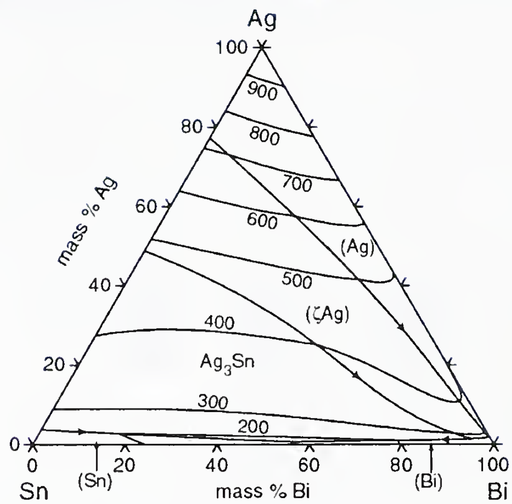
Commercial alloys rarely consist of only two elements and some contain up to 10 elements. Thus thermodynamic databases that permit extrapolation of binary and ternary systems to higher order systems can be invaluable in the design of new materials. Alloy systems of current interest to significant industrial communities are being studied; viz., Pb-free solders, Ni-base superalloys, and metal/Group III nitride compound semiconductors. The approach gives reasonable predictions for complex alloys, enables a compact storage method for data, and provides input to kinetic models for materials processing.

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

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

During the past year, the existing thermodynamics databases for solders and superalloys were expanded and the Ga-N system was evaluated in support of a Division project on interconnects.

- A refined thermodynamic description for the Sn-rich part of the Sn-Ag-Cu system was developed.
- Descriptions of the relevant binary systems involving Ag and Cu were added to the existing database for solders. The database file now includes Sn-Ag-Bi-Cu-Pb.



Liquidus projection of the Sn-Bi-Ag system extrapolated from the thermodynmic description of the binary systems

- Pages for the Metallurgy Division Webbook with emphasis on solder alloys were compiled.
- The congruent melting point of the CoTi (B2) phase was measured and used in the reassessment of the thermodynamic description of the Co-Ti system.
- The 9 component database (Ni-Al-Cr-Co-Mo-Re-Ta-Ti-W) for superalloys was improved to match experimentally observed liquidus, solidus and solvus temperatures for the γ (fcc) and γ' ($L1_2$) phases.
- The thermodynamic description for the Hf solubility in the disordered solution phases was added to the existing thermodynamic database for Ni-base superalloys.
- The thermodynamic description of the Ni-Al-Cr-B system was revised based on experimental results on transient liquid phase bonding that were obtained for samples with selected ternary and quaternary compositions.
- The thermodynamic description of the Ga-N system was evaluated and used for the calculation of the phase diagram at various partial pressures of nitrogen.

Contributors and Collaborators

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FORMING OF LIGHTWEIGHT MATERIALS

Automobile manufacturing is a materials-intensive industry that involves about 10 % of the U.S. workforce. In spite of the use of the most advanced, cost effective technologies, this competitive industry still has productivity issues related to measurement science and data. Chief among these is the difficulty encountered in die manufacture for forming of sheet metal. In a recent Advanced Technology Program sponsored workshop (The Road Ahead, June 20-22, 2000, at USCAR Headquarters), the main obstacle to reducing the time between accepting a new design and actual production of parts was identified as producing working die sets. This problem exists even for traditional alloys with which the industry is familiar. To benefit from the weight saving advantages of high-strength steel and aluminum alloys, a whole new level of formability measurement methods and data is needed, together with a better understanding of the physics behind metal deformation.

To meet these industrial needs, the Metallurgy Division has developed a program that encompasses standard formability test methods, multiscale, physically-based constitutive laws, and consolidation of aluminum-matrix composites. In the past year, we have established a sheet-metal formability laboratory. A state-of-the-art formability testing machine equipped with an advanced surface displacement analysis system permits us to investigate industrially important measurement problems in formability and pursue standard test methods for formability. The facility provides test samples of biaxially deformed metal for other aspects of this program. For example, deformation-induced surface roughening of sheet metal is a poorly understood phenomenon that is highly relevant to industry. We are currently performing controlled experiments on biaxially strained sheets to develop a surface roughening database and a generic model that industry has identified as a need of high priority. On a more fundamental level, we are using MSEL's advanced characterization capabilities (TEM, Synchrotron Radiation, NCNR) to understand the basic dislocation patterning responsible for the observed behavior of metals. A predictive model based on percolation theory has been developed from the measurements and observations. All aspects of the research at NIST will impact our customers by improving the commercially available, finite-element computer codes that are heavily used by this industry. A key element in the design of this program is that an insight or advancement gained in one area can be immediately used in a piecewise fashion in the design process, i.e., total success of the program is not required to have an impact. Other means of transferring this technology, such as through standardizing organizations and by direct interaction with industrial counterparts, are being pursued. While targeting the auto industry, our research will have extended applications to all other industries that employ metal forming in their production lines.

Contact Information: **Richard J. Fields**

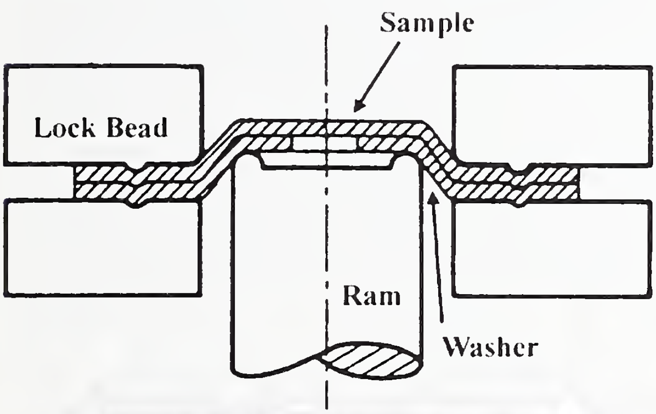
Standard Test Method Development for Sheet Metal Formability

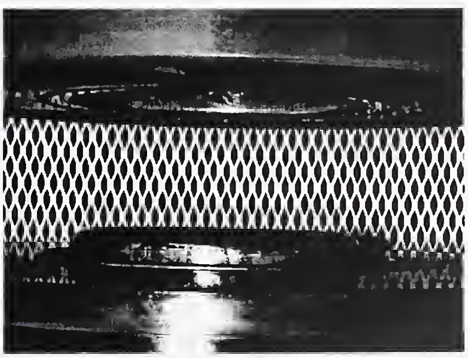
Tim Foecke

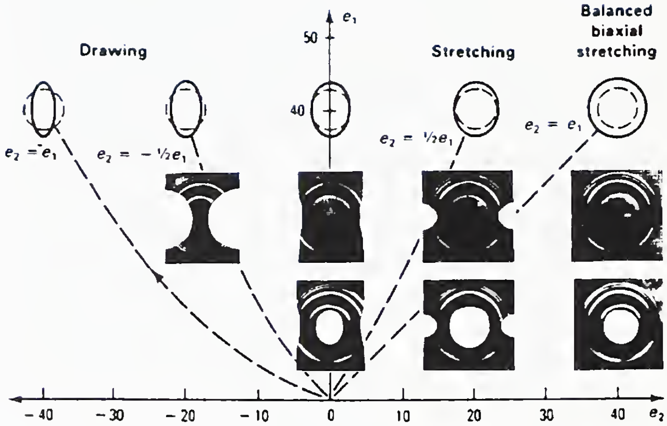
In order to meet the Partnership for a New Generation of Vehicles goals for fuel efficiency, the U.S. automotive industry is moving to lighter, high strength materials for auto bodies. However, their lack of experience in forming these materials translates into difficulty in making accurate dies for producing body parts. NIST discussions with industry have revealed that accurate material properties, and a way to incorporate them into finite element models of sheet metal forming processes, are critical needs for the US auto industry. This project seeks to develop new standard tests and metrology to accurately determine sheet metal mechanical response under forming conditions.

In order for the U.S. automotive industry to be able to transition to new lightweight materials for formed sheet metal parts, they must be able to mechanically characterize the starting materials under forming conditions, and input this information into die design models. The Metallurgy Division has initiated a project intended to develop a sheet metal formability test, along with associated metrology, that can be standardized and easily used by industry.

Our efforts are focussed on a modified Marciniak geometry bi-axial tension test. The test uses a test blank and a support washer, clamped around the edge and stretched by a central ram. By modifying the geometry of the blank and washer, we are able to produce strain states that vary continuously from balanced biaxial through plane strain to nearly drawing conditions. Using this testing scheme, one can easily produce an in-plane forming limit curve using a







Possible bi-axial strain states that can be produced using the current modified Marciniak tooling.

single tooling set and machine. Critical to our test development is the use of a vision-based surface displacement analysis system. This continuously measures the motion of surface features on the deforming sheet and generates a 2-D plot of surface strain. Since the measurements can be performed *in situ*, the results can be displayed as a forming response space rather than a simple forming limit curve. Thus mechanical behavior at strain states from beginning to just before failure can be measured.

Our current work investigates the uniformity of biaxial strain states for a given blank and washer geometry, the effect of strain rate on uniformity and strain state, and the effect of burrs and defects on premature localization.

Samples produced by this equipment are also used in other facets of the formability program to study friction, surface roughening and texture changes as a function of strain state and history in a number of sheet metal material systems. These parameters are all needed for accurate modeling of sheet metal forming.

Contributors and Collaborators

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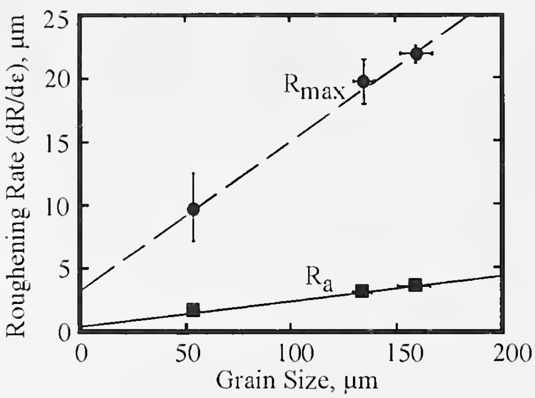
Surface Roughening and Homogeneity of Plastic Deformation

Richard E. Ricker

The automotive industry has determined that the existing data, measurement methods, and basic understanding of the metallurgical factors that influence friction, tearing, and surface finish during stamping are insufficient to meet the needs of the finite element models they are developing to reduce the costs of die design and enable the utilization of lighter metals and new alloys. This project explores the origins of inhomogeneous deformation and how to quantify or predict this behavior for use in finite element codes.

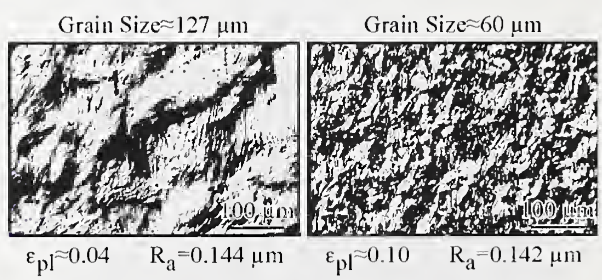
During FY2000, experiments were conducted to determine the influence of uniaxial strain on flow localization and surface roughening in Al alloys. The surface roughening behavior of a commercial Al alloy (AA5052) during uniaxial tension was investigated in two as-received (commercial) heat treatments and after additional heat treatments designed to produce microstructures with different grain sizes, but similar strength levels. The results were then analyzed to determine the influence of uniaxial strain and grain size on surface roughness in this alloy. Initial experiments on the influence of biaxial strain and different strain ratios on surface roughness were also conducted on this alloy and the results are being used to design future experiments.



The influence of grain size on the rate of surface roughening of Al alloy 5052 deformed uniaxially.

Investigators on this project met with industry representatives and discussed methods of estimating the friction between a sheet of metal and a die as the metal deforms plastically, the data required, and measurement methods. Following this meeting, a system was designed and fabricated for these measurements. This system should enable the measurement of the friction observed during plastic deformation over different die draw bead materials and geometries. This system will be evaluated in the coming year and it should provide useful data on die friction and enable evaluation of the mechanisms of die wear and the metallurgical factors influencing friction and wear during deformation.

During a meeting of the industry consortium working on the NIST Advanced Technology Program funded Springback Predictability Project, the finite element models presented were shown to consistently underpredict the measured springback by a small percentage and the magnitude of the underprediction differed for steel and aluminum. At this meeting, there was disagreement concerning whether the "underprediction" could be due to deformation-induced changes in the elastic modulus. To resolve this question and enable more accurate prediction of springback, we designed a simple three-point bend apparatus to measure load and sample springback as a function of time during unloading. For this simple geometry, we predicted the recovery using elastic equations and found that they consistently underpredicted the observed springback by about the same percentage as the finite element models and varied with steel and aluminum in the same manner. We concluded that the underprediction was due to an effect which had not been accounted for in the modeling, namely time-dependent elastic recovery, or anelasticity. This interpretation of the origin of the finite element model underpredictions was well received when presented at the next meeting of the project. Anelastic recovery can be incorporated into finite element codes by substituting a relaxed modulus that contains elastic and anelastic displacement components for the elastic modulus. To further clarify how this effect should be accounted for, we have started measurements of the magnitude of anelastic recovery as a function of metallurgical variables for forming alloys.



Surface topographies for deformed aluminum alloys with different grain sizes.

Contributors and Collaborators

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Fundamental Studies of Plastic Deformation

Lyle Levine

A substantial increase in the use of aluminum alloys and high strength steels in automobiles would greatly increase fuel efficiency. The primary reason why this has not yet been done is a lack of accurate deformation models for use in designing the stamping dies. An improved understanding of the fundamental processes that are responsible for the mechanical properties would allow the development of such a model. This project is developing a physically based model of plastic deformation using a combination of statistical physics approaches and advanced measurement techniques.

Plastic deformation of metals (as in cold rolling, stamping, drawing, extruding, metal fatigue, etc.) is a topic of great importance to industries worldwide, and improvements in the basic technology would have a significant effect on our economy. As one example, stamped metal parts comprise about 1/3 of the weight of an automobile. If the currently used mild steel could be replaced by aluminum alloys or high strength steels, auto weight could be reduced considerably, thus greatly increasing fuel economy.

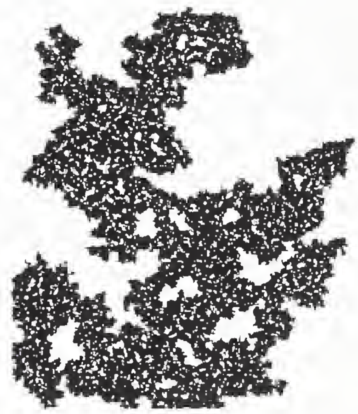
The design of new metal products is often accomplished by computer simulation of the production process using empirically derived constitutive equations. Unfortunately, existing constitutive equations cannot accurately predict the material behavior, and many tryout and redesign steps are required. For stamped aluminum parts for automobiles, this trial and error process is prohibitively expensive and more accurate constitutive laws are required. We are working on developing constitutive laws that are based upon the underlying physical processes that produce the observed mechanical behaviors.

When metals deform plastically, large numbers of defects called dislocations are formed (up to $10^{15}/cm^2$). These dislocations interact via long-range (1/r) stress fields, forming complex three dimensional structures that evolve during deformation. The observed mechanical properties come from the transport of mobile dislocations through this complex system of dislocation structures. Trying to make sense of this process is one of the most difficult problems in materials physics, and researchers have been working on it for most of the 20th century. Recent advances in computers, experimental techniques, and statistical physics have generated hope that a new plateau of understanding may now be within reach.

Our project includes both experimental and theoretical components that will be described below. NIST has also taken the lead in organizing a world-wide effort in this field. We recently ran *Dislocations 2000: An International Conference on the Fundamentals of Plastic Deformation.* This was the largest conference on dislocations ever held. This conference is described in more detail in the Accomplishments section of this report.

On the experimental side, we have developed several synchrotron X-ray techniques for studying dislocation structure evolution *in situ* in bulk thickness metal samples. These include dislocations ultra-small-angle X-ray scattering (USAXS) and high-resolution X-ray topography. Our most recent breakthrough was this fiscal year's development of USAXS imaging, a completely new class of X-ray imaging technique. A description of USAXS imaging can also be found in the Accomplishments section. At present, we are gearing up for a major expansion in our experimental work in FY 2001, in support of our theoretical component.

On the theoretical side, we have shown that the deformation of metals can be considered as a self-organizing critical process where the transport of dislocations through the sample occurs in bursts of collective motion. Our model for this, called strain percolation theory, describes the propagation of strain through the metal (see Figure).



Predicted strain distribution in a deformed metal.

A major recent discovery is that the existence of macroscopic strain requires that the system must exist slightly above the critical point in the supercritical regime. This behavior has been explored using extensive computer simulations and the system is well behaved for a limited range above the critical point. In this regime, the strain behavior is much simpler than at the critical point, thus greatly simplifying the problem of developing useable constitutive laws for metal deformation.

Contributors and Collaborators

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Process Models for Particle-Reinforced Composites

Richard Fields

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

Major research efforts within the U.S. auto industry are driven by the need to reduce the weight of future vehicles to meet the U. S. Council for Automotive Research (USCAR) and Partnership for a New Generation of Vehicles (PNGV) goals. This can most readily be accomplished by the substitution of lightweight materials for the heavy materials currently used. This project aids the commercial development of a low cost powder processing technology for aluminum alloy and particle reinforced aluminum (PRA) parts. The aim is to substitute aluminum alloy and aluminum composite powder metallurgy (PM) materials for iron-based PM products. This approach has been recognized by the auto industry, and the technical barriers to success have been identified: the cost of existing powder processing routes is too high, and efforts to produce acceptable parts using press-and-sinter and direct powder forging are underway. The NIST part of this effort is focused on modeling each step in these consolidation processes from powder to fully dense part. Modeling provides the basis for knowing what properties and parameters of a powder or a process need to be measured in order to more rapidly design successful processes and to monitor consistency. Physical modeling of the process can be used with a cost model to make decisions that optimize cost and properties. The modeling is complex and has been carried out with significant academic and industrial collaboration. NIST's primary role has been to coordinate the modeling efforts between academia and industry, validate the models, and provide industry with working models and a preliminary data base. In collaboration with MatSys Inc., the modeling is being made available to industry in a user-friendly, commercially supported software package.

The NIST powder consolidation modeling effort has established a validated set of equations that describe the densification of reinforced (or unreinforced) metal powder in terms of the processing conditions. These equations are used in a commercial software package that accurately models potential processes and that saves U.S. industry time and money otherwise spent on trial-and-error investigations.

NIST reports its results quarterly to an industrial consortium consisting of the three U.S. auto producers, Valimet, Stackpole, Saint Gobain, Hoeganaes, and Mascotech. This group was organized by USCAR and tracked by PNGV.

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

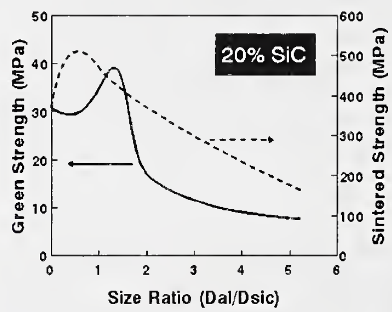

Figure 1. Strength versus size ratio.

As part of the modeling of die filling and powder flow, a Phase II Small Business Innovation Research project developed a method of more uniformly filling dies. This has resulted in commercially available feedshoe technology that can improve the mass uniformity of pressed powder parts by a factor of four with a corresponding reduction in part distortion. This project will be completed in FY2001.

Contributors and Collaborators

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MAGNETIC MATERIALS

Magnetic materials are pervasive throughout our society. They are used in magnetic recording media and devices, in all motors and transformers, on credit cards, in numerous types of magnetic sensors, in magnetic resonance imaging (MRI) machines, in microwave communications, in magnetic separation, and in magnetic cooling. Magnetic materials include metals, ceramics and polymers at different size scales ranging from large castings to particulates, thin films, multilayers and nanocomposites.

In the present trend to make devices smaller, new magnetic materials are constantly being developed. One critical need for implementation of these materials is the development of the measurement science needed for their characterization. This is the focus of the Magnetic Materials Program. Proper measurements of key magnetic properties, determination of the fundamental science behind the magnetic behavior of these new materials, analyses of the durability and performance of magnetic devices and development of Standard Reference Materials are key elements of this program. Some information is only obtainable by the use of unique measurement tools at NIST like the neutron diffraction facilities at NCNR, or the magneto-optic indicator film apparatus for observation of magnetic domain motion. Of particular interest is understanding the magnetic behavior of low dimensional systems, in which one or more characteristic dimensions have been reduced to nanometer sizes.

Areas of present study include preparation, characterization, and modeling of multilayers and other low-dimensional systems for optimized giant magnetoresistance effect and magnetocaloric effect, and spintronic systems wherein spin dependent magnetic devices are integrated directly into semiconductor chips. Giant magnetostriction alloys, prepared using combinatorial methods, are similarly analyzed. Observation and micromagnetic modeling of magnetic domains play a key role in understanding magnetization statics and dynamics. Nanotribology of magnetic hard disks measures friction, stiction, and wear. Advanced magnetic measurements are developed for a wide range of materials including weld metal ferrite standards, and are applied to a wide range of magnetic phenomena including magnetic exchange bias, magnetic susceptibility of small samples at high frequencies, and magnetization time response to a change in magnetic field. Magnetic measurement standards are prepared and certified.

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

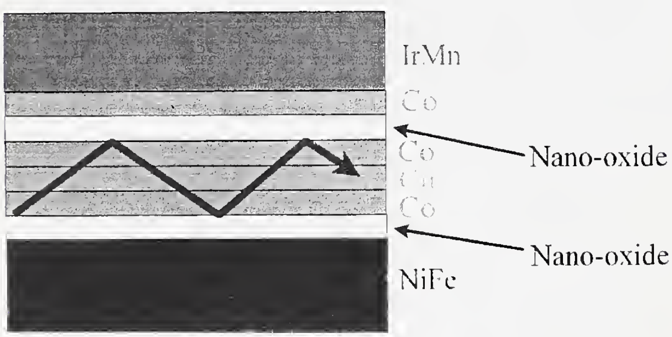
Contact Information: **Robert D. Shull**

Giant Magnetoresistance Materials

William F. Egelhoff, Jr.

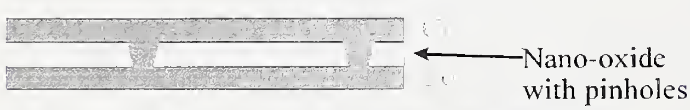
The objective of this project is to provide assistance to U.S. companies that manufacture products based on the giant magnetoresistance (GMR) effect. GMR-based devices are used primarily in computer hard-disk drives, but emerging markets include non-volatile memory chips, magnetic field sensors, and ultrahigh speed isolators. We help these companies learn how to produce improved GMR materials. Our work provides U.S. companies with significant competitive help by investigating the science underlying the manufacturing process, something these companies cannot adequately do on their own.

The use of the giant magnetoresistance (GMR) effect in thin film materials is expanding rapidly and U.S. manufacturers are facing stiff international competition in the race to develop the best GMR materials. To assist U.S. industry in understanding the materials science issues which affect GMR device performance, NIST set up a major new research facility, known as the Magnetic Engineering Research Facility (MERF), which is the most elaborately instrumented magnetic thin-film research facility ever constructed. Research at MERF is closely coordinated with U.S. industry. As one example, this year Veeco/CVC, the world's largest producer of GMR manufacturing equipment, collaborated with us to investigate and clarify the thickness dependence of specular nano-scale oxide layers in GMR materials. The discovery that specular nano-scale oxide layers could increase the GMR was made at MERF a few years ago, and the hard-disk drive industry is now pushing hard to take advantage of this effect. In a typical GMR material, the nano-scale oxide layers reflect



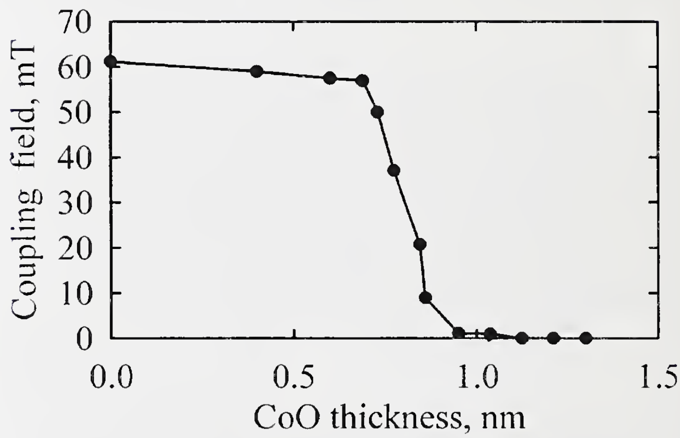
Geometry of a typical GMR material.

Electrons specularly to trap them in the Co/Cu/Co region, which is the most active for the GMR effect. Measurements at MERF on the magnetic coupling between two Co films separated by a nano-scale oxide indicated that pinholes play a critical role by providing magnetic coupling across the nano-scale oxide.



Pinholes provide magnetic coupling across a nano-scale oxide.

This coupling is crucial for the Co layers above and below the Cu layer to be subject to the influence of the IrMn pinning layer and the NiFe softening layer, respectively, so the GMR material will work properly.



A dramatic decrease in the coupling field occurs as the pinholes disappear with increasing CoO film thickness, preventing proper operation of a GMR device.

However, these pinholes also have a negative effect: they leak current, so the specular scattering is not entirely effective in confining the electrons to the Co/Cu/Co region. As a result, the very large increases in GMR values that could potentially be achieved by perfectly optimized nano-scale oxide layers will probably never materialize. It seems that other directions will be more promising as new routes to achieving the much larger values of magnetoresistance needed in the future. Among these new routes are devices based on the injection of spin-polarized electrons into semiconductors (a field known as Spintronics) and ballistic magnetoresistance in magnetic nano-contacts. These areas are actively under investigation at MERF to give further guidance to U.S. industry.

These examples illustrate how NIST magnetics research can help U.S. industry identify the most promising new research directions and avoid expensive unproductive efforts.

Contributors and Collaborators

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7 Corporations, 2 Federal Laboratories, 8 U.S. Universities, 9 International Universities

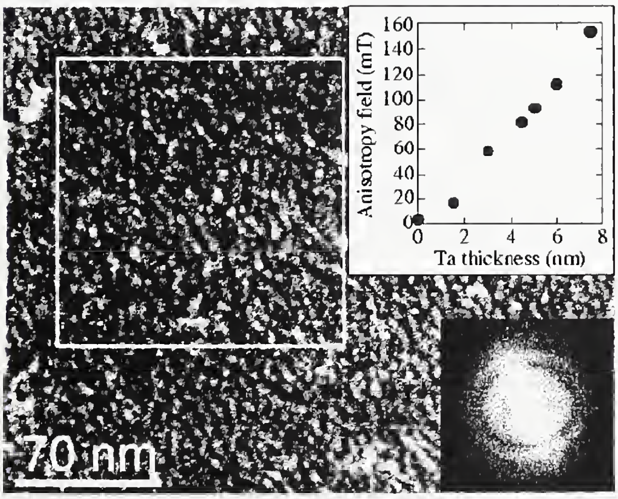
Processing and Micromagnetics of Thin Magnetic Films

For many applications of magnetic thin films in devices, it is important to be able to control the magnetization direction of a thin film in a way that is insensitive to elevated temperatures. We are providing measurement methods, computational methods, and data on the thermal stability, magnetization control and micromagnetics of thin magnetic films to the magnetic recording, magnetic sensor, and other magneto-electronic industries.

Robert D. McMichael

This project is concerned with the thermal stability of "spin valve" multilayer films, the micromagnetics of magnetization control in thin films, and dynamic measurements of thin magnetic films. In FY2000, the emphasis has been on exchange biasing, and novel magnetization control methods, and micromagnetics.

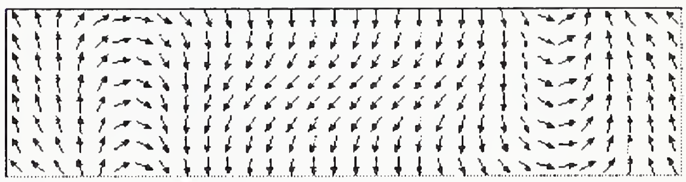
Exchange biasing, which is driven by magnetic interactions across a ferromagnet/antiferromagnet interface, is a commonly used method for magnetization control. Measurement methods and meaningful characterization of the exchange biasing and alternative methods for magnetization control are important for device design and manufacturing. We are nearing completion of a collaborative activity with NIST Physics Laboratory to develop effective models and meaningful measurement methods to characterize exchange bias bilayers. The recent emphasis has been on thermal excitation of antiferromagnetic instabilities, and their effects in hysteresis loop measurements and ferromagnetic resonance measurements. The thermal stability of exchange bias is especially important for read heads which may experience thermal spikes up to 300 °C.



Plan view TEM micrograph of a spin valve with obliquely sputtered Ta underlayer showing anisotropic structure. Inset: Anisotropy field values for 5 nm Co films as a function of obliquely deposited Ta underlayer thickness.

To control the magnetization in thin films, a strong uniaxial anisotropy is an alternative to exchange biasing. We have discovered a technique for producing strong uniaxial anisotropy in thin films by oblique-incidence deposition of tantalum underlayers, and we have produced anisotropy fields on the order of 0.1 T (1 kOe) in thin films of NiFe and Co. These fields are an order of magnitude larger than the magnetocrystalline anisotropy fields in similar films. We have shown that this method can be used to strongly pin the bottom layer of a spin valve, deposited directly on the tantalum underlayer while affecting other layers relatively weakly. We have found that spin valves using the obliquely sputtered Ta underlayers are structurally stable up to 300 °C and that the anisotropy induced by the tantalum morphology remains strong up to this temperature. Obliquely deposited Ta has many of the properties needed to replace thicker, more corrosion prone, and less thermally stable antiferromagnetic exchange bias layers in spin valve recording heads and sensors.

Our work in standard problems for micromagnetic modeling has continued to gain international attention. Recognizing the importance of the dynamic behavior of thin magnetic films for high bandwidth applications such as magnetic memory cells, we added a fourth, dynamic, problem to our suite of standard problems for computational micromagnetics. This problem was posted on the web in February, and in July we had our first submitted solution from collaborators in Orsay, France. Their results, along with results calculated in an MSEL/ITL collaboration are posted on the muMAG web page, <http://www.ctcms.nist.gov/~rdm/mumag.html>. We plan to expand this activity into calculations of dynamics of inhomogeneous thin films.



Magnetization pattern calculated for standard problem #4 captured as the average magnetization first crosses through zero after a field is applied to the left and 10° downward.

Contributors and Collaborators

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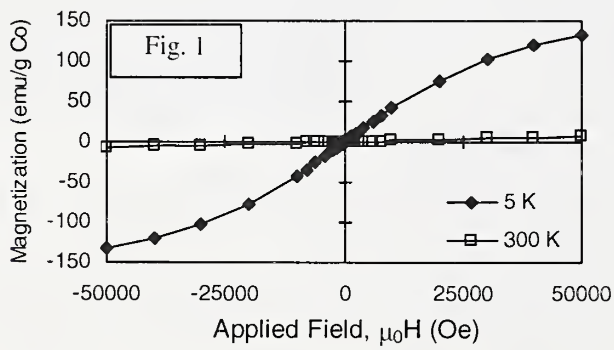
Magnetic Properties of Nanostructured Materials

Robert D. Shull and Richard A. Fry

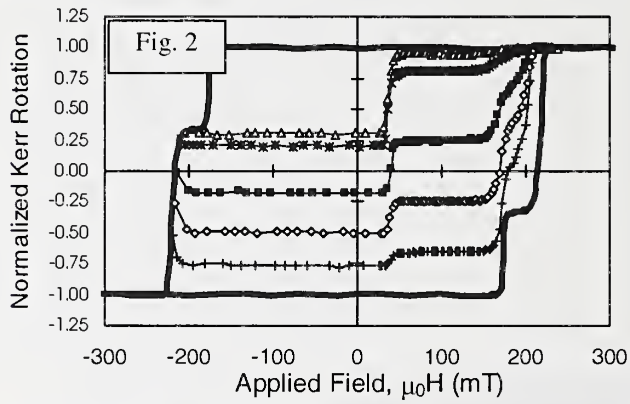
In the past 10 to 15 years improvement in the technology for materials preparation has resulted in the control of morphology and features at the nanometer level. In magnetism, such control allows the fabrication of nm-thick (or separated) composite materials of dissimilar magnetism, leading to materials with novel bulk magnetic character and unusual property combinations. By understanding their behavior and determining proper measurement techniques, we are providing metrology for U.S. industry to take advantage of these new materials.

This project examines the fundamental nature of ferromagnetism at nanometer length scales.

For the first time ever, magnetic dendrimer nanocomposites have been successfully created. This was accomplished by encapsulating nanosized entities of iron, cobalt, and nickel in hydrophobic poly-(amidoamine) (PAMAM) dendrimer hosts and then embedding this in a polystyrene matrix. This technique facilitates the formation of ferromagnetic clusters of well-defined size, while overcoming potential problems relating to the instability of the magnetic structure under the influence of an external electromagnetic field. SQUID magnetometry measurements on these nanocomposites showed that after subtraction of the diamagnetic polymer background, at 300 K all samples exhibited paramagnetic behavior with their magnetization (M) being linear with the applied magnetic field (H) and with the temperature dependence of the susceptibility increasing for decreasing temperatures below 300 K. Curie-Weiss (1/M vs. T) graphs displayed a linear behavior at high temperatures with small deviations from linearity at temperatures below 100 K. The low-temperature behavior indicated either superparamagnetic or soft ferromagnetic behavior (See Fig. 1). These materials are particularly attractive for use in targeted drug delivery because they are biologically benign and now can possess significant magnetic behavior that allows their manipulation.



Ultrathin multilayer films consisting of alternating layers of nanometer-thick cobalt and platinum are known to be promising materials for perpendicular magnetic and magneto-optical recording devices. However, much of the observed magnetic behavior in Co/Pt multilayers remains unexplained. Magneto-optical Kerr effect (MOKE) magnetometry showed in some Co/Pt samples a bimodal magnetization behavior in which the reversal process occurs in two distinct field-dependent steps (see Fig. 2). Analysis of magnetic aftereffect and reversal curves led to the conclusion that two separate magnetic phases are contributing to the magnetization processes in these materials. A model was developed which satisfactorily explains this bimodal magnetic behavior, as well as adding insight into the overall magnetic phenomena occurring in these multilayer materials.



This year, small angle neutron scattering experiments were performed on nanocrystalline Ni which showed magnetic correlations which did not coincide with the grain size, showing grain boundary atoms do not have diminished magnetic strength. Also, measurements performed on magnetic nanofluids were, for the first time, successful at NIST. These showed magnetic strengths which scaled with the concentration.

It is anticipated that as a result of this program, we will develop an improved prediction capability of magnetic properties of magnetic nanomaterials in different morphologies. Success in this area will provide for an improved capability to engineer magnetic properties by design. In addition, it is anticipated that improved characterization techniques for magnetic nanomaterials will be developed, thereby leading to improved quality control by manufacturers.

This year NIST was joined by NSF, ONR, DOC/TA, AFOSR, NIH, and NASA in putting together a National Initiative on Nanotechnology. One of the members of this group (RDS) served on that interagency committee and helped write that Initiative.

Contributors and Collaborators

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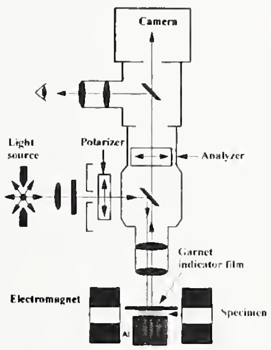
Magneto-Optical Indicator Film (MOIF) Measurements

Alexander J. Shapiro and Robert D. Shull

Understanding of magnetization reversal mechanisms is a fundamental issue in magnetism. For coupled magnetic systems, detailed knowledge of the magnetization reversal processes holds the key to unlocking the potential for many new applications. The magneto-optical indicator film (MOIF) imaging technique developed by NIST and the Institute of Solid State Physics of the Russian Academy of Sciences is a quantitative, simple, fast, and sensitive tool for nondestructive characterization of magnetic microstructures at the micrometer scale and for real-time visualization of the magnetization process elemental events.

Industrial and university laboratories in the U.S. and around the world use the advanced MOIF technique for direct studies of the remagnetization of magnetic materials. We applied this technique to studying the magnetization reversal process in quasi two-dimensional exchange coupled nanocomposite magnetic multilayer systems, in which technologically important effects, such as unidirectional anisotropy, and exchange hardening, which enhances the maximum energy product, have been observed.

In the MOIF technique, a thin film of yttrium iron garnet doped with Bi, having an in-plane magnetization and a large Faraday effect, is placed on the top of a magnetic sample. Since the magneto-static field of the sample under study alters the magnetization of the garnet film, it becomes an indicator of the magnetic field. When polarized light passes through the indicator film and is reflected back by an Al underlayer it undergoes the Faraday rotation which is proportional to a component of the magnetic stray fields perpendicular to the indicator film plane. The resulting intensities of the polarized light are imaged in a polarizing microscope. This allows visualization, for example, of magnetization reversal processes, domain wall nucleation and motion, Bloch lines, and magnetic consequences of crystal defects in magnetic materials.



MOIF Microscope Configuration

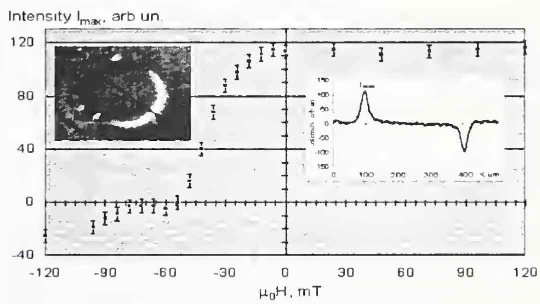
The quality of the magneto-optical imaging can be greatly enhanced by digital image processing: magnetic imperfections of the indicator film and inhomogeneities in the illumination are practically eliminated, image contrast is strongly increased, and quantification of the magnetic information becomes possible (see figure below).

Magnetization reversal processes were studied by the MOIF technique in an exchange-coupled soft and high-coercivity hard ferromagnet (Fe/Sm-Co) as well as in (NiFe/FeMn) ferromagnetic/antiferromagnetic (FM/AFM) bilayers.

The dependence of the magnitude and the orientation of the structure average magnetization has been studied by both cycling and rotating the external magnetic field in exchange-spring permanent magnets (SmCo/Fe). It was discovered that the magnetization reversal of the soft ferromagnet can proceed by formation of not only one-dimensional, but also two-dimensional, exchange spin springs.

In the NiFe/FeMn bilayer, remagnetization is determined by the nucleation and motion of a new type of hybrid domain wall. During the magnetization reversal to the ground state, the untwisting of the exchange spring occurs first at places with the largest anisotropy energy inside the AFM layer because in these locations it is not necessary to nucleate the domain walls in both the FM and AFM layers.

The results are of interest for developing of better permanent magnets, spin-valves, and magnetic field sensors. The MOIF method can be used effectively to determine the structure-property relationships during optimization of manufacturing technologies of nanocomposite materials.



Maximum intensity (shown on the right inset) of the magneto-optic contrast measured along profile line on the MOIF image (in the left inset) vs. field amplitude during magnetization reversal.

Contributors and Collaborators

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MATERIALS FOR MICROELECTRONICS

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

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

- develop and deliver standard measurements and data;
- develop and apply in situ measurements on materials and material assemblies having micrometer- and submicrometer-scale dimensions;
- quantify and document the divergence of material properties from their bulk values as dimensions are reduced and interfaces contribute strongly to properties;
- develop fundamental understanding of materials needed in future microelectronics.

With these objectives in mind, the program presently consists of twenty separate projects that examine and inform industry on key materials-related issues, such as: electrical, thermal, microstructural, and mechanical characteristics of polymer, ceramic, and metal thin films; solders, solderability and solder joint design;[2] interfaces, adhesion and structural behavior; electrodeposition, electromigration and stress voiding; and the characterization of next generation interlevel and gate dielectrics. These projects are conducted in concert with partners from industrial consortia, individual companies, academia, and other government agencies.

The program is strongly coupled with other microelectronics programs within government and industry, including the National Semiconductor Metrology Program (NSMP)[3] at NIST. The NSMP is a national resource responsible for the development and dissemination of new semiconductor measurement technology.

More information about this program, and other NIST activities in Materials for Microelectronics can be found at: (http://www.msel.nist.gov/research.html

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[1] International Technology Roadmap for Semiconductors, 1999, and National Technology Roadmap for Semiconductors, 1994 and 1997, Semiconductor Industry Association, San Jose, CA; National Technology Roadmap for Electronic Interconnections, IPC, Lincolnwood, IL, 1995, 1997; National Electronics Manufacturing Technology Roadmap, National Electronics Manufacturing Initiative, Inc., Herndon, VA, 1996, 1998, 2000.

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

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

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Solder and Solderability Measurements for Microelectronics

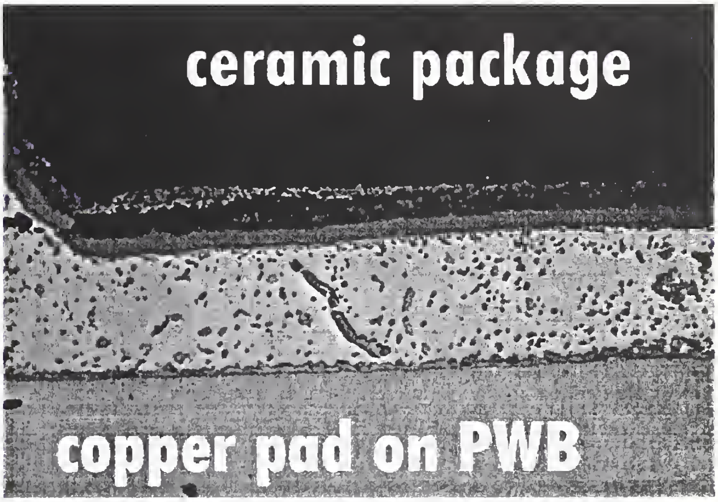
F. W. Gayle, W. J. Boettinger, C. A. Handwerker, U. R. Kattner, and M. E. Williams

Solders and solderability are increasingly tenuous links in the assembly of microelectronics as a consequence of ever shrinking chip and package dimensions and of the movement toward environmentally friendly lead-free solders. We are providing the microelectronics industry with measurement tools and data to address solder problems. A thermodynamic database has been publicly distributed for modeling lead-free solder systems. We also work closely with industry groups on measurement tools needed for development of lead-free solders for use in harsh environments, and provide guidance for adoption of these solders into assembly processes through work with industrial standards organizations.

The U.S. microelectronics industry has clearly articulated the measurement needs for Pb-free solders and for solderability and assembly. For example, the urgency for materials data for Pb-free solders has been specified in the 1997 IPC, 1999 ITRS, 2000 NEMI, and 2000 IPC Lead-Free Solder Roadmaps. The pressure from the Japanese consumer product market and from the E.U. to produce lead-free microelectronics continues to increase. In addition, the lack of understanding and control of current standard solderability measurements has inhibited the development of improved measurements necessary for new solders and for new packaging schemes. These industrial needs are addressed under this NIST project.

NIST has taken a major role working with industry through a NEMI Task Force to identify and move Pb-free solders into practice. NIST co-chairs the NEMI alloy selection group which this year selected standard alloy compositions for U.S. microelectronics assembly (This collaboration is discussed in detail earlier in this report.) NIST is also active in the NCMS High Temperature Fatigue Resistant Solder Consortium and, as in the NEMI Task Force, leads the alloy selection task group. The NCMS consortium, including Ford, Delphi, Allied Signal, Rockwell, Amkor, Heraeus, Johnson Manufacturing, and Indium Corporation, has identified and thermally cycle tested several Pb-free alloys for applications as high as 160 °C. In the past year NIST has been responsible for analyzing microstructure evolution during thermomechanical fatigue. A microstructure of one of the high temperature, high fatigue resistant, lead-free solders after thermal cycling is shown in the figure at the right. The final report is due out in early 2001.

NIST has developed the database necessary to calculate multicomponent phase diagrams essential for Pb-free alloy development. The experimental determination of phase diagrams is a time-consuming, costly task requiring expert interpretation of results. The calculation of phase diagrams significantly reduces the effort required to determine phase evolution in multicomponent systems and can provide quantitative information that is frequently needed in other modeling efforts. During the past year the NIST thermodynamics database for solders was expanded. A refined thermodynamic description for the Sn-rich part of the Sn-Ag-Cu system was developed that was critical for alloy selection by the NEMI Lead-Free Task Force.



Metallographic cross-section of a new lead-free solder developed under the NCMS High-Temperature Fatigue Resistant Solder project. The alloy has excellent thermal fatigue properties.

We are also working in collaboration with IPC Standards Committees (most closely with members from Celestica, Lucent, Raytheon, Rockwell, and Shipley-Ronel) to establish reproducible solderability test standards for board assembly. Activities include providing benchmark experiments for the wetting balance tests to predict on-line solderability for a wide range of surface finishes, lead materials, and solder alloys. New NIST research to develop electrochemical solderability tests and an understanding of whisker formation in Sn-based, Pb-free electroplated surface finishes complements the solderability studies. Highlights from our work include:

- Sources of uncertainty have been established for wetting balance solderability tests, leading to increased repeatability and reproducibility of tests.
- Recent flux studies performed at NIST have led to a change in test procedures for the IPC J-ANSI solderability standard.

Contributors and Collaborators

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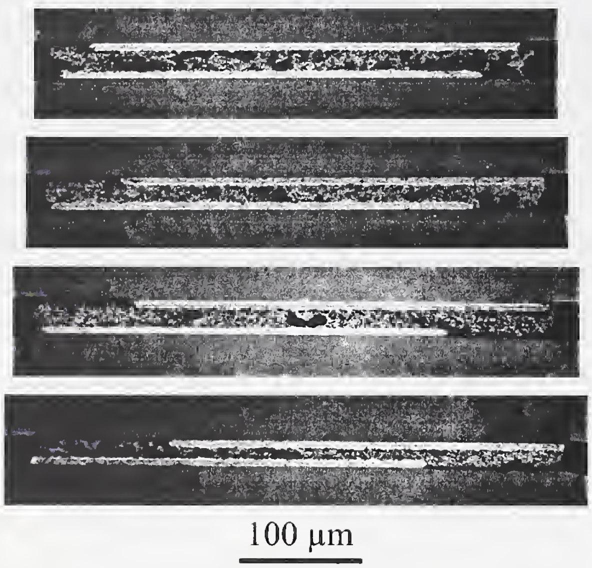
Assembly of IC Chips Utilizing Wafer-Level Underfill

Daniel Josell

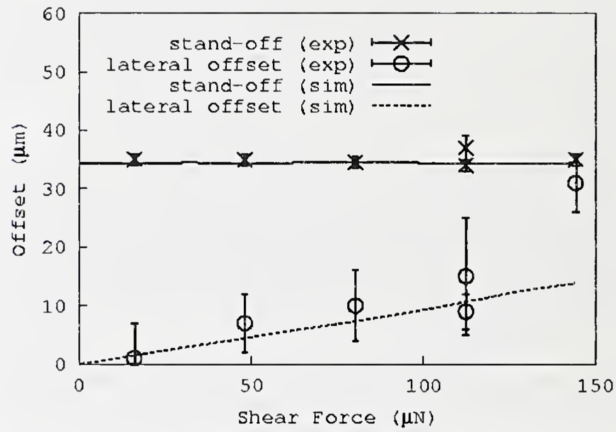
Assembly of advanced area array microelectronic chips and components requires self-alignment of interconnects with restoring forces supplied by the surface tension of molten solder joints. To provide the necessary detailed understanding of the restoring forces provided by misaligned solder joints, we are providing computer simulation as well as experimental studies that verify the accuracy of these simulations. As a result, we demonstrate that the restoring force to be expected during assembly of flip chips with an underfill/solder bump system applied at the wafer level can be accurately predicted using such codes as the free ware Surface Evolver.

This project involves experimental studies and computer modeling of the geometries of solder joints subjected to a range of loading conditions. The applicability of models including only capillary (surface energy) and gravity to flip-chip solder joints has been determined. In addition, the relationship between restoring force and solder joint misalignment obtained in this work determines the ability of flip-chips utilizing wafer-level underfill to achieve self-alignment during reflow operations.



Solder joints made from ~0.0019 mm^3 Pb63Sn37 solder connecting 0.35 mm diameter pads under shear forces from 34 µN to 1.2 mN (top to bottom). Normal force was 1.95 mN.

The experiments measured the capillary realignment forces for different pad dimensions and solder volumes. Solder joints with volumes of eutectic lead-tin solder down to 0.0086 mm^3 were studied with pad diameters down to 0.35 mm. The loading conditions were systematically varied and the post-solidification solder joint geometry measured in order to obtain the force-displacement relatiosnships for the solder joints under both aligned and misaligned conditions. The experimental results were compared to results predicted using the commonly used free ware computer code Surface Evolver. This code considers only capillary and gravitational forces to predict solder joint geometries.



Measured lateral offset (misalignment) and normal offset (standoff height) for ~0.0086 mm^3 Pb63Sn37 solder connecting 0.35 mm diameter pads as functions of applied shear force. The curves are predictions of Surface Evolver.

The predictions of the simulations were shown to be consistent with the results of the experiments, including independently measured contact angles and literature values of the solder surface tension. As a result, this class of computer codes has been shown to be an accurate means of studying solder joint restoring forces for wafer-level underfill applications.

Software based on the freeware Surface Evolver code has been written that allows modeling of relevant joint geometries. This software has been placed in the Center for Theoretical and Computational Materials Science CTCMS web site <http://www.ctcms.nist.gov/~djl/solder/new.html> as part of the library of Evolver files modeling different industrial solder joint geometries. Specific output of this software includes predictions of equilibrium solder joint geometries as well as force-displacement relationships for two pads joined by the solder joint. The user-specified separation between the pads can be such that they are aligned or misaligned. The generality of the joint geometries that can be studied using this code is a significant benefit.

Contributors and Collaborators

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Metallurgy of Electrical Contacts to GaN-based Semiconductors

Albert Davydov and William. J. Boettinger

Effective use of the wide-band-gap GaN-based semiconductors as active layers in short-wave optoelectronic and high-frequency/high-power electronic devices requires improved electrical contact characteristics: lower resistance and higher thermal stability of ohmic contacts to n- and p-GaN. This project investigates the properties of metal/GaN contacts and focuses on correlating electrical performance of metal contacts with the electronic and structural characteristics of the metal/semiconductor interface. A better understanding of these relationships will benefit future efforts to design and optimize thermally stable electrical contacts to nitride-based devices.

The development of suitable ohmic contacts on GaN continues to be a problem due to the large ionization energy of this semiconductor and high Schottky barrier heights between the GaN and metal contact. Until now, limited success has been obtained with various Al/Ti metallizations to n-GaN and n-AlGaN, and Ni,Cr/Pt,Au contacts to p-GaN. Ohmic contact processing often requires brief (less than 5 min) heat treatment of the metal/semiconductor structure in the range of 600 to 1200 °C to reduce the resistance of as-deposited contacts. The optimization of the heat treatment schedule as well as determination of the best metallization composition and sequence are difficult problems that require extensive experimentation. This project aims to develop metallization information that will enable the design of improved electrical contacts to GaN-based semiconductors for optoelectronic and electronic device fabrication. We plan to optimize the search matrix for GaN metallization using high-throughput experimentation and thermodynamic modeling. The high-throughput (combinatorial) approach will involve preparation of a library of contact resistivity for various types of metallizations on n- and p-GaN wafers. The variation with metallization composition and heat treatment schedule will be examined. The thermodynamic approach uses a combination of phase diagram analysis and diffusion kinetic analysis to model the reaction process that occurs at the metal/GaN interface. Prediction and experimental verification of the interfacial phases formed, their thermal stability and their thickness are the goals of this research. We anticipate that coupling experimental information on interfacial reactions with fundamental phase diagram, thermodynamic and kinetic modeling will lead to the development of thermally stable metal contacts to GaN and related materials with improved characteristics for electronic industry needs. As a basis for understanding reactions in this system, work in FY2000 included experimental studies and thermodynamic modeling of the Ni-Ga-N, Al-N, and Ti-Ga-N systems. One important conclusion from this work was that Ni metal does not form a stable couple with gallium nitride, but reacts with GaN to form various nickel gallides.

GaN epitaxial films grown by HVPE and MOCVD on 2" sapphire and SiC substrates have been obtained from the GaN epitaxial films grown by hydride vapor phase epitaxy (HVPE) and metallo-organic chemical vapor deposition (MOCVD) on 5 cm diameter SiC substrates have been obtained from the industrial collaborators for this research. Al/Ti metallization arrays 100 nm thick have been co-deposited by e-beam on n-GaN, using a prototype mask for combinatorial materials library fabrication. Each element of the metal array had a different composition ranging from pure Ti to pure Al (Figures 1, 2). Alloy compositions were verified by scanning electron microscopy/energy dispersive spectroscopy and s-ray diffraction. As-deposited $Ti_{1-x}Al_x$ alloys formed highly textured hcp solid solutions with the c-plane preferred orientation for $x \le 50$ Al and fcc solutions with the (111) orientation for Al atomic fraction $x \ge 75$ %.

Standard lithographic techniques were used on each array to prepare a subarray of metal pads with decreasing spacings to enable measurement of contact resistivity by the transmission line method. Samples are to be subjected to various temperature/time/ambient heat treatments using a rapid thermal annealing furnace. Data collection and analysis will involve the contact resistivity as a function of metallization composition, annealing schedule and sequence of phases formed at the metal/GaN interface, thus enabling understanding and correlation of electrical performance of the metal contacts with the electronic and microstructural characteristics of the metal/semiconductor interface.

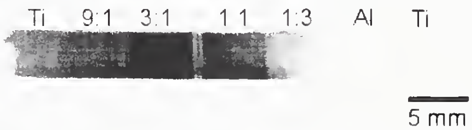

Fig 1. GaN strip with array of Ti:Al metallization pads

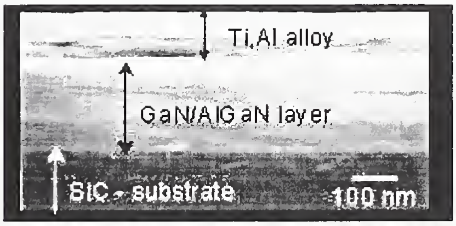

Fig 2. FE-SEM image of the (Ti:Al)/GaN cross-section

Contributors and Collaborators

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Evaluation of Bond Pads for Wire Bonding

Christian Johnson and David Kelley

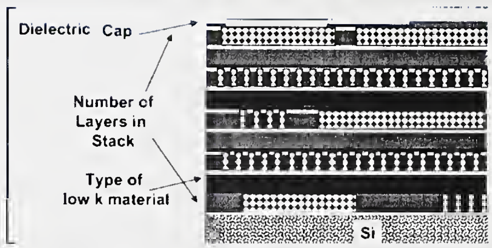
Several problems encountered in wire bonding to advanced damascene copper/low-K devices result from (1) oxidation of the copper pads during handling, wafer sawing, and high temperatures encountered during die attachment and thermosonic bonding, and (2) diffusion of copper into the top surface metal/inhibitor coating. NIST is evaluating the direct deposition of gold onto damascene copper as a top coat oxidation inhibitor while determining the diffusion coefficient of electrodeposited copper into gold for bondability impact.

The introduction of copper and low dielectric constant (LoK) polymers into advanced very large-scale integration copper-damascene chips (see Figure) has created new wire bonding challenges. Oxidation inhibitors are needed to ensure bondability to the top copper surface. In addition, these chips include complex under-pad mechanical support structures with low modulus, low dielectric constant materials positioned underneath the pad. Thermosonic bonding of wires to such pads can result in cracked diffusion barriers, copper diffusion into the LoK polymers, spalling/crazing of the polymers, and bond pad indentation (cupping).

In the past, bonds have been made to aluminum pads over silicon or oxide. This presented an ideal metallurgy and a rigid platform for thermosonic bonding. However, with the introduction of LoK alternatives, copper pads may be positioned over low modulus polymers that are themselves encased in brittle barriers. This can lead to problems with bond yield and/or reliability.

Although there are a number of areas that must be considered in wire bonding to advanced Cu/LoK devices, this project focuses on the top surface metal which is present to promote bondability. Specifically, we are evaluating gold coatings placed directly onto copper as an oxidation inhibitor and determining the impact that interdiffusion of copper and gold may have on long term reliability for wire bonding. Gold-copper bond interfaces have been shown by Lucent Technologies to be more reliable than Au-Al interfaces which are currently used approximately 10^{12} times/year in devices.

The gold deposits to be evaluated will be applied as displacement, electrodeposited, and autocatalytic coatings. Since some of the copper bond pads in a complex stacked device may not have a ground plane connection, which is needed for electrodeposition, autocatalytic gold (only recently developed) would have an advantage. However, the autocatalytic gold process has not been demonstrated on bare copper and has not been attempted for wire bonding applications.



A copper-damascene/LoK metal/dielectric stack, which indicates the complex structures and potential reliability problems that must be contended with during wire bonding.

The project startup tasks being addressed for Cu/LoK wire bonding are:

1. Several bilayer copper/gold samples have been prepared for diffusion studies (oxygen-free high conductivity Cu plated with Cu from a dual damascene process followed by pure electrodeposited Au of varying thickness).

2. Diffusion rate measurements have been started, using temperatures and times typical of those encountered in all subsequent processing/packaging steps. This will serve as a baseline and also indicate any shelf life problems.

3. Surfaces will be characterized by SIMS and Auger to determine the presence and concentration of copper on the surface. This will be correlated with bonding results.

4. Gold ball bonding experiments will be conducted to determine the effect on bondability. Note: the bonding will be carried out at two ultrasonic frequencies.

5 Autocatalytic gold baths will be developed or purchased to repeat above (1 to 4). Methods will be developed for introduction of grain boundary diffusion inhibiting impurities that do not reduce bondability.

As-deposited samples of electrodeposited 24K gold (0.5 µm and 1.0 µm thick) on copper have been successfully wire bonded. These will serve as a baseline. Copper/gold diffusion studies are ongoing and will be correlated to subsequent bonding results. Two papers have been presented (Harman) on the problems associated with wire bonding to advanced Cu/LoK devices.

Contributors and Collaborators

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Measurements for Electrodeposited Copper

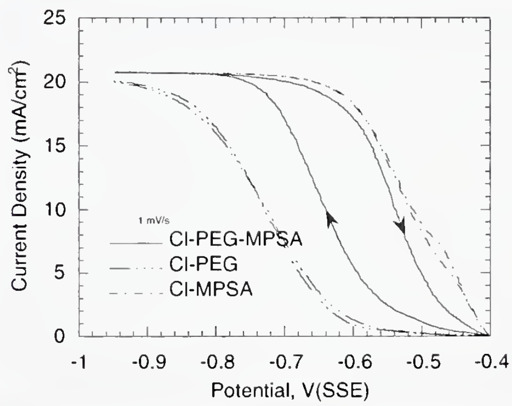
Gery R. Stafford, Thomas P. Moffat, and Daniel Josell

Copper is rapidly being introduced into chip interconnection technology as a replacement for aluminum. Electrodeposition is the preferred deposition method due to its unique ability to superconformally fill high aspect ratio features when organic inhibitors are added to the plating bath. Evaluation of prospective electrolytes could be greatly accelerated by developing a predictive capability for describing the influence of electrolyte species on superconformal deposition, and by developing on-line monitoring tools that will allow industry to determine the additive efficacy and consumption in commercial copper plating baths.

Superconformal electrodeposition of copper in 500 nm deep trenches ranging from 500 to 90 nm in width has been demonstrated using an acid cupric sulfate electrolyte containing chloride (Cl), polyethylene glycol (PEG), and 3-mercapto-1-propanesulfonate (MPSA). In contrast, similar experiments using either an additive-free electrolyte, or an electrolyte containing the binary combinations Cl-PEG or Cl-MPSA, resulted in the formation of a continuous void within the center of the trench. The steady-state i-E characteristics for copper deposition from electrolytes containing various combinations of Cl-PEG-MPSA are shown in the figure below. The addition of Cl-PEG provides significant inhibition of the deposition reaction while the combination of Cl-MPSA leads to an acceleration of the deposition rate. The combined action of all three additives, Cl-PEG-MPSA yields net inhibition and significant hysteresis which reflects the competition between Cl-PEG inhibition and the catalytic effects of Cl-MPSA. The observation of hysteresis is significant because we have been able to correlate its presence to superconformal deposition. Consequently a simple voltammetric measurement may eventually be used to monitor and explore additive efficacy and consumption in commercial copper plating baths.

The hysteresis observed in the voltammetry is due to the competitive adsorption between an inhibiting Cl-PEG surface layer and a catalytic MPSA layer. We have initiated experiments that will eventually allow us to probe the copper – electrolyte interface in the potential region where hysteresis is observed. The nonlinear optical technique of vibrationally resonant sum frequency generation (VR-SFG) is uniquely interface specific and can be applied to the *in situ* study of electrodes. We have successfully measured ex situ VR-SFG spectra of MPSA on both gold and copper substrates. Five resonant features between 2800 and 2950 cm^{-1} can be attributed to the CH_2 groups of the MPSA. *In situ* measurements in 0.01 mol/L $HClO_4$ failed to show these features although a decrease in the non-resonant background due to the substrate was apparent. We attribute this to an all-trans conformation of the MPSA, resulting in unobservable resonance features. An *ex situ* VR-SFG measurement of MPSA on Au, focusing on the symmetric stretch of the sulfonate end group at 1070 cm^{-1}, suggests that the kinetics of MPSA adsorption may be examined, *in situ*, in this way. Future *in situ* VR-SFG measurements will be made under steady state potential control.

A modeling effort is underway to exploit the Division's considerable expertise with phase field models of interface motion. The phase field method has been used to model solidification with considerable success, but this is the first time that this powerful approach has been applied to electrochemistry. This technique abandons the notion of a sharp interface and replaces it with a continuous field variable and governing equation that describes whether a material is solid or liquid as a function of both position and time. This avoids the mathematically difficult problem of tracking an interface whose shape is part of the solution. Intricate morphologies can be solved using simple finite difference techniques on a uniform mesh. Our work is focused on expressing the nonlinear kinetic relationship inherent to electrochemical processes in a manner consistent with the phase field method, verifying the model for simple geometries that have analytical solutions, and simulating the deposition of additive-free solutions into relevant trench geometries. We will then extend the model to account for additive effects, incorporating experimental kinetic data obtained in this project.. This model has the potential of aiding design of complex interface shapes.



A distinct hysteresis loop is observed in the i-E curve for C1-PEG-MPSA electrolyte that is absent for the binary additive combinations.

Contributors and Collaborators

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Electrodeposition of Alloys: Pb-free Solders

Christian Johnson and Maureen Williams

The electrodeposition of metallic alloys has been central to the growth of the electronics and magnetic recording industries. This is largely due to the exceptional properties exhibited by electrodeposited material as well as the favorable economy of scale associated with electrodeposition processes. Composition and microstructure are generally controlled by electrolyte composition, solution hydrodynamics and electrode potential. A technology important to electronics manufacturing is the electrodeposition of Sn-based protective coatings to guarantee solderability.

Through participation in the National Electronics Manufacturing Initiative working group on Pb-free solder alloys, it was learned that significant industrial problems had arisen due to contamination of Pb-free solders by the Pb contained in the protective solder coatings that are used on Cu leads. The protective layer deposited on Cu is usually referred to a pretinned coating and is required to maintain solderability of the component during storage prior to assembly. Thus the development of Pb-free alloy platings to replace Pb-containing protective layers is considered important.

It is well known that the use of pure Sn protective deposits has serious problems. Sn whiskers (1 μm diameter and several mm long) can grow from the Sn plate and cause electrical shorts and failure (see Figure 1). Historically Pb was added to Sn plate to prevent whisker growth as well as to lower cost. In the current research program, it was thus decided to focus this project on Pb-free Sn-rich deposits with alloying additions that would retard whisker formation. The Sn-Cu system was chosen, as the Sn-Cu-Ag is likely to be the Pb-free bulk solder of choice for industrial application. The basic idea is that the substitution of a different solute for Pb in the Sn-rich deposit will also retard whisker growth.

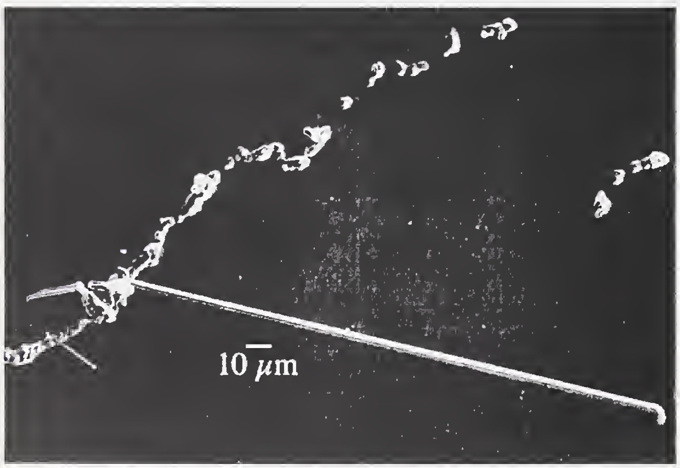

Figure 1. Long whisker growing from bulbous eruption on the surface of a tin deposit.

Whiskers are generally believed to grow to relieve residual stress in electroplated Sn. However it is not at all clear what is the origin of the stress. Grain size and deposit thickness also should play a role. Thus in the process of developing plating methods to control grain size, residual stress and alloy composition, we will elucidate the mechanism for whisker growth and develop suitable plating approaches to prevent their formation.

An initial set of experiments was performed to establish the feasibility of Cu-Sn codeposition from pyrophosphate, commercial sulfate and commercial methanesulfonate electrolytes. In the case of the Sn-based electrolytes containing copper sulfate, one can assume that the copper deposition reaction proceeds at the diffusion-limited current density. The theoretical alloy composition can then be calculated assuming a Cu(II) diffusion coefficient of 5.0×10^{-6} cm^2/sec, a diffusion layer thickness of 100 μm, and a Sn current efficiency of 80%. As expected, the theoretical alloy composition increased linearly with the Cu(II) electrolyte concentration. It is also clear that the experimental alloy compositions deviate from those expected based on calculations that assume a diffusion limited copper reaction. This is likely due to an error in our estimated diffusion layer thickness and indicates that rigorous hydrodynamic control should be implemented in future experiments. If such changes in the experimental set-up are implemented, it is clear that rigorous control of the alloy composition can be obtained.

We have constructed a rotating electrode plating cell to reproducibly deposit Sn and Sn alloy coatings. A variety of substrates including amorphous carbon, vapor deposited Cu and electroplated Cu and Sn will be examined to determine the effect of substrate on deposit microstructure and whisker growth. Special emphasis is being focussed on the characterization of the grain size, surface topography and residual stress. The later is being measured using 'sine-squared -psi' analysis.

We plan in the next year to determine the conditions that lead to whisker formation, such as: intermetallic formation from copper-tin interdiffusion, substrate effects on tin nucleation and impurity inclusion in the tin deposits, either organic or inorganic.

Contributors and Collaborators

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METALS CHARACTERIZATION

Engineering design depends on specification of the properties of the materials that are used, and manufacturers and their suppliers need to agree on how these properties should be measured. In many cases, they depend on measurements that can be traced to Standard Reference Materials (SRMs). This program generates SRMs for several quite different types of measurement. NIST is now providing certified Rockwell hardness test blocks for the C scale and is developing standards for additional scales. NIST is also providing leadership at national and international levels in the development of standardized test procedures and traceability protocols. Standards are also produced for microhardness.

The need for reliable magnetic measurements is becoming increasingly acute because of new technologies involving magnetic phenomena in data storage and microelectronics. Such measurements require calibration of magnetometers using certified magnetic standards in several different shapes and magnetic strengths, and with a wide range in magnetic character. These standards are now being produced under this program.

Coating thickness standards are produced by electrodeposition and are widely used for calibration of coating thickness measuring instruments. Coupons are produced with a wide range of thickness and are bar coded to allow analysis of degradation and life expectancy when the standards are returned for verification.

The Charpy impact machine verification project provides rapid, accurate assessment of test data generated by our customers using NIST SRMs, and, where merited, certifies the conformance of Charpy impact test machines to ASTM Standard E 23. NIST staff participates in ISO Committee TC 164, to ensure that our specimens and procedures remain compatible with associated international and regional standards

NIST provides SRMs for ferrite in stainless steel welds and maintains the system to assign ferrite numbers (FNs) to stainless weld metal specimens, so that the standards sold by NIST will be consistent with previous sets in use around the world.

In the broader sense, a vast range of characterization technologies is needed by U. S. industry to understand the behavior of metals during processing and use. The Metals Characterization Program includes measurements of thermophysical properties of high-temperature materials, advanced magnetic measurement technologies, and measurement and analysis of the deformation properties of nanolayered materials.

The NIST effort in metals characterization has a strong emphasis on electron microscopy, which is capable of revealing microstructures within modern nano-scale materials and atomic-resolution imaging and compositional mapping of complex crystal phases with novel electronic properties. Our NIST microscopy facility is now being enhanced by the addition of a high-resolution field-emission scanning electron microscope capable of resolving features down to 1.5 nm. This FE-SEM maintains high resolution even on uncoated samples, and is equipped with a new detector to provide topographic and compositional images on the nanometer scale.

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Thermophysical Properties During Pulse Heating

Robert J. Schaefer and Daniel Josell

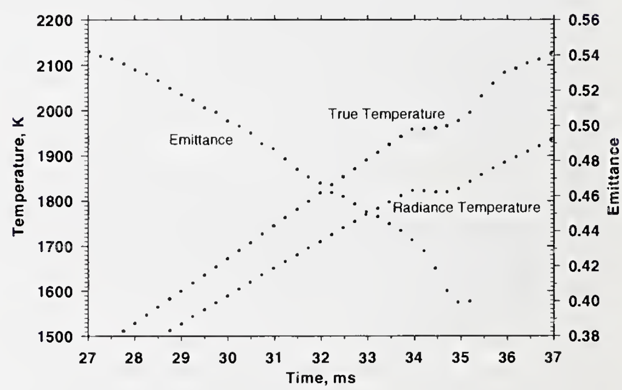
Thermophysical property data are needed as the basis for understanding and modeling many aspects of material behavior, including melting and solidification. This project has developed and applied techniques for measuring several important properties, including specific heat, heat of fusion, and emissivity of high-temperature metallic materials. The measurements have provided benchmark data for pure refractory metals and have recently focussed on emissivity measurements needed for industrial radiometric measurements of process temperatures.

Knowledge of thermophysical properties of metals, such as specific heat capacity, latent heat of fusion, and melting temperature, is essential for a quantitative understanding of how these materials behave during processing and use. For example, these properties are needed for the modeling of metal casting. However, classical thermal analysis techniques for measurement of such properties cannot readily be extended to the high temperatures where data are needed for refractory metals. The NIST high-speed thermophysics laboratory uses electrical resistance self-heating to rapidly pulse heat metal samples to and beyond their melting temperatures, coupled with advanced high-speed radiometric methods to determine the sample temperature, to make benchmark quality measurements of thermophysical properties. Such measurements have been particularly effective for metals such as W, Mo, and Nb with extremely high melting points. During FY2000, the use of a high-speed laser polarimeter to measure normal spectral emittance was demonstrated. The instrument was applied to measurements of properties of niobium and titanium wire-shaped samples heated into their liquid range, the entire experiment being completed in less than 100 μs.

The thermophysics laboratory effort has also focussed on measurements directed toward specific materials problems, including measurements of emissivity properties needed for proper interpretation of two-color pyrometry methods, and the use of coated metal samples to expand the range of applicability of the pulse heating method..

The pulse heating facilities and radiometric instruments of the thermophysics laboratory have been used to determine the wavelength dependence of the emissivity of W and Mo at temperatures up to their melting point. These data were needed to interpret the measurements made by an imaging two-color pyrometer which is used for analysis of thermal spray processes. The usual practice in two-color pyrometry is to make the "gray body" assumption, that the emissivity is independent of wavelength. Simultaneous measurements on heated metal samples were carried out using several radiometric instruments including the two-wavelength imaging pyrometer. These measurements provided calibration for the imaging pyrometer and showed how to account for the error resulting from the gray body assumption, which if uncorrected would introduce a systematic error of 50 K at 1600 K and almost 300 K at 3654 K.

Two types of coated samples were found to yield data not previously obtainable by pulse heating experiments. The first approach uses the coating to permit study of the underlying wire properties (e.g., to study high vapor pressure materials). The second approach uses the wire as a substrate to permit study of the coating properties (e.g., for materials that are nonconductive or difficult to fabricate in bulk). The first approach, using a tungsten coating, was applied to a study of the melting behavior of chromium. In this case, melting of the substrate material is revealed by a plateau in the temperature-time data. The second approach was used in a study of titanium coatings on molybdenum wires. In this case the temperature rises steadily past the melting point of the titanium, but a sharp decrease in the spectral emissivity reveals the melting of the coating (see Figure).



Melting data for a 24 μm thick coating of Ti-19 at. %Al on a Mo rod substrate.

Contributors and Collaborators

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Mechanical Properties of Multilayered and Nanomaterials

Tim Foecke, Don Kramer, and Dan Josell

Mechanical performance of layered structures is important to large sectors of U.S. industry: reliability of microelectronic devices, tribology of magnetic media, and integrity of aerospace thin film coatings. Predictive design of mechanical properties relies heavily on knowledge about how these materials deform and fracture at very fine scales. Research in this project is aimed at determining what deformation mechanisms operate in these classes of materials as a function of layer thickness and constitutent materials using novel experimental techniques. This information will be useful in designing devices and modeling layered systems.

Nanomaterials have been found to exhibit a number of extraordinary mechanical properties relative to larger grain bulk materials. Strengths and hardnesses that are many times that of either constituent bulk material have been observed in nanograined (3D) and nanolayered (1D) structures. In particular, multilayered materials with wavelengths in the micron and submicron regime offer exciting opportunities, because the ability to fabricate these materials using PVD or electrodeposition makes these materials economically viable to produce. Also, one can use pairings of materials that are immiscible, and not able to be conventionally processed.

Prior work in this program saw the development of a novel *in situ* TEM deformation geometry and the first observations of dislocation generation and motion in any nanoscale material system. We are expanding on this early work to determine the effect of layer thickness, interfacial character and constituent materials on the deformation and fracture micromechanisms that operate in these material systems.

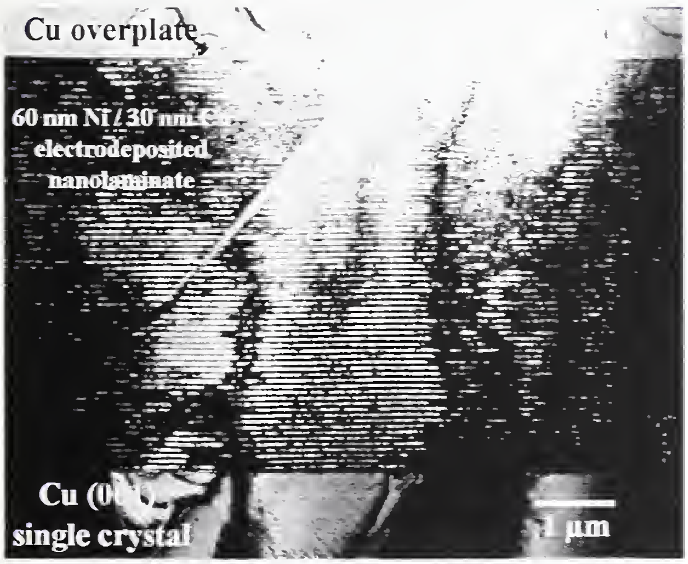

Image of crack in Cu/Ni nanolaminate formed during *in situ* TEM deformation experiment.

A universal observation regarding nanophase materials is that they exhibit very little macroscopic ductility preceding failure, even in structures composed of inherently ductile materials. Results from the *in situ* TEM deformation experiments have begun to reveal the physics behind this behavior. It is seen that near the crack path, local strains are actually very high, but that the deformation is concentrated within an extremely narrow region along the crack path.

This can be explained when one considers the limitation on the dislocation mean free path provided by the interfaces bounding the layer. Under this model, the plastic zone width should equal roughly 2 times the layer thickness, which is what is seen in the TEM. Further work is in progress to examine the effect of layer geometry on enhancing toughness in nanolayered structures.

The results from our mechanical property determinations are being used by theory groups at Ohio State University and Los Alamos National Laboratory to modify their models of these structures. These groups are now concentrating on the details of how dislocations interact with interfaces, and how interfaces act as barriers to dislocation motion.

Another facet of the program deals with the high-temperature structural stability and mechanical behavior of Nb/Nb_5Si_3 microlaminated materials. Work performed in conjunction with The Johns Hopkins University has determined how to form these structures so that they are stable for hundreds of hours at temperatures exceeding 1300 degrees Celsius.

The Air Force is intensely interested in this class of materials for use as a strong, damage tolerant critical coating on jet engine turbine blades, and is investigating whether microlaminated silicide/refractory metal microlaminates may be used to form hollow turbine blades in the absence of any superalloy substrate.

Contributors and Collaborators

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Hardness Standardization Rockwell, Vickers, Knoop

Samuel R. Low and Christian Johnson

U.S. industry needs to be able to make measurements that are traceable to national standards and compatible with the measurements made in other countries. This need is being emphasized by the requirements of quality standards such as ISO 17025. For the measurement of hardness, NIST is meeting this need by standardizing U.S. national hardness scales, producing hardness reference standards, and providing assistance and guidance to U.S. industry through national and international standards activities.

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

At the international level, we are participating in a newly formed Working Group on Hardness under the International Committee for Weights and Measures (CIPM), its primary goal to standardize hardness worldwide. We are also leading the U.S. delegation to the ISO committee on hardness testing of metals, which oversees the test method standards for most common hardness tests. Because NIST is the Secretariat for the hardness committee of the International Organization for Legal Metrology (OIML), we are currently rewriting the OIML hardness standards to be used by countries desiring to regulate hardness.

Rockwell hardness SRMs for the HRC scale.

Our primary task at the national level is to standardize the U.S. national hardness scales and to provide a means to transfer the scale values to industry. Currently, we are producing test block Standard Reference Materials® (SRMs) for the Rockwell, Vickers and Knoop hardness scales, as well as developing new reference standards.

Magnified view of Knoop indentation in a new gold micro-hardness test block developed for the electronics industry.

We are providing microhardness Vickers and Knoop SRMs, which are produced using electrodeposition technology to provide metal with uniform properties and microstructure. Presently, electroformed copper and nickel standards are eal the physics behind this behavior. It is seen that near the crack path, local strains are actually very high, but that the defo A mirror finish is attained by single-point diamond turning of the soft 24 K gold surface.

The release of the NIST Rockwell C scale (HRC) SRMs has had a large impact on U.S. industry by shifting the U.S. HRC hardness scale to be more closely in-line with other industrialized countries. This year, due to the importance of the NIST hardness standards to U.S. industry, the ASTM has revised the Rockwell hardness standard (ASTM E18) to now require that measurements and calibrations be traceable to the NIST hardness scales when transfer standards are available.

We are collaborating with the Manufacturing Engineering Laboratory to accurately measure the geometry of hardness indenters (a major error source in hardness testing). This year, we have begun work with a U.S. company that recently received a Phase II SBIR award from NIST to develop an improved method for producing Rockwell diamond indenters.

We are collaborating with National Voluntary Laboratory Accreditation Program to develop an accreditation program for hardness calibration laboratories. This year, we participated as the technical expert in the successful accreditation of two U.S. secondary level hardness calibration laboratories.

Contributors and Collaborators

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Magnetic Properties and Standard Reference Materials

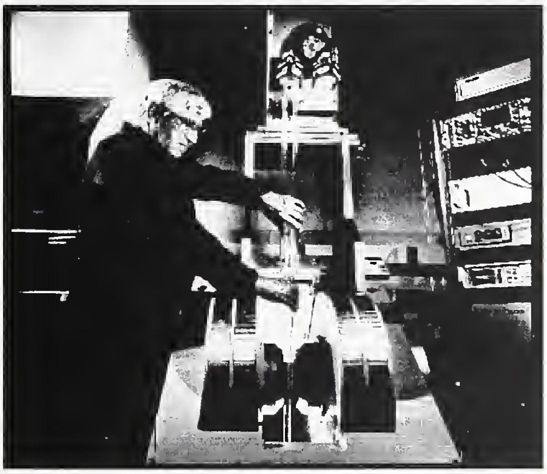
R. D. Shull and R. D. McMichael

Users of magnetic materials, including the recording industry, the permanent magnet industry, and the manufacturers of electric motors and transformers of all types, need standard reference materials (SRM's) to calibrate instruments used to measure the critical magnetic properties of their starting materials. The magnetic materials group is in the process of developing such standards. Methods for improving the efficiency and accuracy of measuring and characterizing magnetic materials of industrial importance are also under investigation.

In this project, measurement methods and magnetic standards are developed that are important to the scientific and industrial communities working in magnetism. The work is done in collaboration with scientists from universities, industry, and other Divisions at NIST. In FY2000, the emphasis has been on development and production of standard reference materials, methods for characterization of magnetostriction and time dependent magnetization and microstructural effects.

Commercial instruments for the measurement of magnetic properties are relative instruments which rely on known samples for their calibration. To certify standard samples for such instruments, an absolute magnetometer was developed and assembled at NIST. A picture of this instrument is shown below.

Recent modifications to the absolute magnetometer to improve its sensitivity will enable certification of reference materials for the calibration of very sensitive alternating gradient magnetometers and SQUID magnetometers. Paramagnetic platinum and very small ferromagnetic yttrium iron garnet spheres are under development. To date two SRM's have been issued, a nickel sphere (SRM 772a) and a nickel disc (SRM 762).



Methods for the characterization of accommodation and aftereffect are under development. These effects describe slow variations in magnetization that are important for magnetic data storage and permanent magnets. The purpose this study is to: (1) improve the characterization methods for magnetic recording media, (2) improve the characterization of the long term behavior of permanent magnetic materials, (3) develop reference materials useful for checking instruments designed to give a complete characterization of magnetic hysteresis loop characteristics, and (4) facilitate commerce in magnetic materials through improved agreement between producer and consumer on the measurement of magnetic properties at a lower cost. To these ends, a Preisach-Arrhenius model for the prediction of magnetic stability with changes in temperature was developed. This model gave good predictions between 150 K and room temperature. However, below 150 K experimental data were at variance with the model's predictions. A new model, based on Bose-Einstein statistics was developed. This model gave good results for data obtained on a high density commercial magnetic particle recording tape over the entire measured temperature range. We are now testing the model on other recording media and on a permanent magnetic material.

We previously developed a magnetic measurement that was correlated with the yield stress for steels. A small scale effort is continuing in this area, designed to examine the physical origin of the phenomenon. To test the effects of small deformations on magnetic properties, a series of tensile test specimens of ultra low carbon steel was subjected to small plastic strains (0%, 0.05%, 0.1%, 0.4%, and 1.1%) and the specimens were provided to the State University of New York at Buffalo for investigation of their magnetic domain structure and for comparison of mechanical and magnetic properties. The work at SUNY-Buffalo was sponsored by the American Society for Non-Destructive Testing. The Barkhausen signals due to domain wall motion were sensitive to even the lowest strain values even though no changes in the coercive fields could be detected. The different effects of interstitial carbon and dislocations on the pinning of domain walls were clearly delineated by domain imaging, indicating that magnetic sensing of mechanical properties should be effective in these materials.

Contributors and Collaborators

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Electrodeposited Coating Thickness Standards

Carlos R. Beauchamp

Standard Reference Materials (SRMs) of nonmagnetic coatings over magnetic substrates, with nominal thickness values ranging from 6.0 µm (~ 0.2 mils) to 2000 µm (~ 80 mils), are produced for the organic and inorganic coating industry for nondestructive measurements. SRMs 1358b, 1359b, 1361b, 1362b, 1363b, and 1364b consist of four different coating thickness values and a steel substrate.. Zinc standards for the electrogalvanizing industry are being explored.

The Electrochemical Processing Group is responsible for producing seventeen different thickness standards of nonmagnetic coatings over magnetic substrates, with thicknesses ranging from 6.0 µm (~ 0.2 mils) to 2000 µm (~ 80 mils). Each standard consists of a 1270 µm (~ 50 mils) thick magnetic steel substrate, electroplated with fine-grain copper of varying thickness, and a thin nonmagnetic layer of chromium for wear resistance. These standards are packaged into preconfigured sets of four coupons. Each set consists of different ranges, depending on the needs of our customers. The standards are certified with a maximum expanded uncertainty of 2 % of the mean at the 95 % level of confidence and are used for the calibration of instruments based on the magnetic pull-off technique or those based on magnetic induction.

These standards are used by the organic and inorganic coating industry for non-destructive measurements of non-magnetic coatings over magnetic substrates. Some of the industries using our standards are paint, electronics, aerospace, automotive, steel, nuclear, railroad, welding, and tool and dye. Typical applications where our SRMs provide a critical need include the evaluation of wear in coatings and coating thickness evaluation during the finishing stages or the repair of worn parts. Our coating thickness standards are used to verify coating thickness requirements for corrosion protection as well as thickness tolerances for the successful assembly of coated parts. These standards are also used by coatings industries where properties ranging from electrical and thermal conductivity to solderability are optimized by the thickness of the coating.

In FY2000, our goal was to replenish the inventory of SRM Coating Thickness Standards 1358b, 1359b, 1361b, 1362b, 1363b, and 1364b. This required the fabrication and certification of 817 units. At this time, about 70 percent of the required 3,268 individual coupons have been measured and it is anticipated that all 817 units for FY2000 as well as the 77 units promised for FY2001 will be delivered by January of 2001.

This year, we also initiated an outreach effort to motivate instrument manufacturers, standards producers, and users to discuss their current needs and to determine how well the current coating thickness product line serves their needs.

We are also providing a long overdue service to this industry by providing a Best Practices Guide that addresses the critical metrology issues associated with the magnetic induction measurement and the recommended use of our coating thickness standards.

This year, we have also continued our effort to provide coating thickness and composition standards to the electrogalvanizing industry. Zinc on steel coupons measuring 3 cm x 3 cm are requested so that gravimetric procedures used in the weigh-strip-weigh method of determining zinc thickness can be properly evaluated. A second standard, used for on-line x-ray fluorescence measurements, is also being developed. Efforts at this moment are focusing on gaining tighter control over the thickness uniformity and crystal orientation of the zinc electrodeposit. The critical bath chemistry and deposition parameters that result in the proper crystal orientation have been determined.

Coating Thickness Standard Reference Materials available sets and their corresponding nominal thickness.

SRM	Coating Thickness Values			
1358b	20 µm (0.8 mils)	80 µm (3.1 mils)	255 µm (9.8 mils)	1000 µm (39 mils)
1359b	48 µm (2.0 mils)	140 µm (5.5 mils)	505 µm (20 mils)	800 µm (32 mils)
1361b	6 µm (0.2 mils)	12 µm (0.5 mils)	25 µm (1.0 mils)	48 µm (2.0 mils)
1362b	40 µm (1.6 mils)	80 µm (3.1 mils)	140 µm (5.5 mils)	205 µm (7.9 mils)
1363b	255 µm (9.8 mils)	385 µm (16 mils)	505 µm (20 mils)	635 µm (26 mils)
1364b	800 µm (32 mils)	1000 µm (39 mils)	1525 µm (59 mils)	1935 µm (79 mils)

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Nanoscale Characterization: Electron Microscopy

John E. Bonevich

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

Atomic-scale structure and compositional characterization of materials can lend crucial insights to the control of their properties. For instance, direct observation of local structures by transmission electron microscopy (TEM) provides an important information feedback to the optimization of crystal growth and processing techniques. Various characteristics may be observed such as crystal structure and orientation, grain size and morphology, defects, stacking faults, twins and grain boundaries, second phase particles -- their structure, composition and internal defect structure, compositional variations and the atomic structure of surfaces and interfaces.

The MSEL Electron Microscopy Facility consists of two transmission electron microscopes, a specimen preparation laboratory, and an image analysis/computational laboratory. The state-of-the-art JEOL3010 UHR-TEM has atomic scale resolution as well as detectors for analytical characterization of thin foil specimens. An X-ray detector provides compositional analysis and an energy selecting imaging filter (IF) allows compositional mapping at atomic resolution.

Highlights from the EM Facility include:

- The IF has been used to reveal how oblique deposition of Ta underlayers promotes large scale magnetic anisotropy in subsequent Co deposition in thin films (see Figure 1).

- The Facility has been enhanced by the addition of a computer-controlled ion mill with an ion-beam terminator and liquid nitrogen cold stage. The XLA-2000 mill has allowed successful preparation of Ti-Al multilayers without forming fcc-Ti artifacts noted elsewhere (see Figure 2).

- Investigations on Cu electrodeposition processes for on-chip interconnects have been initiated. Superfilling in vias from 500 nm to 90 nm was demonstrated. For precise preparation of these specimens, we have established a collaboration with the Institute for Plasma Research to gain access to focussed ion beam (FIB) facilities.

- Linewidth standard reference materials have been characterized for the semiconductor electronics industry. The reference features are based on {111} planes of Si wafers. Atomic resolution lattice counting provides an absolute measurement of width traceable to the meter.

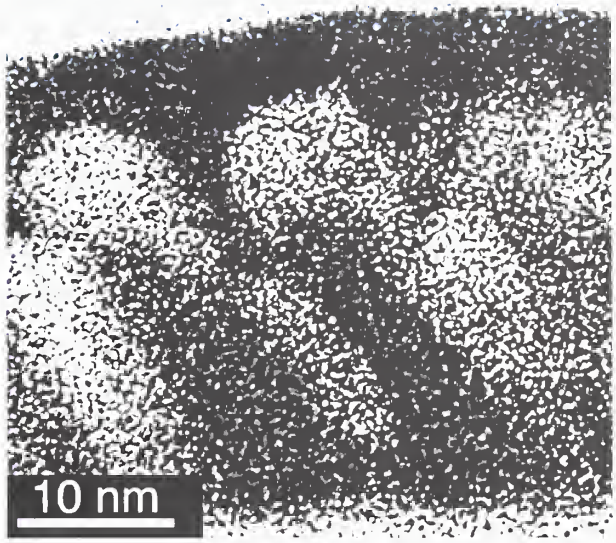

Fig. 1. Oblique deposition of Ta underlayer (dark) promotes discontinuous Co layering (light) in a magnetic thin films.

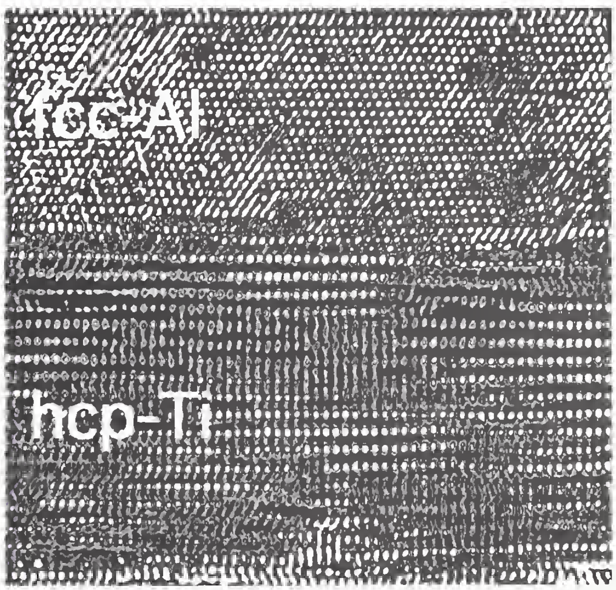

Fig. 2. Ti and Al multilayered materials retain their bulk, equilibrium structures even as thinned TEM specimens.

Contributors and Collaborators

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METALS PROCESSING

The Metals Processing Program directs its attention to problems identified as important by industries ranging as widely as automotive, aerospace, coating, and microelectronics. The general nature of the problem is to understand the processing steps that will lead to products having the desired form and properties, at an acceptable cost. The types of processes considered range from melting and solidification of castings or single crystals to powder production and consolidation, and coating production by thermal spray and electrodeposition. The work thus uses NIST expertise in a wide range of disciplines, including thermodynamics, electrochemistry, fluid mechanics, diffusion, x-ray, and thermal analysis, and many others.

The use of metals and their alloys is based on physical properties that are developed through careful design of their processing cycle. This cycle can include many steps including a formation process such as solidification or electrodeposition, a heat-treatment process, and a deformation process such as rolling or stamping. In each of these processes, the distribution of crystal phases, the grain structure, the alloy's compositional segregation, and the defect structure are altered, with resulting changes in properties such as strength, ductility, corrosion resistance, and conductivity, which properties form the basic rationale for the use of metals in industrial products. The Metals Processing Program focuses on measurements and predictive models needed by industry to design improved processing methods, provide better process control, develop improved alloy and coating properties, and reduce costs.

This program applies advanced sensor and measurement systems to monitoring, diagnostics, and control of processes such as thermal spray, welding, and electrodeposition. All of these areas are important to the automotive industry, where low cost, high reliability, and rapid development of new products are critical. Sensors, usable in either a laboratory or industrial environment, are developed and applied to better understanding of processing phenomena or to feedback and control systems. Modeling plays a central role in several projects, allowing prediction of the correlation between processing conditions and the material response. Current modeling effort includes prediction of solidification, grain growth, and electrodeposition geometries by the phase field method, and prediction of solute diffusion in multicomponent materials.

Metals Processing projects with an especially strong focus on areas that are of special interest to MSEL have evolved to become part of other program areas such as Materials for Microelectronics and Forming of Lightweight Materials. Because processing plays such a basic role in determining the properties and performance of metals, we expect this program to continue providing a foundation for advanced metals technologies.

Contact Information: **Stephen D. Ridder**

Modeling of Solidification and Microstructure Development

W. Boettinger, J. Warren and S. R. Coriell

Most properties of structural and functional materials depend on the distribution of composition, phases and grain orientations on the scale of 1 to 100 μm. Models of alloy solidification, crystal growth processes and heat treatment are being developed using several methods. These models are providing information to aid industry in designing production systems that increase product yield and performance.

Modeling of microstructures produced by solidification and other processes involves mathematical solution of equations for heat/fluid flow and solute diffusion. Boundary conditions on external surfaces reflect the macroscopic processing conditions. Boundary conditions at internal interfaces corresponding to the liquid-crystal (grain) or grain-grain interfaces. These internal interfaces are moving boundaries and require boundary conditions with thermodynamic and kinetic character. For solid-solid transformations, stress and strain replace fluid flow as a consideration.

We use two methods to solve these problems in which the internal interfaces are modeled as either sharp or diffuse. The former is more traditional and often provides analytical solution of problems. The latter (called the phase field method) requires numerical methods but more easily deals with complex interface shapes. This project has produced 14 publications on microstructure development in FY 2000.

Dendritic growth is always present in castings and determines the scale of segregation and involves extremely complex interface shapes. Several of the accomplishments of FY 2000 deal with this subject. Diffuse interface modeling has lead to the following accomplishments.

- The phase field models have been extended to describe the growth and final impingement of differently oriented dendritic grains. Knowledge obtained near the end of solidification has practical applications in predicting porosity and hot tearing of castings. It also predicts the final grain size.
- 3-D alloy dendrites have been successfully modeled with the phase field method using parallel computing methods (see Figure).

Sharp interface modeling has led to the following accomplishments.

- The dendrite tip shape has been described with four-fold axial perturbations of a paraboloid that agree with recently published measurements made in microgravity.
- In collaboration with M. Rappaz (EPFL, Switzerland) a method has been developed to treat dendritic solidification of grains of multicomponent alloys. This method is appropriate for insertion into commercial casting modeling software.
- The Jackson-Hunt model of eutectic growth has been extended to treat different phase densities, which give rise to fluid flow. The calculated flow pattern is found to alter the solute diffusion profiles. The interface undercooling and volume fractions are very different than those predicted by the original theory.
- A simple Rayleigh number based method was developed to predict freckles in directional solidified superalloy castings. The method has been implemented into a commercial software code, ProCAST®, to guide selection of alloys and process conditions to avoid these defects.
- Electrical pulsing is a measurement technique to delineate the crystal-melt interface shape in optically opaque semiconductor materials. A numerical algorithm is used to predict the solute distributions created by the pulsing method. These results permit experimentalists to determine the optimal pulse amplitude and frequency for the delineation technique.
- Northrop Grumman Corporation is developing a single crystal mercurous chloride acousto-optic tunable filter for use in a hyperspectral camera. NIST scientists are refining models of physical vapor transport of mercurous chloride in order to optimize the processing conditions for growth of large crystals.

View of a simulated 3-D alloy dendrite with liquid removed. The colors represent variations of concentration along the liquid-solid interface that are also proportional to that incorporated into the frozen solid.

Contributors and Collaborators

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Sensors and Diagnostics for Thermal Spray

Reliable control of thermal spray process parameters has been identified as a key to production of reproducible products including protective coatings. We are developing and evaluating advanced sensor and diagnostic systems to measure parameters such as particle temperatures and velocities and substrate characteristics during thermal spray processes. We identify sources of variability in process parameters and develop control strategies to produce a more reproducible and reliable product.

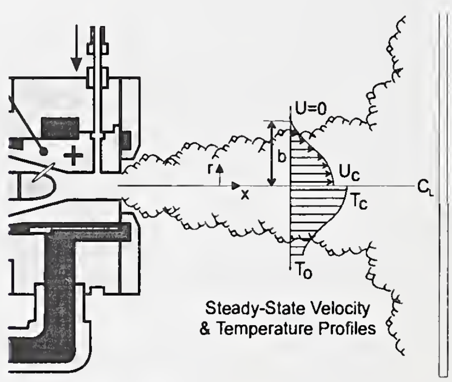
Stephen D. Ridder

Thermal spray is a process in which material particles or droplets are heated and propelled toward a substrate to form a coating or a bulk deposit. Several types of thermal spray systems are now available but a problem common to many of them is the difficulty of obtaining reproducible deposits when using control based on settings of the input parameters to the spray gun, such as voltage and gas pressure. We are working with sensors which can measure parameters of the gun, the spray plume, and the substrate, and identify sources of variability in these parameters and their effect on deposit properties. Because so many parameters affect the quality of coatings applied by thermal spray, an integrated system for control of the spray system input settings and monitoring of the output has been developed.

One component of our program is a two-color imaging pyrometer which has a capability for time-resolved measurements currently lacking in other commercial instruments for particle temperature and velocity measurement. These measurements have shown significant variations in the instantaneous average temperature and velocity of the particles in the plume of an air plasma spray gun. Other sensors include a schlieren system for analysis of gas flow densities and a Coriolis meter for analysis of powder flow rates. The latter has time and flow rate resolution much better than conventional systems based on the changing weight of the powder supply hopper. These have revealed additional types of variability in plasma spray plumes, such as those due to unsteady rates of flow in the powder feed system.

Although two-color pyrometry is the only method currently available for measuring the temperatures of rapidly moving particles with unknown sizes, two-color pyrometry measurements are subject to several sources of error, including errors due to ignorance of the emissivity of the material under study. It is generally assumed, for lack of any more specific knowledge, that the emissivity is independent of wavelength. We have measured the wavelength dependence of emissivity of several metals, which is needed for accurate conversion of two-color pyrometry measurements into absolute temperatures, at temperatures up to their melting points. The measurements have shown that the usual assumption that the emissivity is independent of wavelength can result in a temperature error which increases with temperature and can be several hundred Kelvins at the melting point of tungsten.

Substrate preparation and condition are critical parts of successful coating application. Recent experiments and computer simulations have indicated that the behavior of droplets striking on a substrate is a strong function of substrate temperature and topography. Non-contact sensors capable of measuring these parameters are under development. Radiometric measurement of substrate temperatures is particularly challenging because of the presence of reflected light from the spray plume and because of variations in the surface emissivity. These problems are being addressed through detector designs incorporating appropriate light shielding, wavelength selection, and reflection of modulated light sources.



Particle acceleration and heating are governed by the velocity (U) and temperature (T) distribution in the plasma jet.

Contributors and Collaborators

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Tailored Metallic Powders

There is an intensive search for new materials properties which will be "tailored" by designing its microstructural components. The success of "creating" such materials is strongly dependent on how well we understand the relationships among properties, processing and microstructure. The objective of this research is to develop measurement techniques for the structural and chemical characterization of microengineered powders.

L.A. Bendersky and J.H.J. Scott (CSTL)

The objective of this research is to develop measurement techniques for the structural and chemical characterization of microengineered powders – powders that are either intrinsically nanoscale or combine nanoscale coatings/layers with conventional micropowders. The availability of such measurement techniques will lead to improved understanding of critical microengineered powder fabrication processes such as chemical vapor deposition, physical vapor deposition, multilayer formation, powder agglomeration and sintering, interfacial reactions, and grain growth.

Significant progress has been made in a number of areas in FY 2000. Some highlights of these results are presented below:

• Recently, an electron backscatter diffraction (EBSD) system was developed for the scanning electron microscopy that uses a 1024 x 1024 charge-coupled device camera coupled to a thin phosphor. In this system, crystallographic information on small particles is determined from the EBSD pattern and coupled with the elemental information from energy or wavelength dispersive x-ray spectrometry. Identification of the crystalline phase of a small particle is then made through a link to a commercial diffraction database. Previously this system has been applied almost exclusively to conventional, bulk samples that have a polished, flat surface.

• We developed a 2-dimensional valence mapping technique based on electron energy loss spectroscopy and energy-filtered imaging. A six-window energy-filtering transmission electron microscopy imaging procedure was used to map the valence of Mn in cryptomelane KMn_8O_{16}, a material of interest to the lithium ion battery (Figure 1). In the case of this sample, the L3 and L2 white lines are produced by electronic transitions from 2p3/2 to 3d3/23d5/2 and from 2p1/2 to 3d3/2 states, respectively. The intensity of the lines is a measure of the density of states in the 3d bands, and their ratio is a measure of valence. Background-subtracted L3/L2 ratio values of 4, 2.25 and 2.0 have been experimentally shown to correspond to valences of Mn2+, Mn3+ and Mn4+.

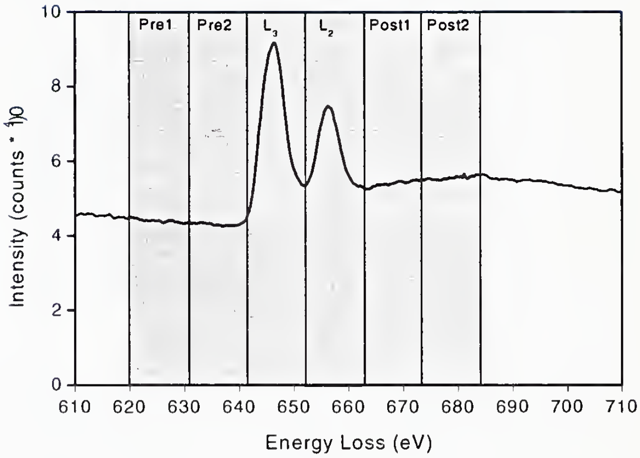

FIG. 1 Electron energy-loss spectrum of cryptomelane KMn_8O_{16}. The six labeled regions indicate the energy windows of the energy-filtered image acquisition..

• We characterized the general morphology of voids in rutile nanoparticles by obtaining images of the voids in several orientations. Orientation of such particles is challenging due to their small size and difficulty in tracking them in a field of many other nanoparticles. Several nanoparticles containing voids were oriented down zone axes including [100], [110], [001], [101], [102], [111], and [211]. By combining the information derived from the two-dimensional projection of the voids in these orientations, a three-dimensional void morphology was derived. The images are consistent with a four-sided prism with dipyramidal terminations with {110} facets predominating in the prism and {101} facets predominating at the dipyramidal terminations.

In the coming year these new techniques will be applied to engineered metallic powders recently fabricated within the industry to validate the techniques and guide the development of additional characterization techniques.

Contributors and Collaborators

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Electrodeposition of Aluminum Alloys

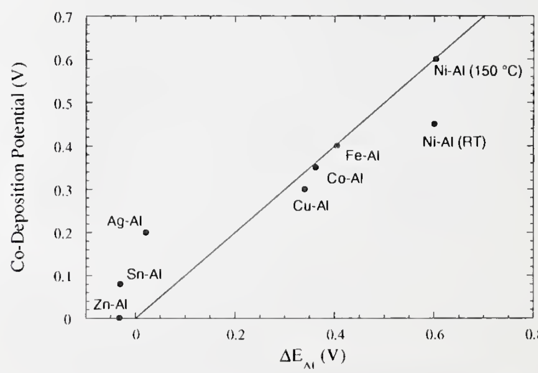
Gery R. Stafford

Aluminum and many of its alloys can impart excellent corrosion protection when applied as a thin coating to other materials. Typical coating technologies include hot dipping, flame spray and physical vapor deposition. Electrodeposition may offer an inexpensive method for producing homogeneous and fine-grained aluminum-based thin films if a low-temperature, low-vapor pressure non-aqueous electrolyte can be developed. Guidelines are needed to predict the deposition conditions for aluminum-based alloys.

Several molten salt systems have been investigated for the electrodeposition of aluminum and its alloys. Binary mixtures of $AlCl_3$ and alkali metal chlorides are molten at temperatures as low as 108 °C. Systems which are molten at room temperature can be obtained when the alkali chloride is replaced with certain unsymmetrical quaternary ammonium chloride salts such as 1-methyl-3-ethylimidazolium chloride (MeEtimCl). These molten salt electrolytes may not only lead to low temperature processes for the electrodeposition of aluminum alloy thin films, but they also provide an excellent medium for carrying out fundamental alloy deposition studies without interference from hydrogen evolution and passivating oxides.

This year we have focused on aluminum-transition metal alloy deposition from the room temperature $AlCl_3$- MeEtimCl electrolyte. The mechanism leading to alloy formation involves the underpotential deposition (UPD) of aluminum during the mass-transport-limited electrodeposition of the transition metal. Several binary alloys of technological importance in the electronics and electrogalvanizing industries are known to form by way of a similar underpotential co-deposition mechanism. If certain assumptions are made, the underpotential shift for aluminum should be directly proportional to the partial molar free energy of aluminum in the alloy. Consequently, one should be able to predict deposition potentials from existing thermodynamic descriptions of alloys. The figure shows a plot of experimentally observed co-deposition potentials versus the calculated underpotential shift (ΔE_{Al}) for aluminum, based on the partial molar free energy of aluminum in the alloy. The calculated alloy deposition potentials are in good agreement with those observed experimentally for Cu-Al, Co-Al, Fe-Al and Ni-Al deposited at high temperature. The temperature dependence in the Ni-Al system is due to a kinetic limitation in the Al co-deposition reaction that has been reported for Ni-Al in the room-temperature melt. It is predicted that no and little alloy formation would be expected for bct Sn-Al and fcc Ag-Al, respectively, whereas some degree of alloying has been observed experimentally in both systems. In the case of Ag-Al, this discrepancy may be due to the deposition of an intermetallic compound whose free energy was not considered in the thermodynamic treatment.

This year we have also examined the electrochemical dissolution of niobium into $AlCl_3$-NaCl at 190 °C in an effort to develop a moderate-temperature electrolyte capable of producing a variety of Al-Nb alloys. Aluminum-refractory metal alloys produced by physical vapor deposition have shown excellent resistance to pitting corrosion in chloride environments. We have found that niobium oxidation begins at about 1.10 V vs. Al with active dissolution beginning at about 1.5 V. Electrochemical impedance analysis suggests that dissolution occurs by way of a two-step electrochemical process involving an adsorbed intermediate. This is an intriguing result since refractory metals have historically been considered inert in chloroaluminate electrolytes. Although it appears that niobium can be dissolved indefinitely, the sustainable concentration of an electroactive species that can be used for the deposition of Al-Nb alloys is limited. This is likely due to either low solubility or chemical instability in the electrolyte. Alloys containing a Nb atomic fraction of up to 60.5 % have been electrodeposited. The Nb content of the alloy varies inversely with the applied current density, suggesting that the niobium deposition reaction is diffusion limited. The structures of these alloys and the electroactive niobium complex in solution are currently under investigation.



Experimentally observed co-deposition potentials versus the calculated ΔE_{Al} values for alloys having a composition of 0.01 atomic fraction aluminum.

Contributors and Collaborators

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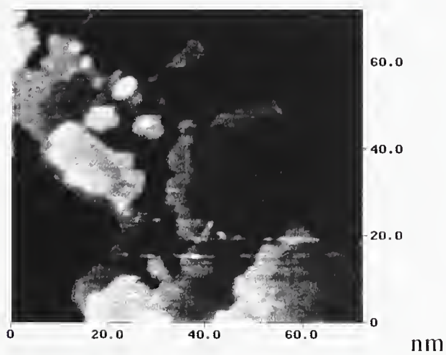
Electrochemical Processing of Nanostructural Materials

Electrochemical methods hold promise for the synthesis and characterization of materials and structures of reduced dimensionality – nanomaterials. Magnetoresistive device architectures ranging from multilayers to spin valves are being examined. Exploring the utility of surfactants and segregation phenomena in controlling homo- and hetero-epitaxial film growth represents a central aspect of this activity.

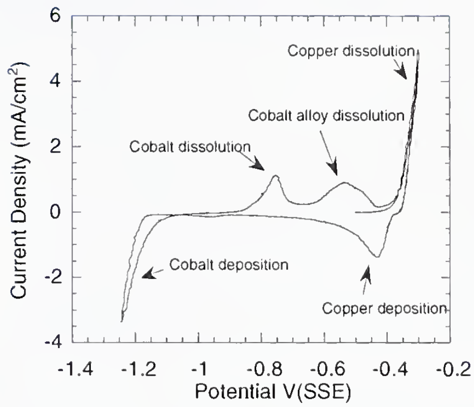
Thomas P. Moffat

In the past decade the influence of surfactants on morphological evolution during metal-on-metal epitaxy in UHV systems has received much attention. In particular, low surface energy metals, such as lead, are known to be active surfactants for control of homoepitaxial growth of late transition metals such as copper. Underpotential deposition (upd) of lead as well as anion adsorption on copper is being used as a model system for studying the applicability of this strategy in electrodeposition. We have used *in situ* scanning tunneling microscopy to reveal several important phenomena associated with lead upd. For example, lead upd on a halide covered Cu(100) surface results in the formation of a two dimensional alloy which subsequently undergoes a dealloying transition as the lead coverage approaches its saturation value. This 2-D phase transition leads to a large change in the step density of the surface and thus may be implemented to minimize the roughness evolution during deposition. Similar studies on Cu(111) reveal sharp changes in the step dynamics and surface mobility with lead coverage.



STM image showing the decoration and alloying at steps on Cu(100) surface by underpotential deposition of lead.

Electrochemical synthesis of multilayers is being explored using two model systems, Cu/Co and Cu/Ni, for studying the magnetic and mechanical properties of laminated systems. Unique attributes of electrochemical deposition are the ability to grow films under conditions of well defined supersaturation, and the ability to probe the defect structure in the materials formed this way by examining the dissolution behavior. Stripping analysis was shown to provide a



Cyclic voltammetry of Cu(100) in acidified cobalt sulfate electrolyte revealing the formation of a Co-Cu alloy.

sensitive probe of the defect generation and associated morphological changes that accompany strain relief during heteroepitiaxial deposition. Likewise, related voltammetric experiments provide evidence of surface segregation and possible compound formation during growth of nominally immiscible Co/Cu multilayers.

In the past year, effort has also been focussed on examining the growth of Co/Cu multilayers on semiconductor substrates with possible application to spintronic devices. In the case of deposition on (100) GaAs, highly textured (100) fcc films may be grown provided the first layer to be deposited is copper. In contrast, if cobalt is directly grown on (100) GaAs, a polycrystalline film results with a (1210) and (1100) texture. However, XTEM indicates formation of an epitaxial 2.5 nm thick bcc variant with cube on cube orientational relationship at the Co/GaAs interface. This normally unstable phase is stabilized by its almost negligible lattice mismatch to the GaAs substrate. Similar observations have been reported for film grown by MBE although the growth rate was 3 to 4 orders of magnitude slower than that used in our studies. Theoretical band structure calculations suggest that bcc cobalt might be attractive for device applications, and the more rapid growth by electrodeposition could make their production more economical.

Contributors and Collaborators

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D. van Heerden (Johns Hopkins University)

Reaction Path Analysis in Multicomponent Systems

Carelyn E. Campbell and William J. Boettinger

A variety of commercially important bonding and reaction processes involve the interdiffusion and concomitant phase formation at metal/metal interfaces, metal/oxide interfaces and metal/vapor interfaces. Prediction of the identity of the transient phases and the rates of reaction for complex multicomponent systems has applications in areas as diverse as transient liquid phase bonding and thermal barrier layers. Models for these reactions based on a comprehensive set of thermodynamic data can be applied to complex systems in which a systematic experimental investigation would be completely impractical.

Several industrially significant multi-component diffusion reactions have been analyzed using models based on thermodynamics and diffusion in multicomponent multiphase systems, as well as compositional analysis of test samples. These reactions include those which occur during the transient liquid phase (TLP) bonding of Ni-based superalloys, the heat treatment of as-cast Ni-based superalloys, and the reaction of Zn with Zircaloy-4.

TLP. To join high temperature turbine materials with a homogeneous composition profile across the joint, TLP bonding uses a thin filler material, which has a significantly lower melting temperature than the bulk material, to wet the base metal. The joint then solidifies isothermally through rapid interdiffusion of an element, such as boron. However, difficulties arise when applying TLP bonding to multicomponent commercial Ni-based superalloys: brittle precipitates may form during the bonding processing degrading the mechanical properties of the joint.

Avoiding these unwanted precipitates requires the correct thermal processing schedule for a given substrate alloy and filler composition, or the correct filler material for a given thermal processing schedule and substrate alloy. To predict the time-dependent diffusion paths, and thus the thermal processing, requires both thermodynamic and kinetic descriptions of the systems. The Ni-based superalloy database developed by the Metallurgy Division has been expanded to include boron. For the binary and ternary systems comprising the Ni-based superalloy system, the available literature diffusion data was used to construct a quaternary diffusion mobility database (Ni-Al-Cr-B).

Numerical simulations of the diffusion paths have been verified with the experimental results on bonding of Ni-Al samples with Ni-B filler alloys. The modeling predicts the formation of an unwanted phase that appears as a transient in the bonding process. The phase exists due to the unusual levels of Al and B that occur for a brief period during the bonding process. This has been published in *Metallurgical Trans-actions* for dissemination to the industrial community. Similar experimental results and correlations with predictions were obtained for Ni-Al samples bonded with a Ni-Cr-B filler material.

Homogenization. As more efficient heat-treating practices of cast Ni-based superalloys are desired by industry, work has been initiated to develop an optimization technique. The correct heat treatment processing of a cast Ni-base superalloy after solidification consists of choosing a heating schedule that, while avoiding incipient melting, minimizes either the power expenditure or the heating time to achieve a homogeneous single phase structure. The first step in optimizing this process is the ability to describe the composition dependence of the diffusion coefficients. To accomplish this, a diffusion mobility database was constructed to be compatible with our existing thermodynamic database. The initial database evaluates Ni-binary interactions in the FCC (γ) phase for the Ni-Al-Cr-Co-Hf-Mo-Ta-Ti-Re-W system. The work was sponsored by and reported to the Advanced Technology Program (ATP). Future work will expand the diffusion mobility database, use the database to optimize heat treatment cycles, and disseminate the diffusion data in an electronic form compatible with existing public access diffusion codes.

Zn-Zircaloy Reactions. The reaction of zinc paint in contact with the Zircaloy-4 cladding of spent fuel rods is of concern to the U.S. Nuclear Regulatory Commission (NRC) and to the long-term safe storage of radioactive waste. The diffusion reactions occurring between zinc vapor and Zircaloy-4 were investigated in the temperature range of 300 °C to 400 °C. Analysis of the diffusion reactions determined a dependence on both temperature and the initial condition of the Zircaloy-4 tubing. At low temperatures, the formation of nodular Zn_3Zr was observed. The growth rate of the inter-metallic increased significantly as its appearance changed from nodular to a homogenous layer. The presence of an oxide coating on the surface of the Zircaloy-4 tubing effectively reduced the reaction rate with the zinc vapor.

Tensile testing of the as-received and zinc-exposed Zircaloy-4 tubing demonstrated a significant decrease in strength and ductility of the exposed tubing. These decreases were correlated to thickness of the intermetallic layer formed. The results of this work were reported to the NRC in the NUREG/CR-6675 report.

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J. Morral (University of Connecticut)
A. Rabinkin (Honeywell, Inc.)

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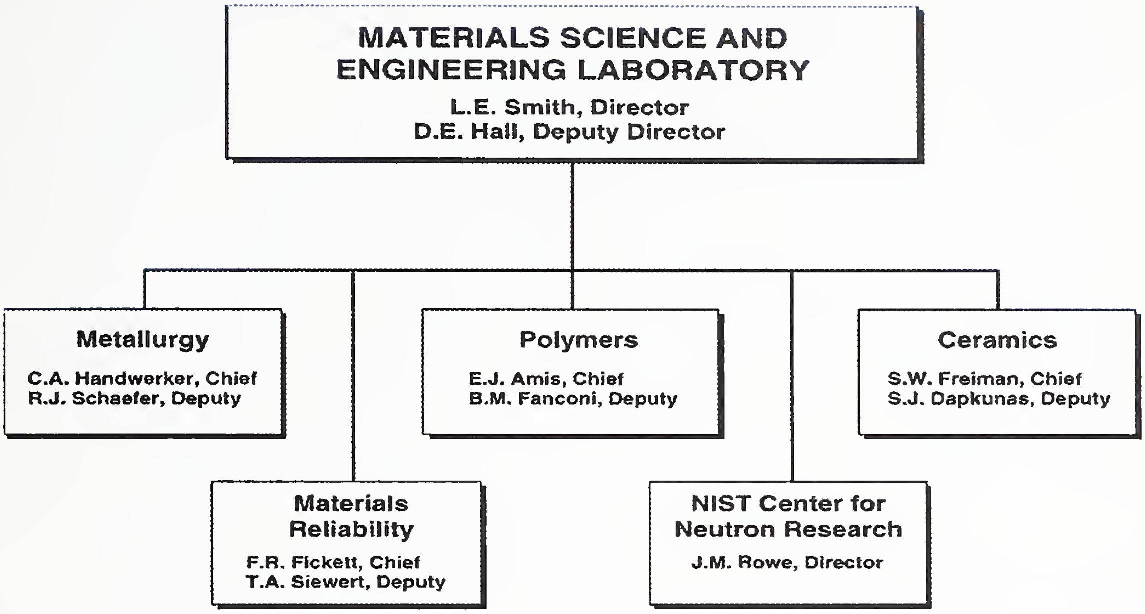

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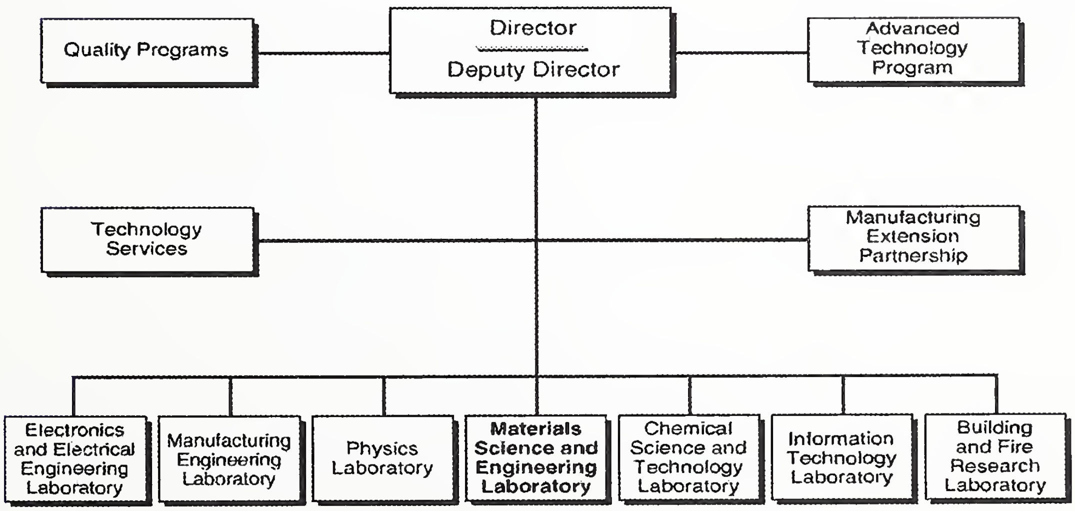

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