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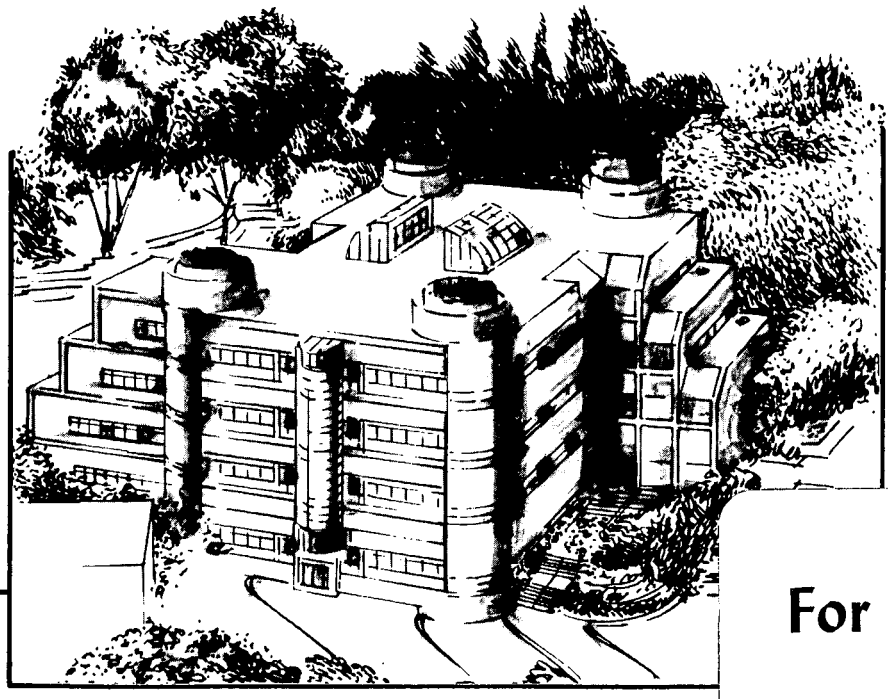
Center for Advanced Materials

CAM ANNUAL REPORT

1988

ELECTRONIC MATERIALS
HIGH-T_c SUPERCONDUCTIVITY
POLYMERS AND COMPOSITES
STRUCTURAL MATERIALS
SURFACE SCIENCE AND CATALYSIS
INDUSTRY PARTICIPATION



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Materials and Chemical Sciences Division
Lawrence Berkeley Laboratory • University of California

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Center for Advanced Materials

Annual Report • 1988

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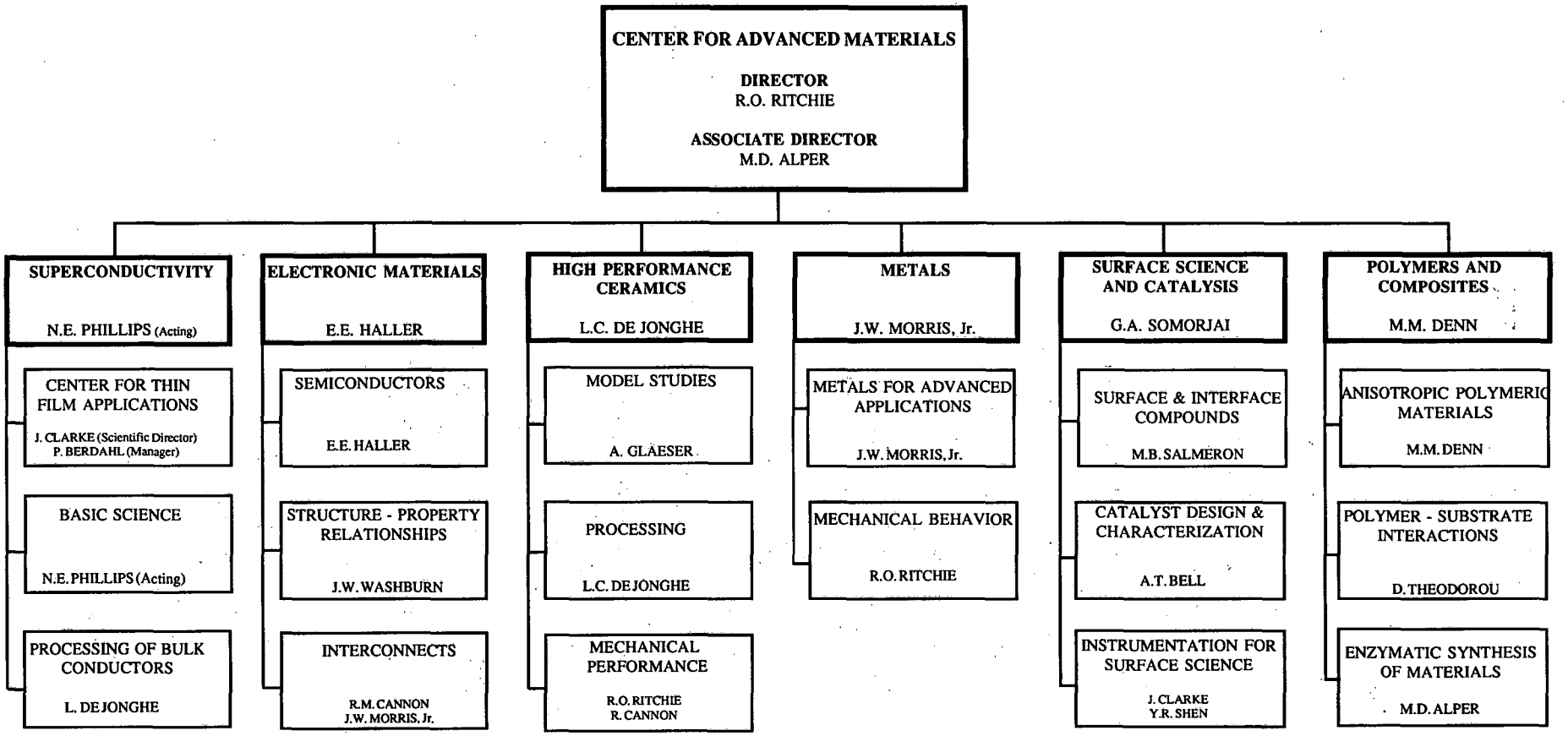

Effective October 1, 1989

Center for Advanced Materials

CAM

The fifth year of the Center for Advanced Materials was marked primarily by the significant scientific accomplishments of the research programs. The reorganization formulated during the previous year restructured the Center into five major programs, and as expected, led to increased collaborations among the investigators. The merger of the Center with the Materials and Molecular Research Division also accomplished its aim of allowing investigators in the two divisions to interact and contribute to projects in both units without administrative barriers. The Center, however, maintains its individual structure within the new Materials and Chemicals Sciences Division. Its mission remains the pursuit of fundamental research in areas of materials science identified by U.S. industry as critical to its continued competitiveness.

The Electronic Materials program continued its work on the growth and characterization of gallium arsenide crystals, and the development of theories to understand the nature and distribution of defects in the crystals. Support from industry included the donation of two sophisticated crystal growth furnaces by Hewlett Packard. Thin film research in the program involving both theoretical modeling and experimental characterization led to the explanation of a number of important phenomena and the Interconnects and Interface group continued its work in analyzing the forces involved in toughening interfaces and the failure of solder joints.

The High-T_c Superconductivity Program continued to make significant contributions to the field in theoretical and experimental work on both bulk materials and thin films and devices. Demonstration of the feasibility of the fabrication of devices based on these high temperature superconductors provided an optimistic note in an area that has been the object of some recent pessimistic views. The Ceramic Processing group developed a new technique for cladding YBCO superconductors for high current applications in work with the Electric Power Research Institute.

The Polymers and Composites program published a number of important studies involving atomistic simulations of polymer surfaces with excellent correlations to experimental results. The new Enzymatic Synthesis of Materials project produced its first fluorinated polymers and successfully began engineering enzymes designed for materials synthesis.

The Structural Materials Program continued work on novel alloys, development of processing methods for advanced ceramics, and characterization of mechanical properties of these materials, including the newly-documented characterization of cyclic fatigue-crack propagation behavior in toughened ceramics.

Finally, the Surface Science and Catalysis program made significant contributions to the understanding of microporous catalysts and the nature of surface structures and interface compounds. Its instrumentation group continued to refine techniques they are developing in scanning tunneling microscopy and nonlinear optics for the analysis of surfaces.

During its first five years, the Center has grown to include over 200 investigators, students, postdoctoral fellows, and technical and administrative staff supported on a budget exceeding eight million dollars. Financial support from industry in FY 1988 exceeded half a million dollars in unrestricted gifts and research contracts, and six industrial fellows worked in CAM laboratories for extended periods of time on the collaborative projects. Center staff published more than 200 papers, presented almost 300 talks at conferences and symposia, and awarded 39 masters and doctoral degrees. Continued and increased interaction with industry is welcome through any of the mechanisms described in the last chapter of this report.

Primary research funding for the Center comes from the Division of Materials Sciences in the Office of Energy Research at the U.S. Department of Energy, but important additional support comes not only from U.S. industry, but also from the Divisions and Offices of Chemical Sciences, Energy Biosciences, Conservation of Renewable Energy and Fossil Energy in the Department of Energy.

Electronic Materials

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Crystal Growth
Thin Films and Interfaces
Interconnects and Interfaces

Electronic Materials

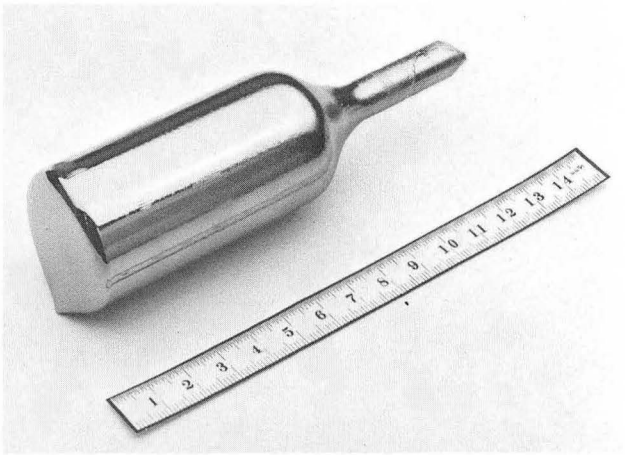
The CAM Electronic Materials Program concentrates on solving scientific problems impeding the development of large-scale digital integrated circuits and optoelectronic devices based on gallium arsenide (GaAs) and related III-V semiconductors. This is an area of research that has been identified in a recent report of the Departments of Energy and Defense as critical to national security and one that poses a number of interesting scientific questions. The CAM research effort in this area focuses on:

- The development of advanced techniques for the **growth and characterization of gallium arsenide crystals** and the study of the nature of structural and electronic defects and the mechanisms of their formation.
- The development of an improved fundamental understanding of the interrelation between processing parameters, the resulting set of structural features and the **electrical behavior of epitaxial thin films**, interfaces, and solid-state devices.
- The study of the chemical, mechanical, and microstructural determinants of the **adhesion and fracture resistance of interconnects and interfaces** including solders.

Many of the properties of compound semiconductors are determined by the presence of intrinsic (native) imperfections of the crystal lattice. The need to understand the microscopic nature of these defects and to develop techniques to control their incorporation during crystal growth or processing is one of the major driving forces in basic and applied semiconductor research.

The ***CRYSTAL GROWTH*** effort relies on a close coupling of crystal growth studies and the characterization of those crystals in order to gain an understanding of the relationships which exist between growth conditions and the structural and electronic properties of the grown crystals. Recent research in this area has led to a number of significant results which include:

- The formulation of a theoretical model of processes controlling defect abundances and defect reactions in semiconductors. The model provides a unified basis for the explanation of a large variety of phenomena in bulk semiconductor crystals, including compensation in particle irradiated semiconductors, limitations of free carrier concentrations, and suppression of dislocation formation by electrically active and isoelectronic dopants.
- The reproducible growth of 1.5" diameter GaAs crystals by a closed ampule, vertical gradient freeze technique. The crystals were grown under controlled arsenic pressure conditions. Low dislocation density material (50% of the crystals have a dislocation density less than $10^3 cm^{-2}$) is routinely grown.
- The establishment of the limitations of the universality of the transition metal energy levels as an internal energy reference in semiconductors. It was shown, both experimentally and theoretically, that light transition metals such as titanium and vanadium provide a more reliable energy reference than heavy transition metals such as nickel.



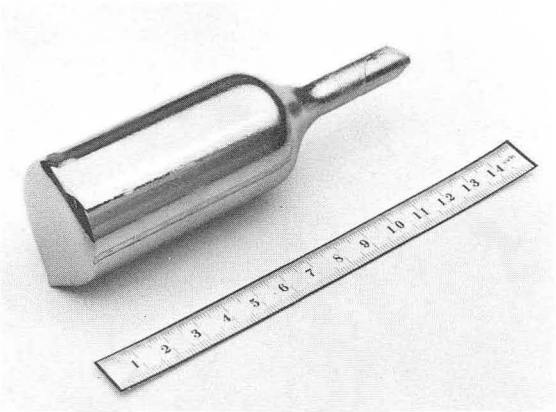
The *THIN FILMS* research effort focuses on studies of the behavior of intrinsic defects near metal-semiconductor and semiconductor-semiconductor interfaces and also in homoepitaxial and heteroepitaxial layers of GaAs and related semiconductors. Particular focus is on Schottky barrier and ohmic contact formation at metal-semiconductor interfaces and epitaxial growth of GaAs, Si and InP. This approach involves electron microscopy at the highest resolution and advanced microanalytical techniques, combined with Rutherford back-scattering, spectroscopic and electrical studies. A number of results were produced:

- The patterned MBE growth of GaAs on Si was shown by TEM observations to result in a two to three order of magnitude reduction of dislocation density, and the virtual elimination of stacking faults.
- Electron microscopy and energy dispersive x-ray spectra of metal n^+ GaAs diodes in combination with electrical measurements demonstrated strong correlations between the GaAs stoichiometry and Schottky barrier height.
- The theoretical model of processes controlling defect abundances and defect reactions in semiconductors was applied to thin films and shown to explain the formation of Schottky barriers and doping-induced superlattice intermixing.

The *INTERCONNECTS AND INTERFACES* effort investigates the physical, chemical and mechanical aspects of interfacial adhesion. A major objective is to develop and verify fundamental models of interfacial decohesion, with emphasis on dissimilar material interfaces such as ceramic-metal bonds. Parallel research is focused on understanding and improving the mechanical properties of solders to decrease the rate of failure due to fatigue resulting from thermal cycling. Notable results in this area this year include:

- The use of Bragg peak simulation methods to characterize the large stress gradients in deposited thin films; these results were critical for assessing the film delamination resistance. X-ray diffraction of the fracture surfaces also elucidated the direct relationship between the crack-tip plastic deformation and the resultant fracture energy for ceramic-metal interfaces.
- The evaluation and refinement of a potent mechanism for toughening interfaces that involve microstructural enhanced plasticity via the creation of bridging ligaments behind a crack front that are triggered by microcracks emplaced into the metal member near the interface.
- The identification of the mechanisms leading to solder joint failure under thermal fatigue conditions.
- The characterization of the mechanical properties and microstructures of several ternary Pb-Sn based solder alloys.
- The characterization of microstructures and interfacial morphologies of In-based solders for cryogenic applications.
- The achievement of microstructural and kinetic characterization of the precipitation reaction and grain growth in Al-2%-Cu thin films.

Figure 1
Single GaAs crystal grown by the vertical gradient freeze technique.



CRYSTAL GROWTH AND DEFECTS

CRYSTAL GROWTH RESEARCH

E.E. Haller, E. Bourret, M. Galiano, J. Guitron

After demonstrating the feasibility of a new approach to vertical, seeded growth of GaAs, studies have focused on understanding the basic science of the growth process and the factors involved in achieving reproducible growth of high quality crystals. A vertical growth configuration with a low temperature zone controlling the As source temperature in the lower part of the furnace, provides a stabilizing environment for fluid flows. The quartz ampoule must provide both structural support and appropriate heat transfer between the heating elements of the furnace and the growing crystal. A design for this structure was developed, consisting of a boron nitride heat pipe and a modular alumina structure shaped to favor heat transfer by either radiation or conduction, depending on the temperature of operation of each module. The crystal growth conditions (temperature gradients, growth rate) were studied in relation to the crystalline perfection of the grown crystal. Since the crystals are confined in a crucible, the surface finish of the crucibles must be such that random nucleation does not occur. Abrasive and cleaning procedures were developed for SiO_2 crucibles which allow the reproducible growth of crystals, free of twins and low-angle grain boundaries. A process to prepare pyrolytic boron nitride (PBN) crucibles is being developed. Making use of the results of these studies, crystals of extremely low dislocation density (50% of each crystal with dislocation density of less

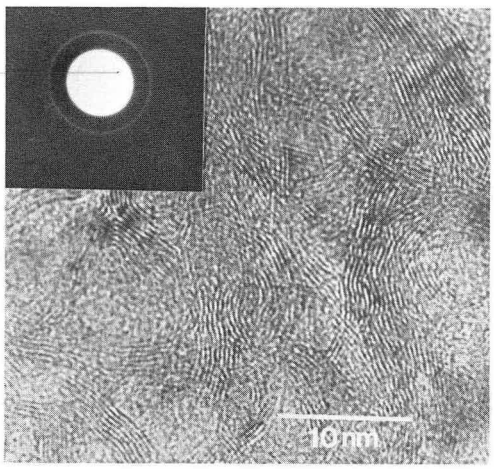


Figure 2
Transmission electron micrograph: lattice imaging and diffraction pattern of a chemical vapor-deposited boron nitride film.

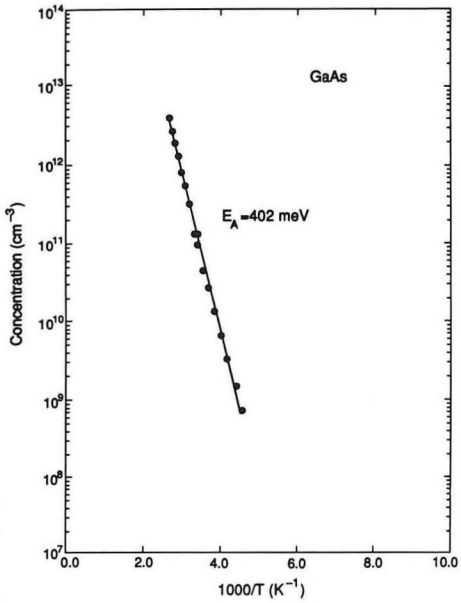


Figure 3
Activation energy of the defects responsible for the electrical properties of GaAs grown by the vertical gradient freeze technique. The concentration has been measured with the variable temperature Hall effect system.

than 1,000 cm^2) have been produced (Figure 1). This is the lowest dislocation density ever reported in the literature for undoped crystals 1.5" in diameter. The crystals were also free of slip lines, indicating that thermal stresses during growth and during post-growth cooling have been reduced below the critical resolved shear stress.

It was demonstrated that the CVD process using BCl_3 and NH_3 can be used for the coating of silica crucibles with 1 to 16 m thick BN films. These films exhibit optical absorption and x-ray diffraction characteristics of h-BN, but TEM lattice imaging of the films reveals a structure that is expected to result in isotropic physical properties (Figure 2). Hall effect and SIMS measurements show a silicon concentration in the GaAs ingots synthesized in these BN coated crucibles is much larger than that found in those synthesized in uncoated crucibles. The source of this additional silicon may stem from impurities in the BCl_3 source gas, from decomposition of the silica parts used during BN film growth, or from silicon in the GaAs melt. Other experimental results suggest that silicon incorporation occurs mainly by vapor phase transport of silicon from the SiO_2 ampule during synthesis.

On the basis of these results, PBN (rather than CVD-BN) was used for elimination of silicon contamination during vertical growth. Various designs, including capping of the charge, lining of the silica ampule, and addition of oxygen have also been investigated to prevent silica decomposition. Crystals of net carrier concentration as low as 10^{10} cm^{-3} have been obtained. The crystals, characterized by variable temperature Hall measurements, show that silicon is no longer a major donor. In these crystals, the Fermi level appears to be pinned at about 0.4 eV which indicates that deep donors EL6 and EL5 play a dominant role in this material (Figure 3). Pinning of the Fermi energy so close to the conduction band reduces the resistivity of the samples compared to semi-insulating materials. The process is currently being modified in an attempt to introduce the deep level EL2 and increase the resistivity of the material.

BASIC STUDIES OF DEFECTS

Amphoteric Native Defect Model

W. Walukiewicz

Based on the concept of amphoteric native defects, a unified model describing a large multiplicity of phenomena in semiconductors was formulated. It has been shown that the formation energies and consequently the abundances of simple native defects are dependent on the

location of the Fermi energy measured with respect to an internal energy reference E_{FS} (Fermi level stabilization energy). The known position of the E_{FS} allows for a quantitative prediction of the trends in the maximum free carrier concentration which can be achieved by intentional doping of a semiconductor. This finding has important consequences for many semiconductor technologies dependent on the availability of material with high dopant activation efficiency.

The same model was used to explain another extensively studied phenomenon known as doping induced superlattice disordering. The Fermi energy shift associated with n-type doping of a GaAs/AlAs superlattice reduces the formation energy of Ga and Al vacancies. The resulting increase in the generation of these vacancies leads to rapid interdiffusion and destruction of the integrity of the superlattice. The diffusion constant of Ga vacancies and the free electron concentration as functions of the donor doping level are shown in Figure 4. Theoretical calculations agree with the available experimental data. A direct manifestation of the fact that triply charged Ga vacancies are responsible for both phenomena is the characteristic third power dependence of the diffusion constant at low doping levels and one-third power dependence of the free carrier concentration at high doping levels.

The concept of amphoteric native defects was applied to the mechanism of dislocation formation in semiconductors, particularly, the problem of doping induced suppression of dislocation formation. This study, prompted by earlier measurements of mechanical properties of undoped as well as silicon and indium doped GaAs, showed that although these dopants are very effective in reducing dislocation density they do not increase the high temperature hardness of the material. These results discounted previously proposed solution-hardening models of dislocation suppression. It was proposed that the formation of dislocation occurs via condensation of vacancies. The process of condensation is controlled by vacancy supersaturation. Doping with either electrically active donors (Si) or isoelectronic impurities (In) leads to the reduction of vacancy formation energy and vacancy supersaturation and thus also to suppression of dislocation density. In the case of doping with electrically active impurities (e.g. GaAs:Si) the reduction of vacancy supersaturation is caused by a shift of the Fermi energy away from E_{FS}. The calculated supersaturations of amphoteric defects V_{Ga} and $As_{Ga}+V_{As}$ in the case of

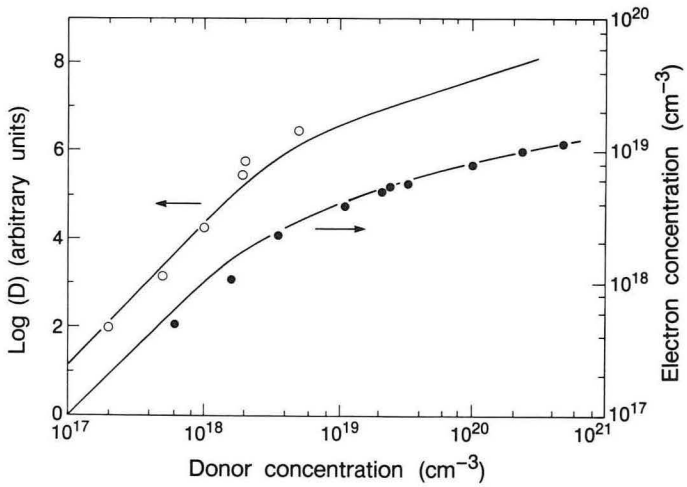


Figure 4
Diffusion constant D of gallium vacancies in the GaAs/AlAs superlattice and free electron concentration as functions of the donor concentration. The solid curves represent the results of theoretical calculations and the full and open circles show the experimental data.

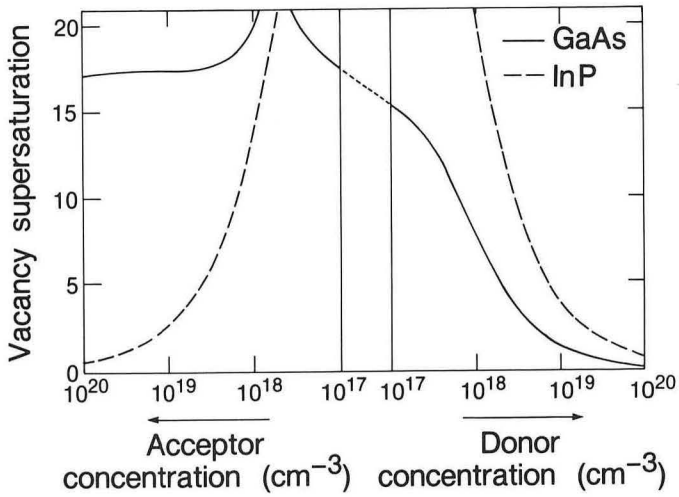


Figure 5
Calculated supersaturation of vacancies as functions of the donor and acceptor doping levels. The dislocation formation is suppressed when the vacancy supersaturation falls below critical supersaturation $S_{v,c}$ = 8. Dislocation free GaAs crystals can be grown for the donor doping exceeding ~10^{18} cm^{-3}.

GaAs, as well as supersaturations for equivalent defects V_{In} and $P_{In}+V_P$ in InP are shown in Figure 5. In GaAs, supersaturation of V_{Ga} is abruptly reduced for donor doping levels exceeding 10^{18} cm^{-3}. Conversely, doping with acceptors is less efficient in reducing the supersaturation of $As_{Ga}+V_{As}$ defects. This result agrees with experiments showing that donors are very effective in reducing the dislocation density, whereas doping with acceptors has no effect or leads to higher dislocation density than in intrinsic GaAs. In the case of InP, it is found that doping with both donors and acceptors reduces the supersaturation and therefore can lead to dislocation suppression. This is again in agreement with the available experimental data which indicates that donors at a concentration of ~10^{19} cm^{-3} completely eliminate dislocations. Unlike in GaAs, doping of InP with acceptors has been found to be even more effective than doping with donors. A substantial reduction of the dislocation density has been observed for the acceptor dopant concentration exceeding 10^{18} cm^{-3}.

Although isoelectronic dopants (GaAs:In) do not directly affect the Fermi energy position, they introduce a spatially inhomogeneous strain which leads to a reduction of the vacancy supersaturation. Doping of GaAs with indium leads to a reduction of defect supersaturations (Figure 6). For high enough doping levels the supersaturation of V_{Ga} in intrinsic

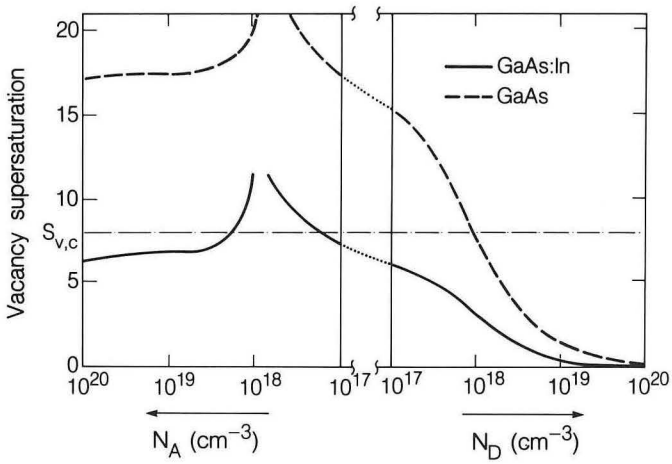


Figure 6
Vacancy supersaturations as functions of the acceptor and donor doping for GaAs and GaAs co-doped with the isoelectronic impurity, In, to the concentration 5x10^{19} cm^{-3}. Co-doping with In reduces the supersaturations so that for intrinsic GaAs (no acceptor or donor dopants) the supersaturation is lower than $S_{v,c}$ = 8. Under such conditions dislocation-free semi-insulating GaAs can be grown.

GaAs is below the threshold value $S_{v,c}$. This explains why isoelectronic doping can lead to dislocation free semi-insulating GaAs.

Annealing Studies of Native Defects in As-Rich GaAs

E. Bourret, R. Gronsky, B.T. Lee

A detailed transmission electron microscopy study of dislocation loops and precipitates in As-rich GaAs crystals has been completed. The study has been complemented by investigations of relationships that exist between structural defects and electrical properties upon annealing of GaAs. Post-annealing has become a routine production process for GaAs devices since it was found that this process results in crystals of more uniform electrical properties. In particular, the distribution of the deep level EL2 and the resistivity become more uniform while the overall EL2 concentration increases. The changes in EL2 concentration and the behavior of As-related structural defects (dislocation loops and precipitates) during bulk annealing in the temperature range 500-900°C were studied. Results indicate that for isochronal bulk annealing at temperatures above 600°C, the concentration of EL2 increases (Figure 7). Evidence of structural characterization demonstrates that this increase in EL2 concentration is associated with the dissolution of extended structural defects containing excess arsenic. It was observed that excess As condenses as point defects, dislocation loops, and/or As precipitates, depending upon the cooling rate from high temperatures and the availability of nucleation sites (dislocations). It was determined that the solvus temperature for the crystal studied, with an excess As concentration of about 10^{16} cm^{-3}, lies between 600 and 700°C.

Pressure Dependence of EL2

D. Bliss, E. Haller, W. Walukiewicz

Systematic measurements of the pressure coefficients of the energy levels of EL2, the major native defect in GaAs were performed conducted. In agreement with previously reported data, it was found that the pressure coefficient of the energy level associated with the first ionization stage of EL2 has a value very close to the pressure coefficient of the conduction band edge. Measurements of the pressure coefficient of the second ionization energy of EL2 were also conducted. Such measurements are difficult because of lower concentrations of EL2 defects in p-type GaAs and because there are a number of impurity states (such as iron and copper) which interfere with the DLTS spectrum of EL2 (+/++). The finding that the second ionization level follows very closely the valence

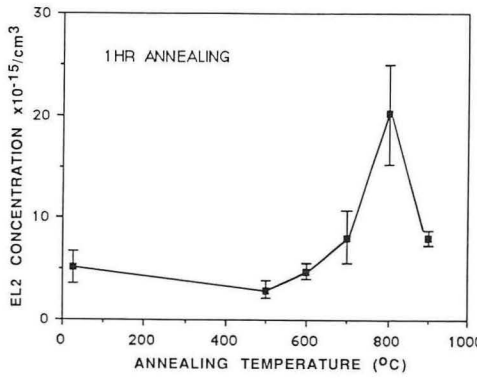


Figure 7
Concentration of the EL2 defect as a function of temperature for 1 hr isochromal annealing cycles.

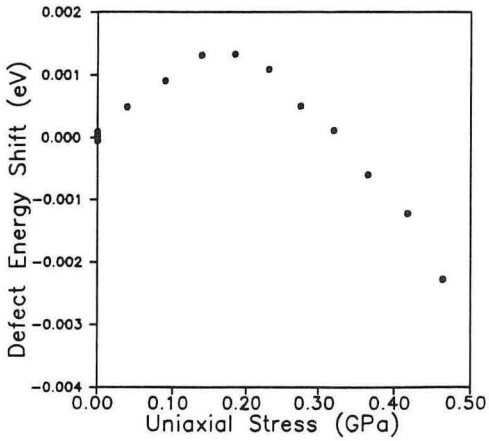


Figure 8
Uniaxial stress induced shift of the second ionization energy of the EL2 defect measured with respect to the valence band edge.

band edge was unexpected (Figure 8). Analysis of this exceedingly different behavior of the first and second ionization energies of EL2 indicates that only the neutral state of the EL2 defect is strongly coupled to the crystal lattice. This is very important information for future theoretical models of EL2 in which the relaxation of the crystal lattice will be included.

Unification of EL2 Properties

M. Hoinkis, E. Weber

The deep double donor, EL2, is the most important and most extensively studied native defect in GaAs. The interest in EL2 was prompted by its technological significance. It was shown in early studies of GaAs that controlled incorporation of EL2 allows for growth of high resistivity crystals which are required as substrates for many GaAs applications. Despite intensive studies conducted in many places all over the world, the microscopic identity of EL2 is not yet firmly established. Several experimental techniques, including zero-phonon line (ZPL) absorption, electron paramagnetic resonance (EPR), magnetic circular diachroism (MCD), and optically detected nuclear double resonance (ODENDOR), are used to study properties of EL2. However, until now, no clear evidence has been provided that all these techniques are detecting the same defect. In collaboration with a group from the Materials Science and Engineering Department at MIT and a group from the University of Paderborn (West Ger-

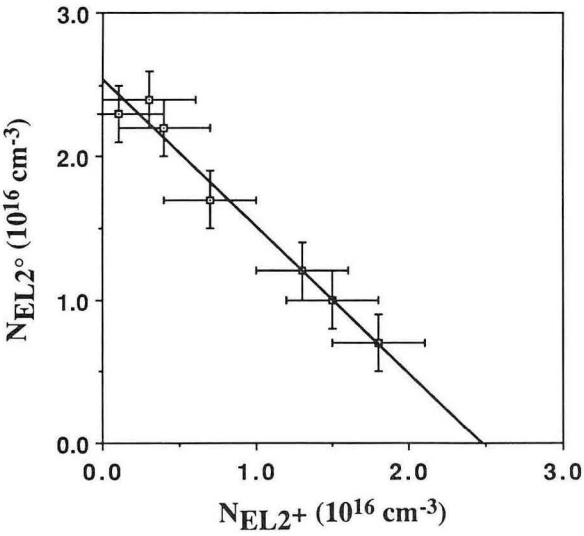


Figure 9
The relationship between the change of the concentration of the neutral $EL2^0$ defect measured with zero phonon line absorption and a change of the concentration of positively charged $EL2^+$ defects measured with electron paramagnetic resonance.

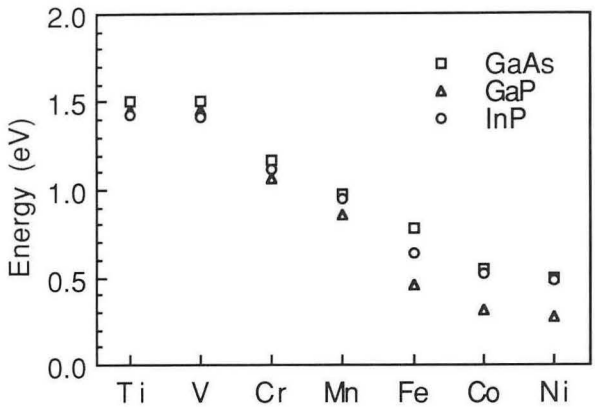


Figure 10
Position of the (3+/2+) acceptor defect state calculated for different transition metals in three representative group III-V semiconductors. The energy is measured with respect to the GaP valence band edge. The defect energy is much less dependent on the host semiconductor for light transition metals (Ti, V) than for heavy ones (Co, Ni).

many), a number of selected, well-characterized, as-grown and thermally treated GaAs crystals were studied. ZPL absorption, EPR and MCD were measured on the same crystals. A good quantitative correlation between a decrease of the ZPL signal which measures the neutral state of EL2 and an increase of the EPR quadruplet signal associated with the singly ionized EL2 defect exists (Figure 9). This proves that all these experimental methods are indeed probing different properties of the same defect. Our experimental results provide guidance and represent a challenge for all microscopic models of EL2 which have to account for various experimentally determined properties.

Universality of the Internal Energy Reference Associated with Transition Metal Energy Levels in Semiconductors

D. Nolte, E.E. Haller, M. Hamera, W. Walukiewicz

The studies of the energy levels of transition metals in III-V semiconductors has been continued. Using experimental and theoretical methods, the hypothesis that the transition metal energy levels in a semiconductor can be used as reference levels for the determination of semiconductor properties such as band offsets and band edge deformation potentials was tested. A study of the stress properties of defect levels caused by intentionally introduced nickel atoms in GaAs with the aim to measure the pressure induced shift of nickel energy levels with respect to the band edges was conducted. It was found that the nickel (2+/1+) defect level has a different pressure coefficient than the (3+/2+) defect levels of vanadium and titanium. This result disproves the commonly accepted assumption that all transition metal defect levels provide equally accurate energy reference levels.

To gain a theoretical understanding of the difference between transition metals, calculations of the transition metal energy levels in three representative group III-V semiconductors (GaAs, InP, and GaP) were performed. The striking result of the calculations is that the positions of the transition metal energy levels are constant when measured with respect to the vacuum level (Figure 10). This is a consequence of the similarity of the gross features (defined by maximum density of states) of the band structure within this class of isovalent semiconductors. It was found, however, that within the group of all transition metals, the lighter metals such as titanium or vanadium are more stable than heavier metals., e.g. nickel. This finding accounts for the experimentally observed difference in the pressure coefficient of the nickel defect level compared with that of titanium and vanadium. Also it points out that the deformation

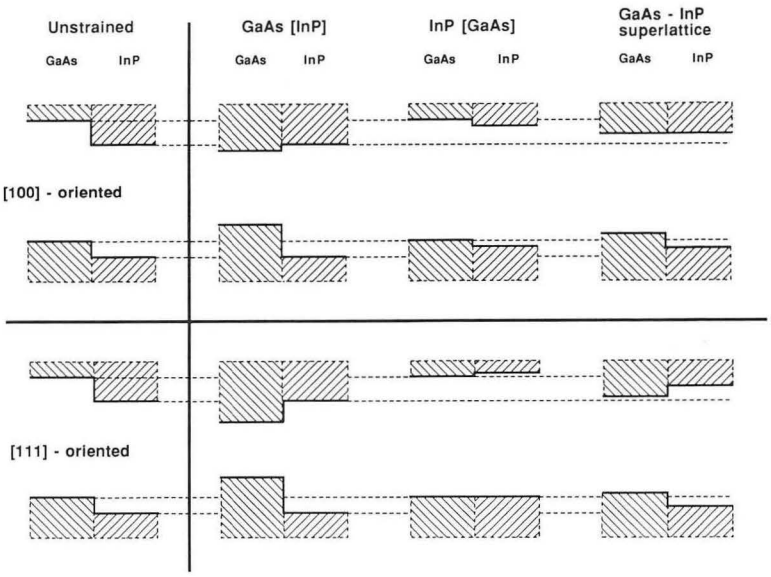


Figure 11
Band offsets for pseudomorphic GaAs grown on InP substrate (GaAs[InP]), pseudomorphic In grown on GaAs (InP[GaAs]) and pseudomorphic GaAs/InP superlattice. Band offsets for the unstrained GaAs/InP interface are also shown for comparison.

potentials determined using titanium and vanadium energy levels are more accurate.

The values of the band edge deformation potentials deduced from the measurements of the pressure coefficients of titanium and vanadium energy levels in GaAs and InP were used to theoretically determine the band offsets for pseudomorphic GaAs/InP grown heterojunctions and for GaAs/InP pseudomorphic superlattices. Accurate values of the band edge deformation potentials are critical for such determination since there is a substantial contribution to the band offsets coming from biaxial strain in the pseudomorphic layers. The band offsets depend on the growth sequence (GaAs on InP or InP on GaAs) and on the growth direction (Figure 11). In particular, it was shown that a biaxial strain strongly affects band offsets for pseudomorphic GaAs grown on InP in the (111) direction. In this case a conversion from the type-II heterojunction (unstrained case) to type-I, in which, due to the reduction in the energy gap of the pseudomorphic GaAs, the conduction band edge of GaAs falls below that of InP. This is an interesting case of a strong confinement of electrons and holes occurring in the same layer.

THIN FILMS AND INTERFACES

OHMIC AND SCHOTTKY CONTACTS TO III-V SEMICONDUCTORS

Theoretical Model for Defect Formation at Metal-Semiconductor Interfaces

W. WALUKIEWICZ

The concept of amphoteric native defects has been employed to study the behavior of intrinsic defects at metal-semiconductor and semiconductor-semiconductor interfaces. Recently, this concept of defects with Fermi energy dependent formation energy was used to describe the initial stages of the Schottky barrier formation occurring at very thin (submonolayer) metal coverages. Assuming that the energy necessary for the formation of defects at the interface is provided in the process of the back-relaxation of the semiconductor surface, we are able to explain the early stages of the Fermi energy pinning. In contrast to previous proposals, and in agreement with experiments, a very slow Fermi level pinning extending over almost three orders of magnitude of the metal coverage is

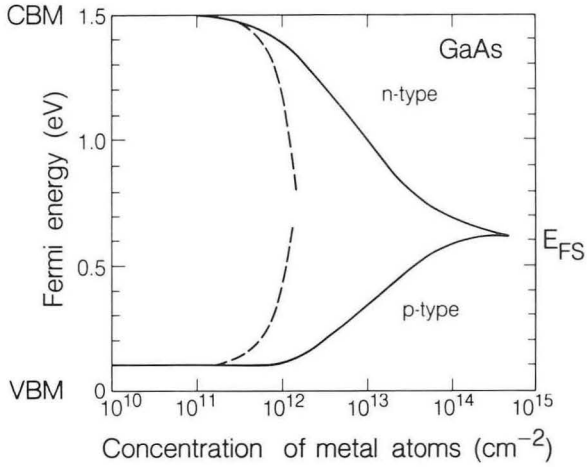


Figure 12
Metal deposition induced Fermi level pinning in n- and p-type GaAs. Calculations based on the amphoteric defect model (solid curves) or predict much slower pinning than those based on standard defect models (broken curves).

predicted by our model calculations (Figure 12). The very distinct asymmetry of the pinning behavior in p- and n-type GaAs, at low temperatures, is a direct consequence of the fact that the diffusivity of the defects generated at the interface is very low and therefore some of those defects can easily recombine in n-type GaAs. As a consequence, the Fermi energy does not become pinned for submonolayer coverages at low temperatures in this material.

Role of Excess Arsenic Near the Semiconductor-Metal Interface

N. Newman, J. Ding, Z. Liliental-Weber, J. Washburn

Metals deposited onto semiconductors generally form rectifying Schottky contacts. The basic mechanism of this barrier formation at these contacts is still not completely understood. It has been generally recognized that the original Schottky model, which predicted that the barrier height would be equal to the difference between the metal work function and the electron affinity of the semiconductor (for n-type semiconductors), is contradicted by experimental results. In the case of GaAs, for example, the pinning position of the Fermi level for many metals, with very different work functions, as well as for oxygen, falls within the unexpectedly narrow range of 0.7 to 1.0 eV below the conduction band minimum.

Many models have been developed to try to explain the observed pinning levels. In order to test these models, an extensive study of thick metal-film (~100 nm) diodes was undertaken. Diodes were produced at Stanford University on clean-cleaved GaAs(110) under UHV conditions with in situ metal deposition to avoid the accumulation of impurities on the semiconductor surface. (In earlier work of this study it was found that even submonolayer coverages of impurities before metal deposition are capable of establishing a barrier, altering the chemistry and morphology at the interface and significantly effecting the current transport mechanism.) The structure of these well-defined Ag, Al, and Au contacts on GaAs was investigated by high resolution and analytical transmission electron microscopy. In all cases the metal/semiconductor interface was atomically abrupt, but the last three to five atomic layers near the interface were reconstructed, indicating a highly strained and defected region near the metal/semiconductor interface.

Analytical TEM EDX results for all systems studied showed that the region within ~100Å of the interface was also slightly As-rich when compared to the bulk (Figure 13). This As-rich condition near the interface was found to diminish with time under the illumination of the electron beam, while no such change in the temporal dependence of the As concentration was found in the bulk. This suggests that a less tightly bound form of As occurs in significant concentrations at or near the interface.

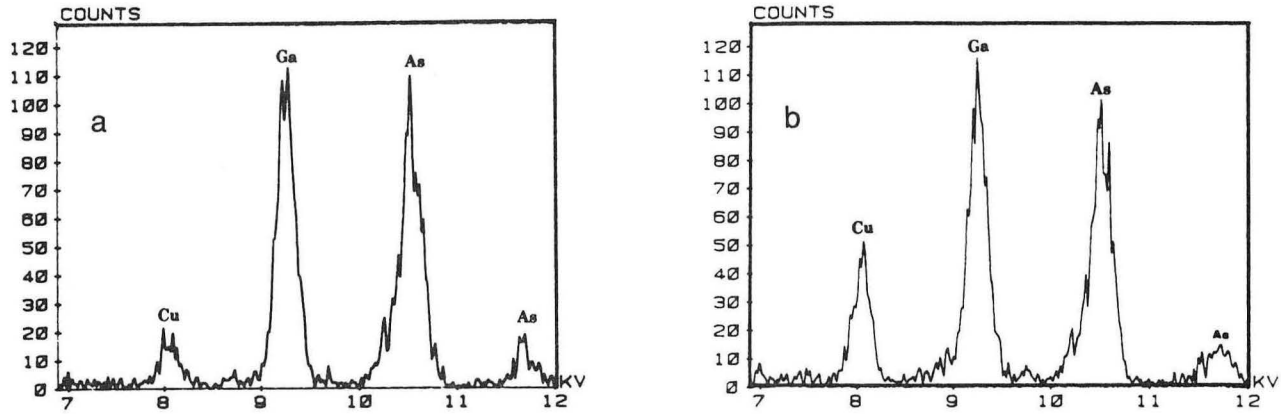


Figure 13
a) Energy dispersive x-ray (EDX) spectrum from the GaAs close to the interface with Au. Note the increased As/Ga ratio near the interface. b) EDX spectrum taken from the GaAs far from the interface. The Cu line in both spectra is an artifact from the sample holder.

Strong correlations between the Ga/As stoichiometry and the changes in barrier height upon annealing were found. In all cases, an increase in excess As near the interface was found to correlate with a decrease in barrier height, whereas a decrease in the excess-As near the interface correlated with an increase in the barrier height.

Coincidence of the experimentally determined energy levels of the As_{Ga} antisite defect at $E_v + 0.52$ eV and E_c-0.75 eV with the Fermi level pinning positions, and the fact that these defects are directly related to the crystal stoichiometry, strongly suggests that anion antisite defects, partly compensated by cation antisite defects, determine the pinning positions observed for metal contacts on state-of-the-art bulk GaAs crystals. There is evidence that a similar mechanism might apply for other compound semiconductors such as InP.

This research, carried out in cooperation with W.E. Spicer's group at Stanford University, further supports his advanced unified defect model fo Schottky barrier formation. The new feature is the identification of the defect producing pinning at 0.75 and 0.5 eV above the valence band maximum as the As_{Ga} antisite. Since the As_{Ga} antisite is a double donor, a minority compensating acceptor is necessary. This has been tentatively ascribed to the Ga_{As} antisite or to gallium Vacancy V_{sa}.

Effect of Surface Contamination on Metal GaAs Interfaces

N. Newman, Z. Liliental-Weber, J. Washburn

A systematic study of the annealing-induced changes in Schottky barrier diodes fabricated on atomically clean or on contaminated surfaces was conducted. Al, Ag, and Au/GaAs(110) diodes were fabricated by *in situ* deposition on both clean n-type GaAs(110) surfaces prepared by cleavage in ultrahigh vacuum and also on contaminated surfaces prepared by cleavage and exposure to the atmosphere for ~1-2 h before metal deposition. The study of these diodes demonstrates that the difference in as-deposited barrier height and also in annealing-induced changes in barrier height depend on whether or not there is an interfacial layer of contamination between the metal and the clean semiconductor surface. Air exposed Ag diodes exhibited the largest change in barrier height (~85 meV) upon aging while UHV-cleaved Ag diodes showed no significant change. The results also demonstrated that interface morphology, epitax-

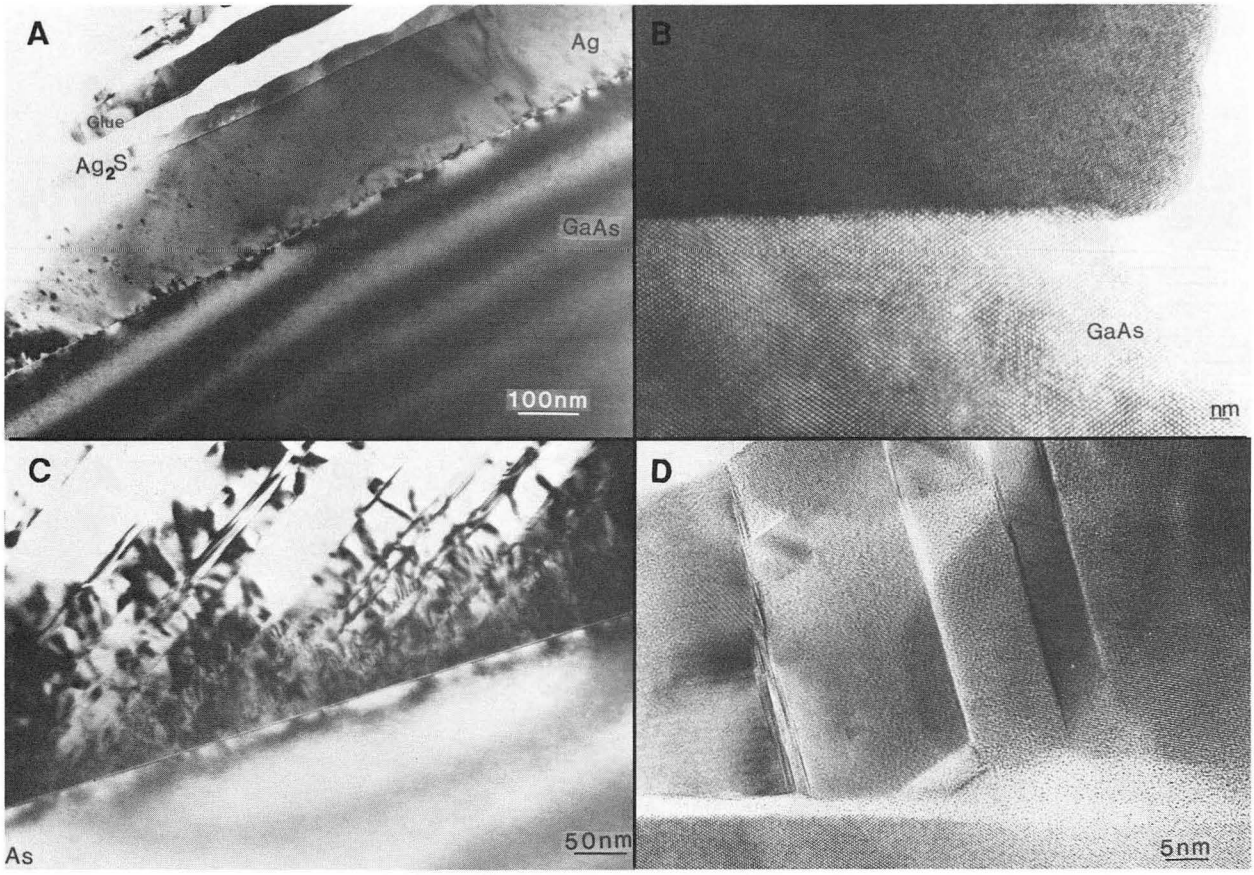


Figure 14
TEM micrographs of the Ag/GaAs interfaces prepared by Ag deposition in situ on UHV-claved (110)GaAs (a,b) and by Ag deposition on air exposed cleaved (110) GaAs (c,d). Note very large grain size in a), abrupt interfaces in b), high density of twins in c), and an oxide layer formed on the interface in d).

ial orientation relationship, and formation of new phases strongly depend on the surface preparation before metal deposition and/or on the annealing environment. Au, Ag, and Al, with similar lattice parameters all show very similar orientation relationships with GaAs when annealed after being deposited *in situ* on a UHV-cleaved GaAs surface. The interface between the metal and the GaAs remains abrupt and planar for all metals investigated when deposited on a UHV-cleaved GaAs substrate (Figure 14). When GaAs is exposed to air before metal deposition the epitaxial orientation relationships are different and protrusions of the metallic phase grow into the GaAs on annealing resulting in a non-planar interface.

This study suggests that the frequently observed problems with reproducibility and stability of Schottky barrier heights on GaAs can be attributed in large part to insufficient cleaning of the water surfaces before metal deposition.

Hydrostatic Pressure Studies of Schottky Barriers in GaAs

W. Shan, K. Yu, W. Hansen, W. Walukiewicz

Using diamond anvil cells pressure dependence of the height of the Schottky barrier formed by depositing platinum on n-type GaAs was measured. The very small working volume of the anvil cell required preparation of extremely small samples, ~10^{-3} mm^3. It was found that at

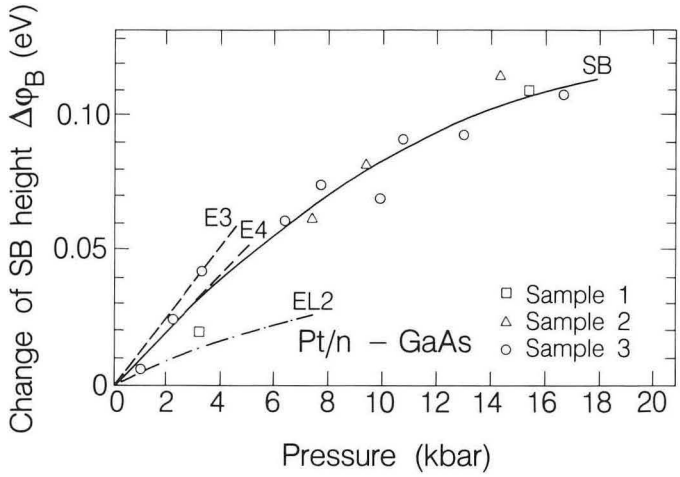


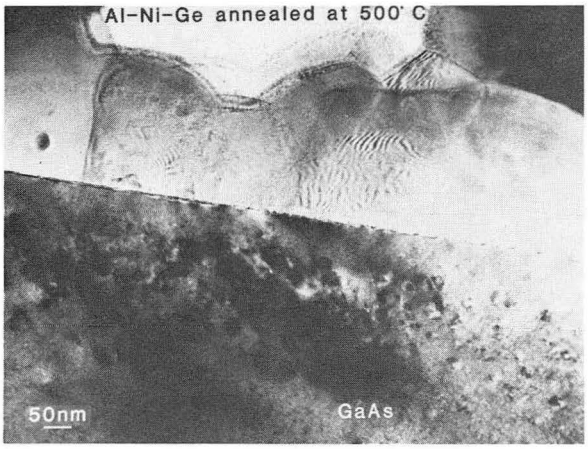
Figure 15
Change of the Schottky barrier height with pressure for three different Pt/GaAs diodes. The energy shifts of EL2 and irradiation induced E3 and E4 defects are also shown.

low stresses the pressure coefficient of the Schottky barrier height is ~110 meV/GPa, a value very close to the pressure coefficient of the energy gap, (118 meV/GPa) and almost exactly the same as the pressure coefficient of the transition metal based energy reference (108 meV/GPa)(Figure 15). This indicates that electronic states responsible for the pinning of the Fermi energy at the metal-semiconductor interface are following the valence band edge under stress. Such information allows for the testing of various models of the Schottky barriers. In particular it has been shown that the energy levels of the defects formed in GaAs during the growth process exhibits different pressure coefficients. It indicates that these grown-in defects do not play a major role in the Fermi level pinning at metal-semiconductor interfaces. On the other hand, the literature data on pressure coefficients of the defects introduced by electron irradiation indicate that the electronic states associated with these defects follow the valence band under stress. Similar behavior of these defects and the defects responsible for pinning of the Fermi energy at metal-semiconductor interfaces supports the amphoteric native defect model for Schottky barrier formation, which claims that simple native defects are responsible for pinning of the Fermi energy at metal-semiconductor interfaces and the compensation of electrical activity in irradiated semiconductors.

The Structure of Al-Ni-Ge Ohmic Contacts

Z. Liliental-Weber, J. Washburn

In cooperation with McDonnell Douglas Microelectronics Center the structure and composition of the recently developed Al-Ni-Ge ohmic contacts to n-GaAs were investigated by transmission electron microscopy combined with secondary ion mass spectroscopy (SIMS) and Auger spectroscopy. The semiconductor/metal-alloy interface of these contacts, in contrast to the widely used Au-Ni-Ge contacts, remains very flat after annealing (500 C, for 1 minute-contact resistance 1.4×10^{-6} Ωcm^2)(Figure 16). The metal deposition sequence is found to be a critical factor in determining the electrical contact properties and the dispersion of the oxide layer on the semiconductor surface after chemical cleaning. Ge doping of the GaAs beneath the contact layer was observed by SIMS, and a tunneling mechanism through the n^+GaAs:Ge layer was proposed to explain the ohmic properties of the contacts.



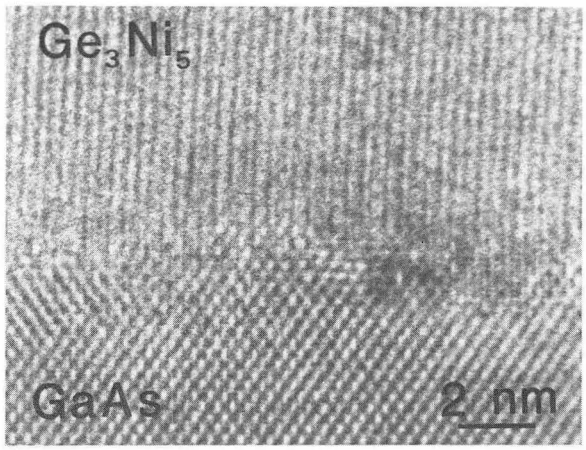


Figure 16
a) TEM micrograph of cross-section of Al-Ni-Ge contact after annealing at 500 C for 1 min, b) high resolution micrograph of the same interface. Note abrupt interface despite the annealing.

CONTROL OF DEFECTS IN EPITAXIAL LAYERS

Facet Formation on (110) Growth of GaAs on GaAs

L. Parechanian-Allen, E.R. Weber, J. Washburn

In cooperation with Varian Associates III-V Device Center, in Santa Clara, CA, and Hewlett Packard Optoelectronics Division, San Jose, CA., facet formation during MBE growth of GaAs on a (110) GaAs substrates was studied through a detailed analysis of the geometry and sequential development of hill and valley faceted growth with increasing thickness of the epitaxial layer. It was shown to be related to the polar nature of the GaAs structure. A growth step on the (110) surface has outermost atoms which can be either As, Ga, or an equal number of both, depending on its orientation on the surface. By tilting the substrate surface 6 degrees away from exact (110) in the correct direction, Ga exposed growth steps can be made to predominate leading to uniform thickness MBE layers which preserve the near planar surface of the substrate and contain far fewer defects.

Origin and Control of Defects in MOCVD and MBE of GaAs on Silicon Substrates

Z. Liliental-Weber, J. Washburn

Growth of GaAs on Si has been recognized as a highly desirable goal for a number of years. However, the large lattice misfit between GaAs and Si and the problems connected with epitaxial growth of a polar crystal on a nonpolar substrate can result in a high density of lattice defects, including antiphase disorder, where some Ga-As bonds are replaced by As-As and Ga-Ga bonds.

Studies were carried out on GaAs grown by MOCVD at Hewlett Packard and Kopin Corporation, on exactly oriented (100) Si wafers and by MBE on wafers tilted by 4 toward (110). In both cases high densities of defects, mostly stacking faults and dislocations, were observed in cross-sectioned samples. Antiphase boundaries (APBs) were also identified in both types of samples by observation of Convergent Beam Electron Diffraction (CBED) patterns.

APBs were shown to be natural obstacles for the propagation of twins and stacking faults into the growing epitaxial layer. Faceting of APBs was observed which suggests anisotropy of the interfacial energy. In most cases extended surface areas of APBs were observed to lie on the energetically favorable (110) planes. High resolution micrographs from edge-on (110) inversion boundaries were taken in (110) and (100) projection (Figure 17). A shift of the lattice image of 0.14 nm along (200) planes was observed in some segments of the boundaries (Figure 16). It was confirmed by image simulation that the visibility of this shift should be limited to a critical sample thickness of 24 3 nm for a 1 MeV accelerating voltage in the ARM. Image processing of the lattice image micrograph of the GaAs/Si interface in (100) projection showed that a/4 single steps were present at the Si surface which initiated the inversion boundaries. It was also shown that APB formation is promoted by Si surface contamination.

This work has also shown that the density of threading dislocations and stacking faults in lattice mismatched heteroepitaxy can be substantially influenced by post-growth annealing treatments and by the insertion of strained layer superlattices. A detailed analysis of the character of the observed dislocations and stacking faults has resulted in a better understanding of the mechanisms for the observed density reduction. The current growth technology is clearly not optimum. It is possible to grow low defect-density lattice mismatched structures with a controlled network of misfit dislocations at the heterointerface by removing the misfit strain. Although a method for reliably eliminating all threading dislocations has not yet been found, this work has produced occasional ~1-μm^2 areas of GaAs/Si structures free of all threading defects.

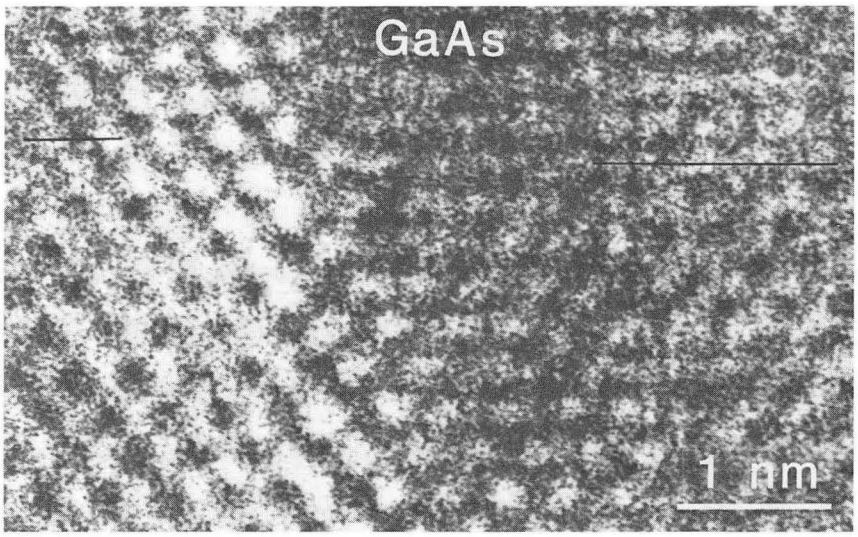


Figure 17
High resolution image of a (110) antiphase boundary in [110] projection. Note the 0.14 nm shift along the (200) planes across the boundary, as shown by two arrows.

CERAMIC AND METAL INTERFACES

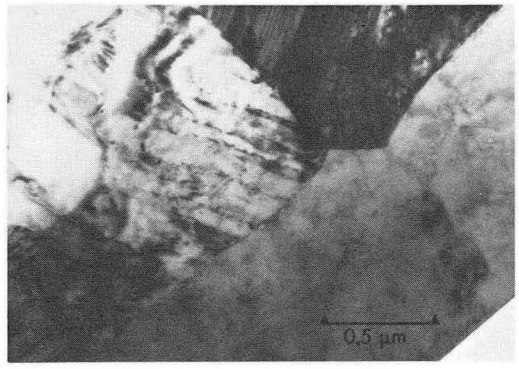
Interfacial Fracture Energies

R. Cannon, R. Fisher, A. Fox

Earlier work in this program has established a framework of the major elements of the interfacial fracture energy and their interdependencies. Parallel effort has included the development of experimental methods and sample fabrication techniques that permit systematic study of mechanisms singly or in desired combinations. Experiments first focused on factors controlling the extension of a single crack at or near a flat interface. The roles of interface morphology and adjacent microstructure have been studied more recently. Theoretical efforts are aimed toward developing micromechanical models, seeking correlations with basic chemical treatments of interfacial bond rupture strength and kinetics, and stimulating study of promising or novel toughening mechanisms. Models being developed reveal a strong interplay among chemical and mechanical factors.

Interfacial toughness is measured using a macroscopic, ceramic-metal-ceramic sandwich specimen, in a double cantilever beam (DCB) geometry. Prescribed modifications of the near-interface microstructure can be made using a photolithographic etching (in the Microfabrication Laboratory, Department of Electrical Engineering and Computer Science at the University of California, at Berkeley) thin film deposition, and diffusion bonding techniques adapting a method earlier reported by A.M. Glaeser of Lawrence Berkeley Laboratory's Materials and Chemical Sciences Division.

Transmission electron microscopy (TEM) and x-ray diffraction have been used to assess the microstructure and residual stresses within the as-bonded copper and near crack plasticity within the Cu for plain Cu/glass bonds (Figure 18). Residual



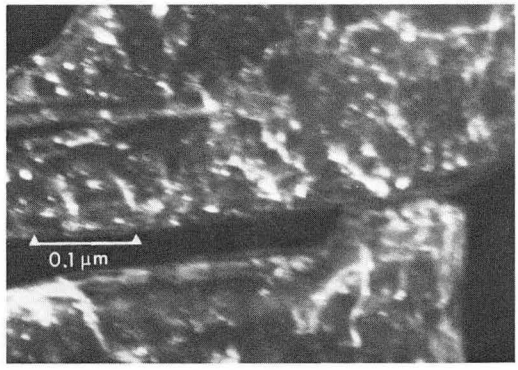


Figure 18
Bright field transmission electron micrograph (a) shows the initial microstructure of the Cu after diffusion bonding the Cu/glass samples. The accompanying dark field micrograph (b) illustrates the high dislocation density which results from fracture of the interface; the dislocation density can exceed $10^{11}/cm^2$ near the fracture surface.

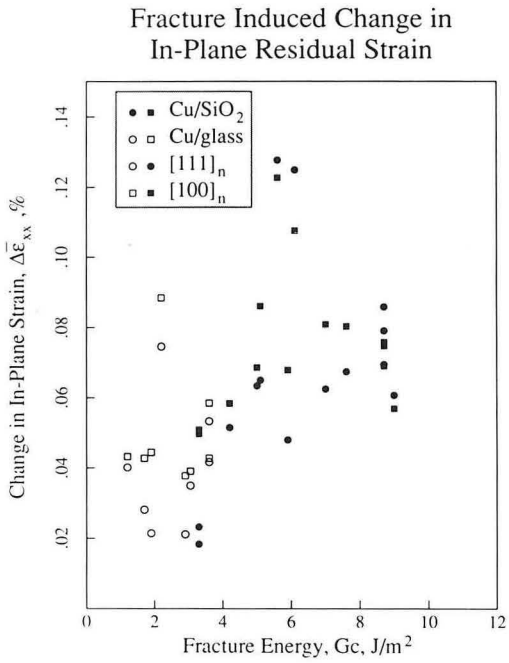


Figure 19
Measurements from x-ray diffraction show that there is a change in the residual stress in the Cu as a result of the crack-tip plasticity accompanying interfacial fracture for Cu/glass bonds. The initial stress state is dictated by yielding in response to the thermal expansion difference upon cooling the samples. A change in residual stress induced by the fracture increases with the fracture toughness. This demonstrates an approximately linear dependence between the interfacial fracture energy and the crack-tip plasticity; the latter is believed to be leveraged by the quality of the interfacial chemical bonds which are highly sensitive to impurities.

stresses deduced from diffraction for the as-bonded Cu are as high as 400 MPa, for glass and SiO2 bonds owing to the thermal expansion mismatch from cooling. Although high, these stresses have been partially relieved by plastic deformation. Similar measurements on the Cu fracture surfaces reveal that a superposed compressive residual stress results from the near-tip plasticity during interfacial fracture (Figure 19). This change in residual stress increases nearly linearly with fracture toughness, G_c, over a measured range of a factor of 10 in G_c. The work associated with the residual stress change is about 20% of the fracture energy. However, this is only a fraction of the plastic work accompanying fracture owing to the redundant nature of crack-tip deformation. Observations in the TEM of much higher dislocation densities in the Cu after fracture (see Figure 18) support this interpretation.

These results support the proposition that plasticity accounts for most of the fracture energy, and that both quantities increase as interfacial chemical bonding is improved. *In situ* fracture tests in UHV and surface spectroscopy measurements on the fracture surfaces, being conducted in collaboration with the CAM Surface Science program are providing information on the role of interfacial impurities, such as residual hydrocarbons or chlorine, that control the interfacial bond scission resistance.

A crack-tip shielding mechanism that can provide one or two orders of magnitude toughening of ceramic-metal interfaces that utilizes crack bridging was demonstrated earlier and further refined. This involved glass-copper interfaces with periodic arrays of microcrack-like-voids produced in the Cu, but near the interfaces.

Near-interface "defects" in the Cu trigger formation of bulged metal-film ligaments that bridge the interfacial crack. The ensuing plastic stretching, and sometimes tearing, of the film provide the toughening, which shows marked R-curve behavior. Three distinct modes of behavior exist, two of which are described by micromechanical models being developed. When fracture occurs exclusively along the interface, the toughening increment increases with the microcrack spacing normalized

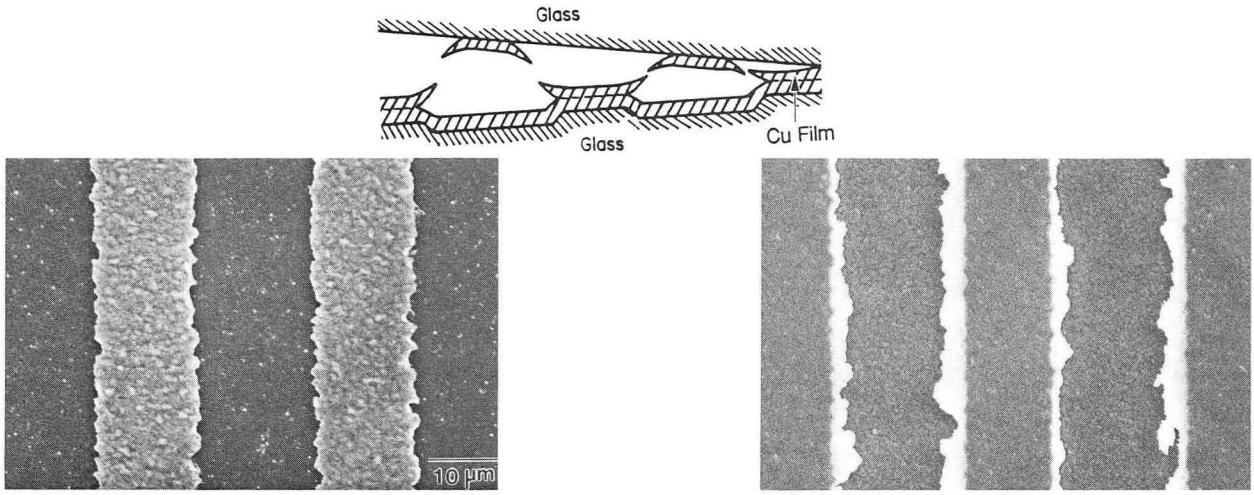


Figure 20
Schematic illustration of microcrack toughening mechanism for ceramic-metal interfaces (a) and corresponding SEM micrographs of Cu (b) and glass (c) fracture surfaces in the regimes where behavior is controlled by ligament tearing.

by the ligament thickness and is nearly proportional to the inherent interfacial toughness (Figures 20, 21). The latter dependence reflects the greater plastic stretching of the ligaments that results from the higher forces required to induce interfacial bond rupture. When ligaments are sufficiently thin, fracture entails tearing them; the toughening increment then depends upon the stress and strain to failure of the metal ligaments and the area of bridging ligaments. A third regime, that obtains for higher inherent interfacial toughness, involves alternate interface and glass fracture and provides less toughening.

This toughening study, conducted in close collaboration with R.O. Ritchie of the CAM Structural Materials Program, also initiated investigation of cyclic fatigue for Cu/glass interfaces. Two important results have emerged. Crack growth along plain Cu-glass interfaces is faster under cyclic loading than expected from the subcritical crack growth under monotonic loading. However, the microcrack toughened interfaces are more resistant to such fatigue crack growth.

Initial measurements of the fracture toughness from DCB tests for copper bonded to as-fired, commercial polycrystalline alumina yielded about 25 J/m2, more than twice that for similar Cu-glass samples. Preliminary observations suggest that residual glass, which is an impurity in the alumina, is present at the ceramic-metal interface and dictates the oxide-metal interfacial chemistry. The high fracture energy relative to that for Cu-glass is attributed to the rougher, as-sintered ceramic surface; such a large deflection effect suggests that local shear stresses associated with deflected cracks increase the plasticity in the Cu. Cooperative studies on the strength of diffusion bonded Pt-Al_2O_3 and Au-Al_2O_3 with B.J. Dalgleish, now at University of California, Santa Barbara, indicate that silicate impurities expedite attaining high bond strengths but are not necessary. These issues are under continued study.

Fracture and Delamination of Thin Films

R. Fisher, R. Cannon, J.-Z. Duan, A. Fox

Evaporated thin films of chromium exhibit large internal stresses when they are deposited at low temperatures (e.g. room temperature for Cr). They will delaminate spontaneously from ceramic substrates when the strain energy released during exfoliation exceeds the fracture energy of the interfacial zone. Thus, knowledge of the internal stress and the critical film thickness at which delamination ensues can provide a useful, relatively simple method of measuring the fracture energy on a microscopic

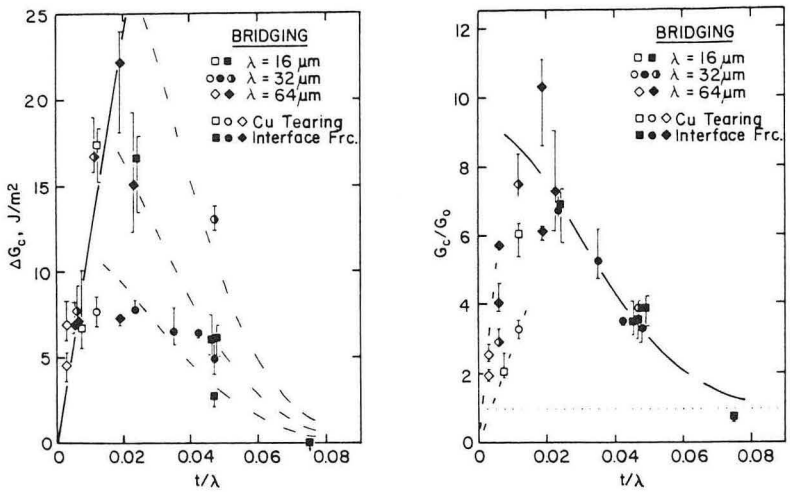


Figure 21
Experimental results illustrate how toughening from microcrack induced bridging varies with the thickness, t, and periodic spacing, λ, of the bridging ligaments. When fracture is entirely along the interface, the toughening increment diminishes with ligament thickness but is proportional to the inherent interfacial toughness, G_o, (which varies randomly for these samples) as illustrated by the normalization in the right portion of the right figure. Conversely, when fracture entails ligament tearing, the toughening increases with ligament thickness until the optimum which occurs at the transition between regimes.

scale. Preliminary fracture energies derived from such observations were plausible. However, the delaminated films curl into very tight scrolls owing to the presence of steep stress gradients through the film. These gradients complicate computation of the fracture energy. The stress fields deduced using x-ray diffraction have been used to study the delamination of bilayer films such that fracture energies can be compared with values from macroscopic tests.

Quantitative measures of the average strain and the strain gradient in vapor-deposited Cr films were derived by comparing simulated and observed Bragg diffraction peaks. The simulation procedure involved integration of the intensity diffracted from successive layers having assumed values of strain. The computation took into account the Bragg angle, x-ray absorption and the grain size change with distance from the substrate as observed by TEM. The strain, which varied from zero at the interface to as much as 0.8% for the Poisson contraction at the film surface for several film thicknesses, was deduced by computer matching of diffracted peak positions and shapes for both Cu and Fe radiation to improve the accuracy (Figure 22). The corresponding maximum in-plane tensile strain is about 2% (6 GPa stress) in agreement with the radii of curvature of the curled films.

The key to successful matching of computed x-ray line shapes with those observed was knowledge of the actual grain size which varied significantly (3x) with depth in the film. The analysis pointed out the erroneous grain size and strain values that are obtained by standard

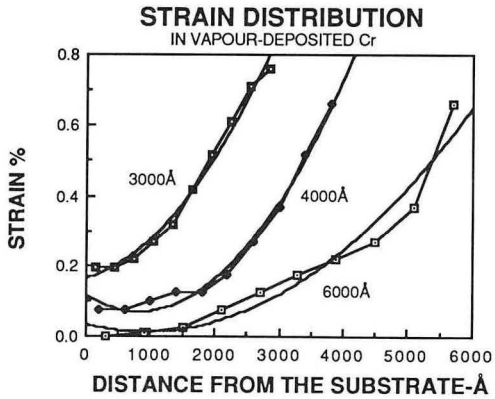


Figure 22
The occurrence and form of steep through-thickness strain gradients in vapour-deposited Cr films was deduced by computer simulation of the asymmetrical shape of X-ray Bragg diffraction peaks. The plot shows the compressive Poisson strains resulting from the tensile in-plane strains.

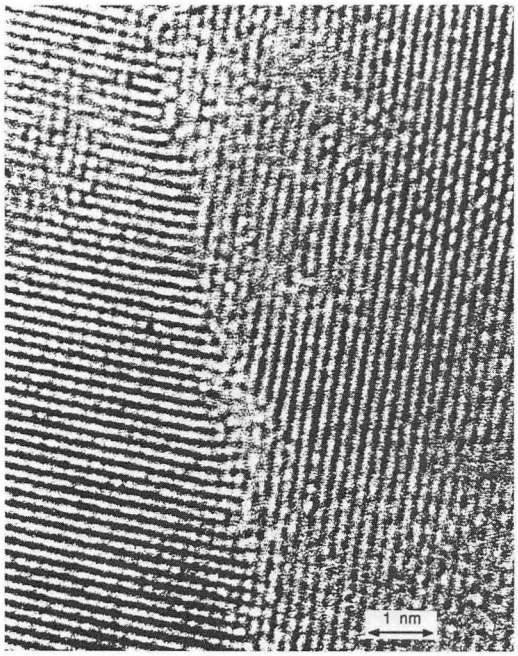


Figure 23 (above)
High resolution electron micrograph, taken on the Atomic Resolution Microscope at the LBL National Center for Electron Microscopy, showing a cross-section view of a Cr film vapour-deposited on a silicon wafer at 200°C. The occurrence of diffuse microvoids, i.e., regions of high vacancy content in the column boundaries, generates large tensile stresses in such films.

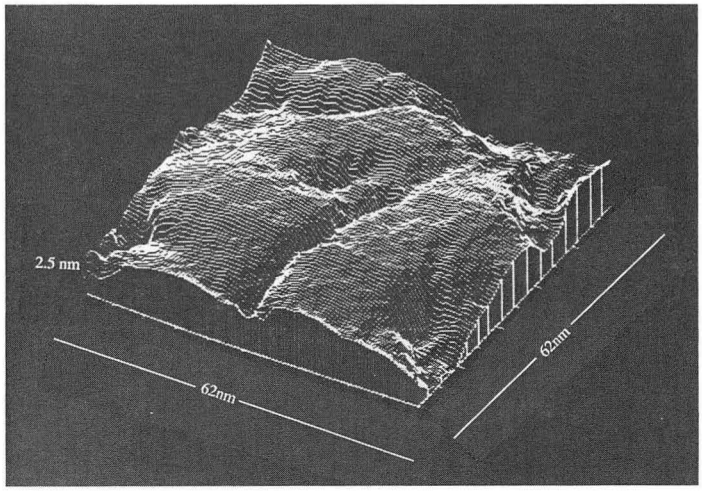


Figure 24 (above)
Scanning Tunneling Microscopy shows the deep grooves between columns in vapour-deposited Cr that lead to cracking when the in-plane tensile stress exceeds the fracture strength of the film.

Warren-Averbach and Cullity methods on samples with non-random spatial variabilities.

The values for Cu/glass interfacial fracture energies obtained from spontaneous delamination studies for Cr deposited onto various intermediate layers of Cu are comparable with separate double cantilever load-separation measurements on bonded couples. However, the surprisingly slight dependence of fracture energy on Cu thickness indicates that shear plays an important role during crack expansion.

The high residual stresses in vapour-deposited thin films are believed to result from the presence of microvoids and excess vacancies in the boundaries between columns. Thus deposition conditions that affect the columnar structure also influence the magnitude and anisotropy of the residual stress pattern. Examinations of deposited films in cross-section using high magnification transmission electron microscopy and the LBL Materials and Chemical Sciences Division Atomic Resolution Microscope (ARM) have provided much information about the dependence of column dimensions and orientation on substrate type and temperature, evaporation rate and deposition angle (Figure 23). The columns consist of clusters of grains with small angle boundaries between them. There is no fixed crystallographic relationship between the columns themselves, beyond the columns tending to be parallel to [110].

The large in-plane tensile stresses, with maximum values at the surface, cause cracking of the films through to the substrate when the stress exceeds the fracture stress. The cracks initiate at deep grooves between the columns which are seen in the STM image presented in Figure 24.

Discontinuous cracking occurs during vapour-deposition of Cr on polymers such as PMA when the fracture stress is reached producing a hierarchy of crack dimensions (Figure 25). Measurements of the crack area (N) and peripheral length (R) have been plotted to derive the fractal dimensions for the fracture process. The D value of 1.50 is midway between 1 for purely 1-dimensional brittle fracture in a thin film and 2 for purely ductile void growth (Figure 26).

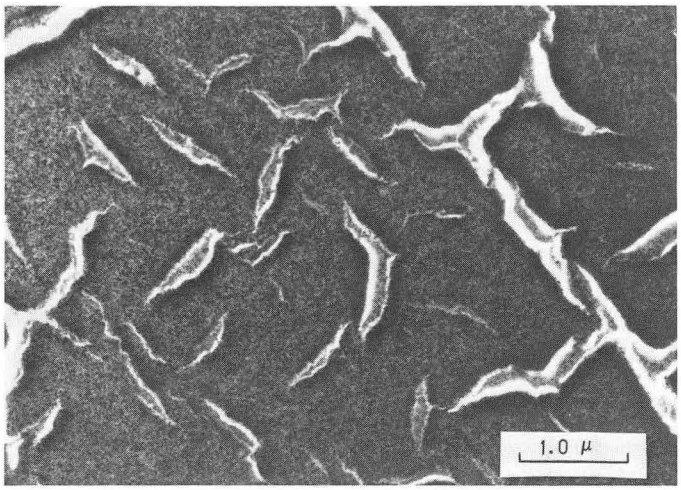


Figure 25
The occurrence of discontinuous cracking of Cr during deposition on polymethacralate (PMA), to relieve stresses developed in the film, is revealed by electron microscope observations of films stripped from the substrate.

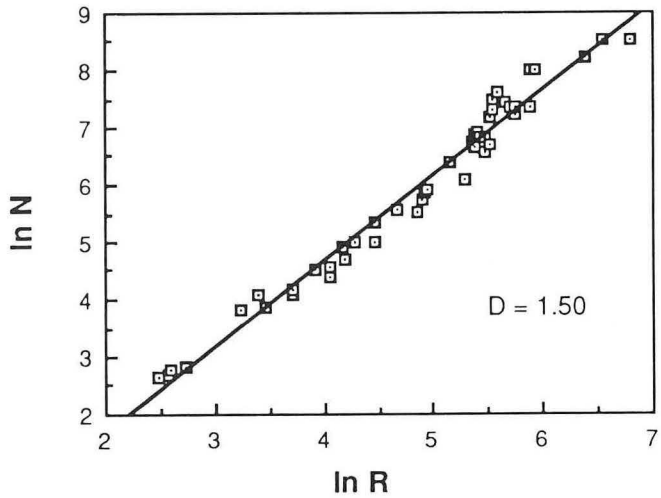


Figure 26
Image analysis of the crack pattern that results during vapour-deposition of Cr on PMA indicates a fractal parameter of 1.5 for the fracture that occurs within the 2-dimensional thin film during deposition.

Interface Fracture During Sintering

R. Cannon, C. Carter

During fabrication of multicomponent devices by sintering, stresses arise owing to incompatibilities in densification behavior of the constituents. Cracking, delayed densification permitting grain growth, and distortion can be undesired consequences. Although workers in several laboratories have been developing methods to analyze these stresses, criteria for failure or flaw formation are lacking. Theoretical analyses have been undertaken that address the latter issues, in particular providing criteria for situations wherein capillarity induced forces cause grain boundary fracture.

The analysis has initially concentrated upon a simplified geometry, i.e. a linear row of sintering particles which permits more precise treatments than do three dimensional compacts. The equilibrium shapes of segments/grains have been calculated exactly for cases wherein the interparticle distances are constrained to varying degrees either mechanically or kinetically (i.e. where only vapor-phase transport or surface diffusion are active). The densification potentials and surface curvatures are calculated exactly for the equilibrium shapes as a function of dihedral angle and the degree of shrinkage.

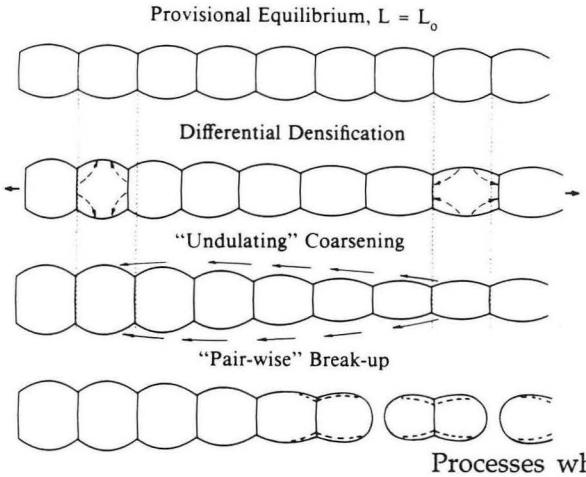


Figure 27
Equilibrium grain shapes for a constrained (fixed-grip) row of sintering particles plus independent modes of instability. A row which has been equilibrated due to surface smoothing or mass flow within each grain (a) can, under constraint, dehomogenize and rupture when one or more grains shrink at the expense of the others, i.e., differential densification (b), or form undulating, radial instabilities when mass is transferred between the grains, i.e., coarsening (c). Either process leads to break-up (d) when a critical grain aspect ratio is attained.

Processes which can dehomogenize a sintering system have been investigated by a thermodynamic stability analysis on the same geometry. Conditions for the occurrence of coarsening, differential densification, and combinations thereof are calculated (Figures 27, 28). Regimes exist where a sintering system is relatively stable to heterogeneities as well as regimes for which a system is highly unstable. In the latter regimes, rupture of a constrained chain would ensue from spontaneous growth of heterogeneities. Effects of diffusional transport coefficients, applied forces, and dihedral angle on the evolution of microstructure emerge. Densifying mass transport mechanisms (e.g. lattice or boundary diffusion) produce microstructural evolutions distinct from those derived from nondensifying mechanisms (e.g. surface transport).

Interface Fracture of Wire Bonds

R. Fisher, C.G. Shirley, S. Ahmed

A technology exchange program that was conducted with personnel from Intel's IC fabrication facility at Chandler AZ was concluded during FY88. The study, in collaboration with Glen Shirley and Syad Ahmed of Intel, involved analysis of the measured shear and tensile pull loads and examination of the various fracture paths that resulted from different bonding and test conditions with reference to interfacial fracture mechanics. Studies showed that both high and low bonder force settings caused subsurface damage to the silicon and resulted in low bond strength. Even with optimum bonder conditions, the fracture toughness was estimated to be only 1-2 J/m2 suggesting that it may be possible to develop some improvements in bond strength.

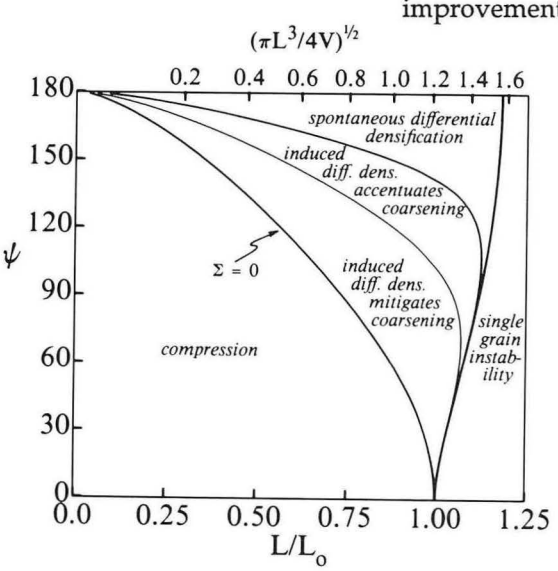


Figure 28
Map showing susceptibility to mechanical instabilities for an initially homogeneous row of grains with lengths L for each dihedral angle. The processes associated with each regime are illustrated for the single grain instability in figure 27d, and for spontaneous differential densification in Figure 27b. Spontaneous coarsening, Figure 27c, is energetically possible everywhere in the diagram. In two regimes, coarsening induced differential densification, shown above, can respectively, accentuate or mitigate the growth of perturbations leading to rupture. For specific systems, the kinetics will dictate which of these energetically possible instabilities will dominate.

Solder Contacts

J.W. Morris, Jr.

Pb-Sn solders are widely used for electrical contacts because of their low melting points, good adhesion characteristics, good plasticity and reasonable electrical conductivity. However, some of these very properties that make them desirable—malleability and low melting points—also make them liable to failure by thermal fatigue in service. The integrity of a solder contact is critical to reliable device operation. Improved solder joint reliability requires the development of accelerated tests that accurately predict fatigue life and the development of new, fatigue resistant solders. Current research is directed towards gaining a fundamental understanding of the thermal fatigue mechanism that is sufficient to guide the attainment of these goals. Thermal fatigue and creep experiments on experimental joint configurations in conjunction with extensive microstructural characterization of the solder microstructure have been conducted to evaluate the microstructure/property relationship for this alloy system for various temperature and loading histories. Results obtained here form the basis for an understanding of the failure mechanism operative under thermal fatigue conditions.

Stability of the Solder Microstructure

T. Summers, L. Louie, J.W. Morris, Jr.

The effect of storage on the solder joint reliability is of concern to the electronic industry. Room temperature corresponds to about .7 of the melting temperature of eutectic and near eutectic tin-lead alloys. Exposure to such high homologous temperatures is expected to influence the solder microstructure and in turn its mechanical properties. Therefore, before investigating the mechanical properties of these solders the effect of room temperature aging was deemed necessary. Several double shear specimens were made, under identical preparation conditions and allowed to age at room temperature for one, seven, and sixteen weeks (Figure 29). The microstructure appears to have coarsened with aging but due to the morphology of the microstructure the extent of coarsening is

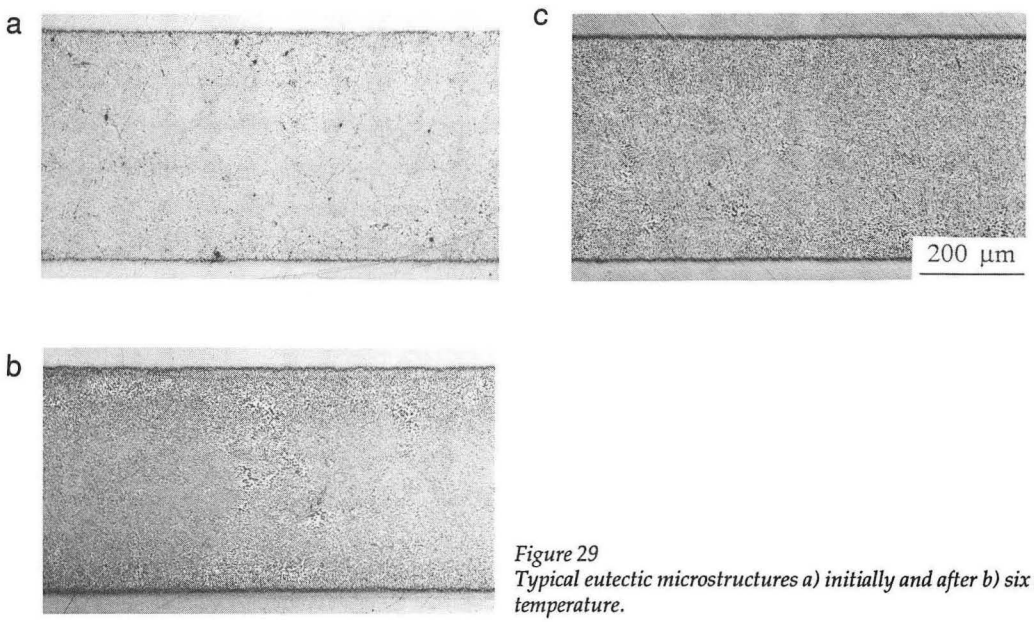


Figure 29
Typical eutectic microstructures a) initially and after b) six and c)sixteen weeks at room temperature.

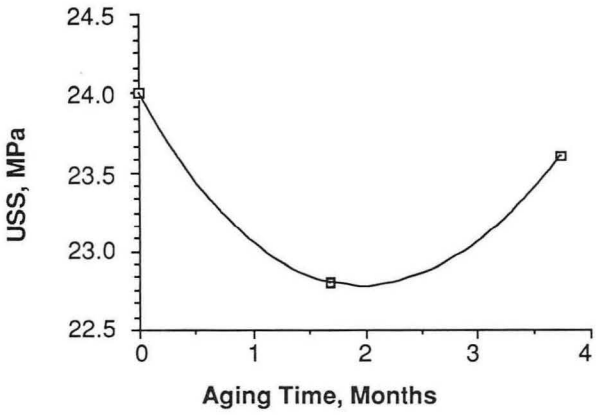


Figure 30
Shear Strength of a 63Sn-37Pb solder joint as a function of time at room temperature.

difficult to measure (Figure 30). Each datum point corresponds to an average of 3 specimens. The shear strength of a given alloy is relatively independent of room temperature aging and will not be affected by more than 5% provided the specimens are tested within the first 3 months after they are made. Work is still in progress to investigate any further effects of room temperature aging on the shear strength.

Thermal Fatigue Failure in Shear

D. Frear, D. Grivas, J.W. Morris, Jr.

The thermal fatigue of solder joints has been investigated in this laboratory. Research performed on near eutectic 60Sn 40Pb solders shows that failure in these solders occurs through the bulk of the joints. For solder joints possessing an interfacial intermetallic layer that is a significant fraction of the joint thickness, the failure may be accelerated by cracking through the intermetallic layer.

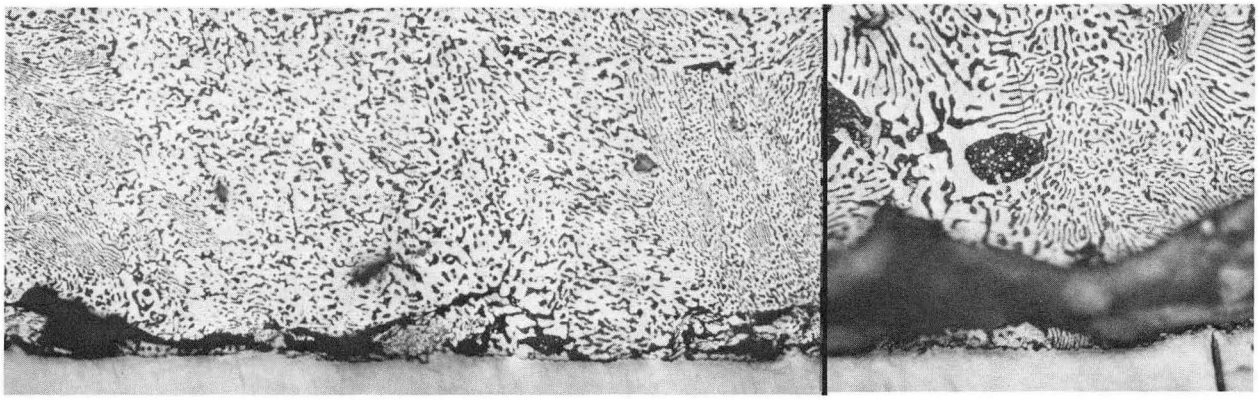
Fatigue failure is largely determined by microstructural changes that take place during the thermal cycle. The mechanism of thermal fatigue is intimately connected with the evolution of the microstructure and is a result of inhomogeneous shear deformation and associated microstructural coarsening. Inhomogeneous shear deformation in the solder results in inhomogeneous coarsening of the eutectic microstructure. Since the microstructure softens as it coarsens, shear deformation concentrates in coarsened regions, in turn causing more rapid coarsening. Failure occurs exclusively through this coarsened microstructure.

Improved solders should deform more homogeneously under load, hence minimizing the strain concentration that lead to coarsening and should be compositionally modified to resist coarsening at normal operating temperatures.

Thermal Fatigue Failure in Tension-Compression

D. Frear, D. Grivas, J.W. Morris, Jr.

Solder joints tested under thermal fatigue in tension-compression did not reveal preferential coarsening similar to that observed in shear. The coarsening is more general and tends to concentrate along the colony boundaries. Fatigue failure in tension initiates more rapidly than in shear and tends to occur by crack growth through the brittle intermetallic layer (Figure 31). Contrasting the shear fatigue data to the tension compression fatigue data, it appears that solder joints are more liable to fail in the brittle intermetallic layer. These results suggest that solder joints be designed to minimize tensile loading across the intermetallic layer.



250 Cycles **50 μm** **500 Cycles** **20μm**

Figure 31
A 60Sn-40Pb solder joint thermally fatigued in tension. The failure occurs through the brittle intermetallic layer at the copper/solder interface.

Creep in Shear of Experimental Solder Joints

D. Tribula, D. Grivas, L. Louie, J.W. Morris, Jr.

The microstructural coarsening observed in thermal fatigue was also observed during unidirectional creep in shear. Since creep experiments are relatively simple to conduct and analyze, they have been used to investigate the formation and growth of coarsented bands.

The inhomogeneous deformation associated with these local microstructural changes is a result this highly localized deformation that drives a recrystallization and subsequent coarsening of the as-solidified microstructure (Figure 32). The microstructure within this band bears no resemblance to the as-solidified eutectic material present elsewhere within the

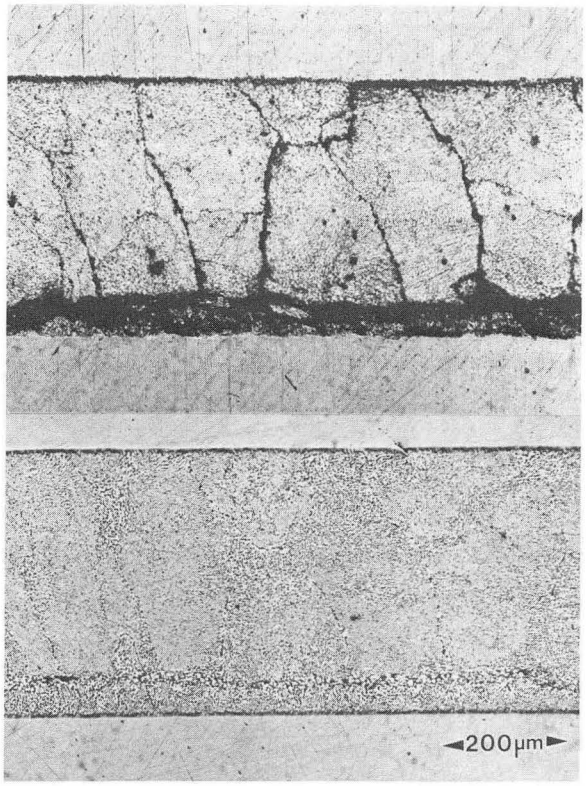


Figure 32
The deformation pattern (top) and associated microstructure (bottom) that develops within a 63Sn-37Pb solder joint as it is crept in shear. The deformation is localized to a plane parallel to the copper solder interface and its location corresponds exactly to the location of the coarsened band.

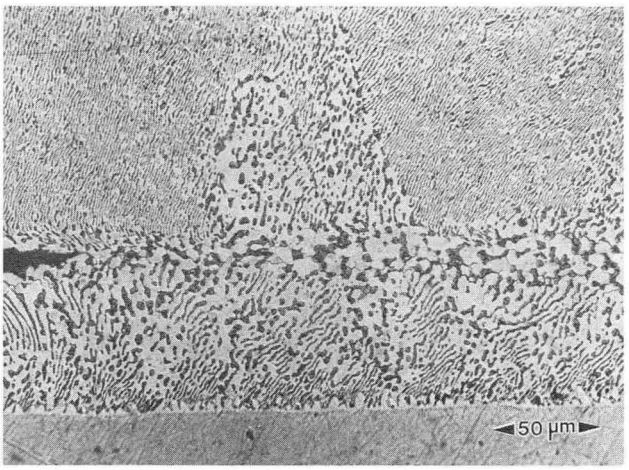


Figure 33
The microstructure within the coarsened band. The microstructure is characteristic of a recrystallized Pb-Sn microstructure. No resemblance to the initial as-solidified microstructure is evident within this coarsened band.

joint (Figure 33). Growth of the coarsened band occurs by progressive recrystallization and coarsening of the deformed as-solidified material. Since the recrystallized material is soft compared to the eutectic material its bahaviour is very much like that of a narrow crack. The plastic strain of a crack under simple shear loading conditions (mode II), is narrow and confines the deformation to the plane of the crack. It follows that the recrystallized band tends to remain plane and narrow while it extends itself along the a shear plane, as is observed. These observations are in agreement with those obtained for thermally fatigued solder joints, both service failures and experimental joints tested in this laboratory. Based on these observations, it is expected that improved, fatigue resistant solders should posses micostructures that exhibit more uniform deformation characteristics which are more stable under thermo-mechanical processing.

Solders for Cryogenic Surface Mount Devices

D. Grivas, J.W. Morris, Jr.

Microelectronic devices that operate at cryogenic temperatures are not subjected to the modes of thermal fatigue described above. At such low operating temperatures, while the microstructure of the solder is stable the shear strength of the bulk solder increases with the potential consequence that the locus of failures may shift to the intermetallic layer. The intermetallic composition and morphology was investigated for 60Sn-40Pb, 75In-25Pb, and 60Sn-40In solder alloys joining copper plates. The Indium based alloys are of interest due to their relative low melting points and chemical insensitivity to gold and silver. Indium lead solders are particularly suitable for use in step soldering due to their wide range of melting temperatures. Joints on copper were tested in shear; all three solders failed in a ductile manner through the bulk rather than along the interface. All solder alloys investigated develop intermetallic layers at the solder copper interface. The morphologies of the intermetallics on the solder side are similar, and consist of whisker-like intermetallics that grow out into the solder (Figure 34). In the 60Sn-40Pb the intermetallic whiskers were identified as Cu_6Sn_5, in the 75In-25Pb as InCu, and in the 60Sn-40In a mixture of intermetallic phases containing Cu, In, and Sn. Hollow rods of Cu_6Sn_5 intermetallics were observed in the bulk 60Sn 40Pb. For specimens tested at 77 K these rods were found not to cause substantial deterioration in the strength of the solder.

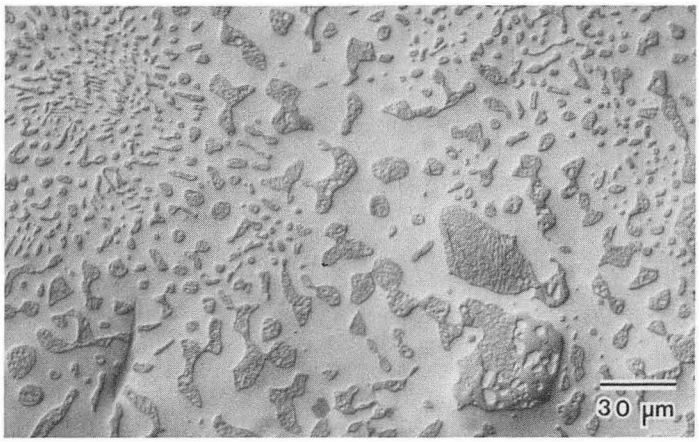


Figure 34
The microstructure of a 58Sn-40Pb-2In solder alloy. Note the diffuse character of the eutectic colonies.

THIN FILM METALLIZATION

J. Sanchez, T. McKnelly, J. Bowen, J.W. Morris, Jr.

Sputter deposited aluminum thin film alloys are the standard metallization materials used for local electrical interconnects and current bus lines in LSI and VLSI silicon based integrated circuit devices. However the reliability of these patterned metal lines continues to be a concern for both present and future circuit designs. Electromigration induced short and open circuit failures, and stress induced voids and hillocks are examples of failure mechanisms that continue to plague device manufacturers and to limit future circuit design criteria. The drive for increased chip complexity, circuit speed and level (or 'scale') of integration leads to increasing reliability requirements for future VLSI metallization structures and systems. However the understanding of the role of the thin metal film microstructure in these failure mechanisms has not kept pace with device reliability requirements.

The approach undertaken in this program is to initially focus on the microstructural characterization of these material systems as a function of processing and alloy content. We may then use this characterization information and apply it to patterned thin film circuits undergoing, for example, electromigration stressing in order to determine which features of the film microstructure influence and control the failure processes. Eventually the understanding of the processing and alloy effects on microstucture and failure mechanisms will lead to the design of more reliable metallization systems in integrated circuits.

Microstructural Characterization of Al 2% Cu Thin Films

J. Sanchez, T. McKnelly, J. Bowen, J.W. Morris, Jr.

Work completed in FY88 includes the transmission electron microscopic (TEM) characterization of grain size, grain growth, and precipitate reactions in sputter deposited Al 2% Cu thin films as a function of film thickness and thermal annealing conditions. A TEM plan view shows the fine grained aluminum matrix with a uniform distribution of Al_2Cu (θ) phase particles in the as deposited film (Figure 35). Annealing of this film in the range 300 °C to 475 °C allows for rapid grain growth in the aluminum matrix and for redistribution of the θ phase into several different mor-

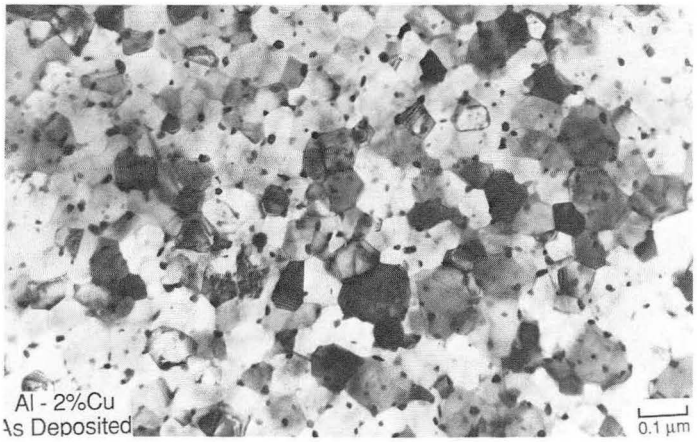


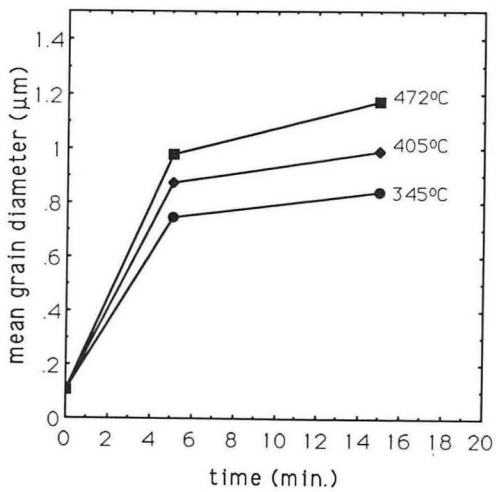
Figure 35
TEM plan view micrograph of sputter deposited Al 2% Cu thin film, 0.8 m thick, in the as deposited condition, showing the small and uniform aluminum grain size with the evenly distributed Al2Cu θ (dark) phase with spherical morphology.

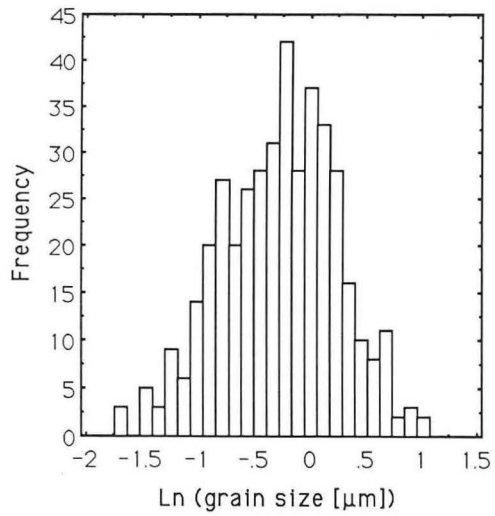
phologies which are dependent upon the precise annealing thermal treatment.

Aluminum grain size and size distribution as a function of annealing treatment is shown in figure 36. Kinetic analysis of the data indicates that the grain growth process has "saturated" for the times and temperatures examined here. Previous work by others has typically shown that films with larger grain sizes and more uniform size distributions are more electromigration failure resistant. The work completed here has characterized this growth process for a typical film used in VLSI applications.

Annealing of the as deposited films in the two phase region of the phase diagram, at a temperature high enough to allow for rapid copper diffusion but low enough to prevent θ particle dissolution, produces a blocky θ phase morphology at grain triple points via an Ostwald coarsening process (Figure 37). Annealing at higher temperatures (at or above 400 °C) allows for θ phase dissolution, with θ phase heterogeneous reprecipitation on cooling. This dissolution-reprecipitation process produces elongated θ precipitates along grain boundaries (Figure 38). These θ morphological differences should affect electromigration resistance in these films, since most models for the retardation effect of copper on electromigration failure rates rely strongly on specific copper-aluminum grain boundary interactions. Ongoing work in our laboratory will try to

Figure 36 (below)
a) Mean Al grain diameter as a function of annealing time and temperature for a 0.4 m thick sputter deposited Al 2% Cu thin film. Measurements were taken from TEM micrographs using the linear intercept method. b) Grain size distribution for an Al 2% Cu thin film annealed at 345 °C for 5 minutes, showing the log-normal grain size distribution.





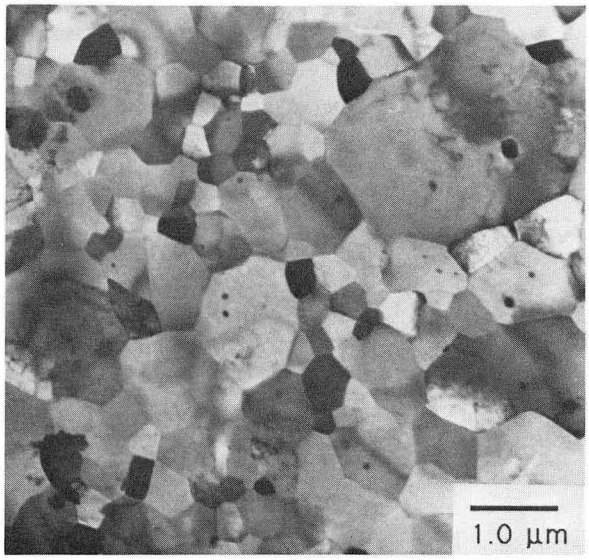


Figure 37
Blocky θ phase (Al_2Cu) formed at Aluminum grain boundary triple points by a coarsening reaction during annealing 345°C for 15 minutes.

determine this θ morphological effect on electromigration failure times. Finally, in collaboration with Materials Research Corporation, we will investigate the influence of high deposition temperature and bias on film microstructure for Al-Cu and Al-Cu-Si alloys. Subsequent electromigration testing of these films will help to clarify the role of film microstructure on electromigration reliability.

Accelerated Electromigration Testing of Aluminum Alloy Thin Films

J. Sanchez, T. McKnelly, J. Bowen, J.W. Morris, Jr.

Results and progress for FY88 include the design, fabrication, and the operation of an electromigration test station with associated electronics for sample stressing and data retrieval. Further, aluminum based thin film circuits were fabricated, and accelerated (i.e., high temperature and high current density) electromigration testing of these circuits was begun. The test circuit pattern chosen, designed and fabricated is an array of 50 parallel lines ("PLA") which allows for electrical stressing of line widths from 1.0 m to 10.0 m at current densities up to 5x10 ^{6} A/cm^2. The critical advantages of this test pattern include the simulataneous testing of a statistically significant number of similar lines, many lines optimally

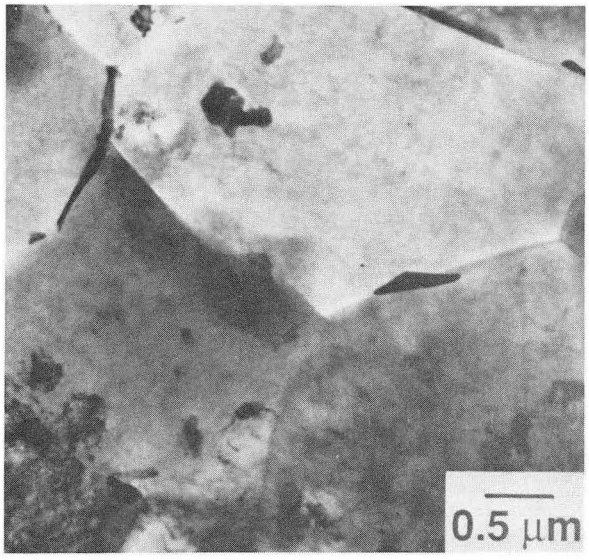


Figure 38
Elongated θ phase formed by heterogeneous precipitation along grain boundaries during cooling after annealing at temperatures above ~400°C.

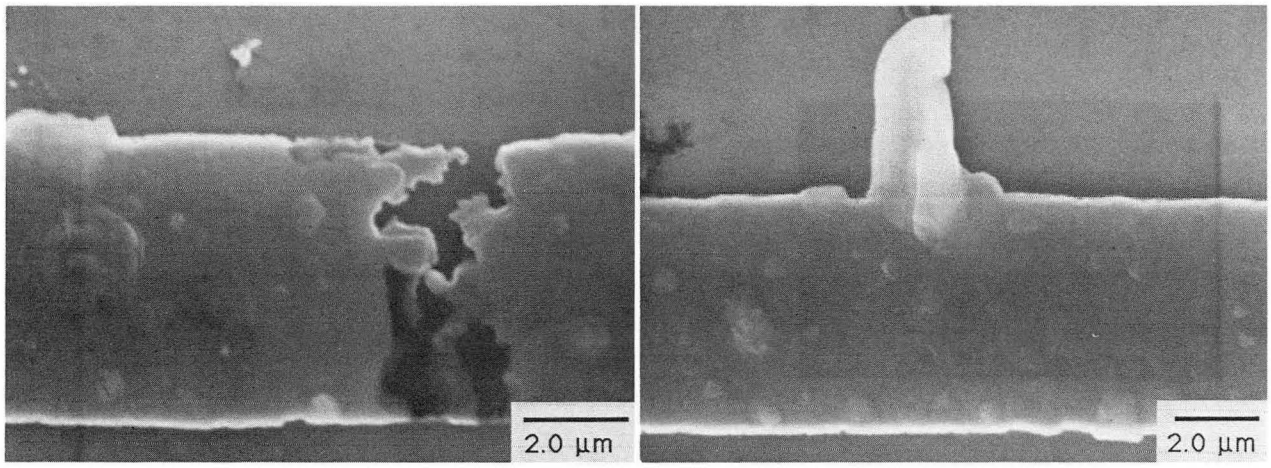


Figure 39
SEM micrographs of electromigration damage in a aluminum line, 0.5 m thick and 6.0 m wide, after current stressing at 0.8x10 ^{6} A/cm^{2}. at 250°C. a) Void damage leading to open circuit failure. b) Whisker or hillock damage leading to a short circuit failure.

spaced for subsequent TEM sample preparation, and preserved failure sites on the tested lines which allow for microscopic investigation. Failure sites and several failure modes were tested on pure aluminum lines at 225°C (Figure 39).

Data from electromigration tests carried out on pure aluminum films, tested from 200°C to 250°C at current densities from 0.8 to 1.3 E6 x 10^6 A/cm^2, are shown in figure 36. Analysis of these results show an activation energy of 0.55 eV, and a current density exponent of approximately 2.5. Plans for continued work include testing of Al-2% Cu film circuits with different θ morphologies as described above, and the testing of ternary Al-Cu-Si thin film alloys.

Continuing work also includes TEM investigation of failure sites on tested lines for various alloy systems. For example, we anticipate TEM microscopic evidence for the beneficial effects of Cu additions (or θ morphological effects) on aluminum film electromigration lifetimes. Grain boundary structural effects and surface damage such as whisker (Figure 40) and hillock growth will also be investigated, since for some material systems an interlevel short circuit (due to a whisker or hillock) is the predominant electromigration failure mechanism.

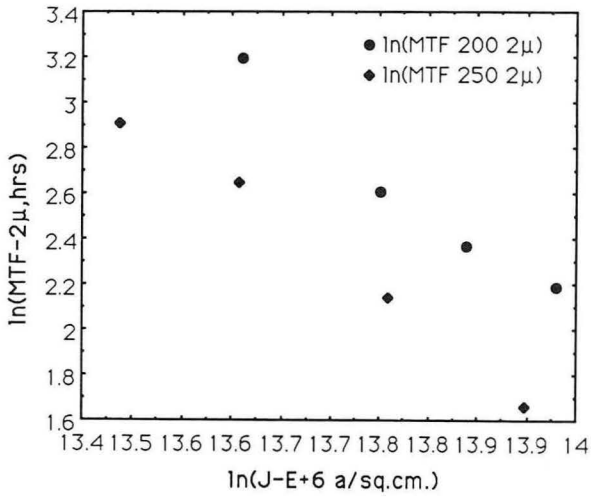


Figure 40
Electromigration median time to failure (MTF) data for open circuit failure as a function of testing temperature and electrical current density. Test circuits are pure aluminum films 0.5 m thick with 2.0 m wide stripes, and are in the fully annealed condition. Each data point is the median of failure times for 50 individual open circuit failures.

STAFF

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Administrative Support	Margaret Ragsdale

AWARDS

- Jack Washburn was elected to the Bohmische Physical Society.

INDUSTRY INTERACTIONS

Research Contracts

- The Interconnects project is working with IBM in investigating the adherence of ceramic-metal interfaces as characterized by the fracture energies for such interfaces.

Equipment Donations

- Two crystal-growing furnaces were donated to the Semiconductors project by Hewlett-Packard's Microwave Technology Division in Santa Rosa .

Advisory Board

Robert A. Burmeister (Chairman)	Hewlett Packard Laboratories
Robert S. Bauer	Xerox Corporation, PARC
Walter Brown	ATT Bell Laboratories
John Carruthers	Intel Corporation
Richard A. Reynolds	DARPA
R. Noel Thomas	Westinghouse R & D Center
August Witt	Massachusetts Institute of Technology

Industrial Collaborations

- Scientists from Rockwell Science Center collaborated on studies of the factors determining the spalling resistance of thermal protection coatings on advanced aerospace alloys.
- Studies were conducted with Intel Corporation on the failure modes occurring during wire bond testing.
- In a collaboration with McDonnell Douglas Microelectronics Center, the structure and composition of the recently developed Al-Ni-Ge ohmic contacts to N-GaAs were investigated by transmission electron microscopy combined with secondary ion mass spectroscopy and Auger spectroscopy.
- In collaboration with Varian Associates, and Hewlett Packard Optoelectronics Division, facet formation during MBE growth of GaAs on a (110) GaAs substrate was studied.
- In collaboration with Materials Research Corporation, the influence of high deposition temperature and bias on film microstructure for Al-Cu and Al-Cu-Si alloys was studied.

Industrial Fellows

- David W. Bliss of M/A-Com worked with the gallium arsenide crystal growth project.
- R. Crooks of Rockwell International worked with the Interconnects group on the adhesion of thermal barrier coatings for advanced aircraft.
- C. Glenn Shirley of Intel Corporation worked with the Interconnects group on the reliability of integrated circuit devices.

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Liliental-Weber, Z., *Suppression of Defect Propagation in Heteroepitaxial Structures by Strained Layer Superlattices*, Thomson-CSF, Paris, France, June 1988.

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*Joint study with R.O. Ritchie of the CAM Structural Materials Program.

High-T_C Superconductivity

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Basic Science
Thin Films and Thin-Film Devices
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High-T_C Superconductivity

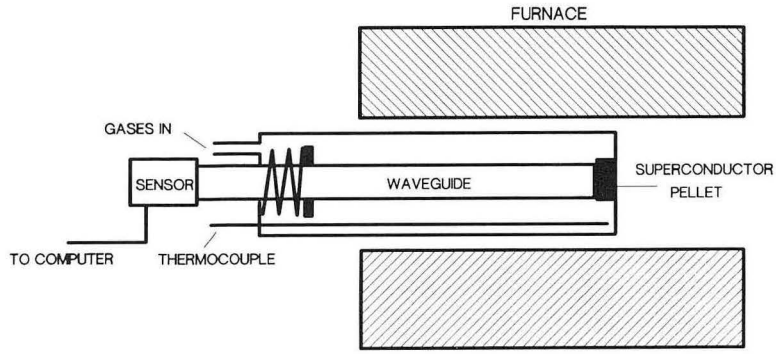
The CAM High-Temperature Superconductivity Program is directed to the development of a fundamental understanding of the new high-critical-temperature (high-T_C) superconductors, by both experimental and theoretical investigations, and to the development of the knowledge necessary for the utilization of these materials in applications in electronics and electrical power systems.

The current research areas are:

- ***BASIC SCIENCE***, which includes theory, measurement of physical properties, and materials synthesis.
- ***THIN FILMS AND THIN-FILM DEVICES***
- ***CERAMIC PROCESSING***
- ***ELECTRON MICROSCOPY***

Notable accomplishments of the Program during the past year include:

- Observation of the superconducting energy gap in $Bi_2Sr_2CaCu_2O_8$ single crystals, by measurement of high-resolution photoemission spectra and by tunneling.
- Bulk synthesis, using high pressure oxygen, of the superconducting 1-2-4 compounds R $Ba_2Cu_4O_8$, with R = Y, Nd, Sm, Eu, Gd, Dy, Ho, Er, and Tm
- Synthesis of $La_{2-x}M_xCuO_4$ (M = Ca, Sr, Ba) and $Ba_{1-x}K_xBiO_3$ utilizing fused NaOH/KOH melts at temperatures as low as 300°C.
- Demonstration of feasibility of a high-T_C superconducting bolometer. An optimized bolometer at 77 K detecting 20 μm radiation should provide one to two orders of magnitude improvement in signal-to-noise ratio over comparable detectors.



- Measurement of magnetic flux noise and flux creep in YBCO ($YBa_2Cu_3O_7$) films. The noise is believed to result from hopping of flux vortices along grain boundaries, and can be reduced by the use of films with large grain size, c-axis orientation, and high critical current density.
- Demonstration of thermocompression bonding of aluminum cladding to YBCO. A thin layer of silver prevents chemical interaction between the highly oxidizing superconductor and the reducing normal metal.
- Identification, using advanced transmission electron microscopy, of the lower-T_C (polytypoid) compounds which tend to form next to the grain boundaries in Bi-Ca-Sr-Cu-O. Microscopy also shows that these undesired phases can be eliminated by substitution of Pb for Bi.
- Demonstration that the "linear" term in the specific heat of the Bi-Sr-Ca-Cu oxides is at least an order of magnitude smaller than in $YBa_2Cu_3O_7$.

The majority of the research is conducted by staff of the Materials and Chemical Sciences Division of the Laboratory, but the effort involves very significant participation by investigators in the Applied Science Division (Berdahl, Hunt, Rubin, Russo), the Physics Division (D. Morris), and the Accelerator and Fusion Research Division (Brown). Funding sources for the research are likewise diverse: Division of Materials Science in the Office of Energy Research of the US Department of Energy (DOE); Office of Energy Storage and Distribution, Conservation and Renewable Energy at DOE; Electric Power Research Institute; Office of Naval Research; Defense Advanced Research Projects Agency; and private sources. In the research descriptions which follow, principal investigators' names are used merely to identify research groups; a clearer picture of the individuals responsible for each research achievement may be found in the bibliography.

BASIC SCIENCE

M. Cohen, D. de Fontaine, L. Falicov, C. Jeffries, V. Kresin, J. Michaels, D. Morris, J.W. Morris, Jr., N. Phillips, A. Pines, A. Portis, P. Richards, A. Stacy, G. Thomas, E. Weber, P. Yu, A. Zettl

Theory

The theoretical work includes fundamental microscopic calculations and phenomenological calculations of superconducting properties, as well as computations of oxygen ordering in $YBa_2Cu_3O_x$. Close collaborations with experimentalists are maintained.

Kresin's proposed explanation of the observed high superconducting transition temperatures has been elaborated by him in a collaboration with H. Morawitz (IBM, Almaden). In their view, the attraction responsible for charge carrier pairing is due to the exchange of both phonons and plasmons. The structure of the plasmon and phonon bands in conducting highly anisotropic layered materials was investigated and a generalized Eliashberg equation describing the effects of phonons and plasmons was formulated.

The superconducting properties of a material can be investigated by study of the total dielectric function (Cohen). This function describes the interaction between test changes in a solid, including the effects of electronic and lattice polarizability. Properties of the dielectric function determine crystal stability, electron-lattice interactions, and superconductivity. In this work a total dielectric function for the electron-lattice system is derived and used to explore and determine the above solid-state properties and phonon frequencies.

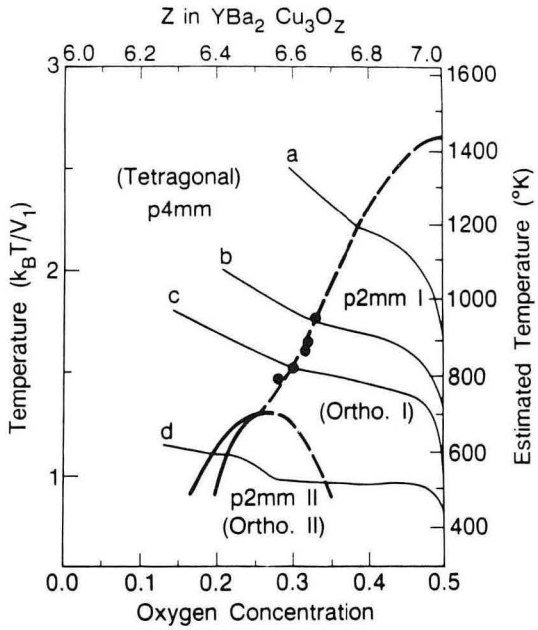
Microscopic calculations were performed with the Hubbard model, including an electron-lattice interaction (Falicov). A very small cluster of four atoms with periodic boundary conditions was examined when the electron hopping is a function of the lattice vibration of the ions. It was discovered that the classical electron-lattice interactions and the electron-electron repulsion tended to cancel one another and favor different ground states. It was also found that some of those ground states can sustain superconductivity of a variety of types, while other ground states, mostly the magnetic ones, do not favor any superconducting pairing.

The phenomenological theory of deformable superconductors was investigated by Falicov. The solution of the Ginzburg-Landau equations for a system that can sustain both superconductivity and a structural transition was obtained. It was found that the interaction between superconductivity and deformation can lead to weak first-order superconducting transitions and to fascinating spatially dependent phenomena: (1) an unexpected magnetostriction at the surface caused by the diamagnetic response of the superconductor and its attendant change in the structural properties; (2) metastable surface superconductivity produced by unreleased stresses at the surface which produce a surface deformation and its attendant surface superconductivity. It was found that while the deformation relaxes over short distances, the superconductivity may extend much deeper into the bulk of the deformable superconductor.

Theoretical calculations in support of experiments continue to be an important activity. Cohen collaborated with Zettl's experimental group to investigate various properties of high temperature superconductors: Using inelastic neutron scattering the electrostatic field near the rare-earth site was examined; the anisotropy of the thermoelectric power of YBaCuO was studied; and a detailed magnetic and resistive study of the isotope effect for LaSrCuO was completed. A theoretical calculation was per-

Figure 1

$YBa_2Cu_3O_x$ pseudo-binary phase diagram calculated by the cluster-variation method. Ortho. I is the 90 K and Ortho. II is the 60 K superconducting phase. Dashed lines are second-order transitions, continuous lines are first-order phase boundaries. Fine lines represent oxygen partial-pressure isotherms at (a) 400 atm, (b) 1 atm, (c) 0.2 atm, and (d) 0.001 atm. Filled circles are transition points determined experimentally.



formed to examine electronic correlations and satellites in photoemission spectra in superconducting oxides. Further analyses of physical properties, based particularly on the small value of the Fermi energy and the layered structure of the high-T_C cuprates, have been presented by Kresin, in a collaboration with G. Deutscher (Tel-Aviv University) and S. Wolf (Naval Research Laboratory). These analyses show, for example, that the electronic heat capacity can be separated from the full heat capacity at high temperatures and used to estimate the electron-phonon coupling constant.

Analysis of the proximity effect, as it should be exhibited by high-T_C superconductors (Kresin), has led to two conclusions. First, it has potential for the enhancement of three-terminal semiconductor (field-effect) devices with proximity effect contacts. Also, it offers a potential mechanism for the enhancement of the low-T_C superconductors in properties such as the critical temperature, critical field, and critical current.

The thermodynamics of oxygen ordering in $YBa_2Cu_3O_z$ is very important for the understanding of the various related phases of this material permitted by the variability of oxygen concentration z. The ordering in the Cu-O basal plane has been investigated as a function of oxygen content and temperature (de Fontaine). Several phase diagrams have been calculated by means of the cluster variation method applied to asymmetric two-dimensional Ising models. The interaction parameters selected guarantee the stability of the orthorhombic structures near z=7, and, for certain choices, also include a doubled-cell phase (Ortho.II) around z=6.5. O-Cu-O correlations were investigated as a function of temperature and concentration. Calculated orthorhombic-to-tetragonal transition temperatures and concentrations for various oxygen partial pressures are in excellent agreement with recent experimental data. The resulting phase diagram is shown in Figure 1.

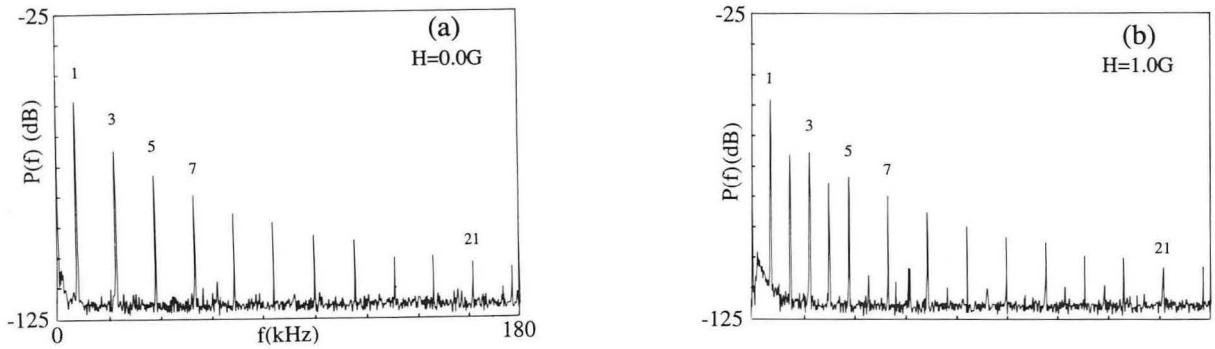


Figure 2

Power spectra for powdered YBa2Cu3O7 at T=77 K, driven by an ac field at f_0=7.7 kHz, of amplitude H_1~14G. (a) dc field H=0.0 G. Odd harmonics, n=3,5 ..., are generated. (b) In a parallel dc field H = 1.0 G, even harmonics, n=2,4 ..., also appear, owing to symmetry breaking by the dc field. The unit of the vertical scale is P(db)=20 $\log_{10} V_s$+13, where V_s is the rms signal voltage.

Theoretical work in the group of J.W. Morris, Jr. has resulted in the proposal of a homologous series of transient ordered structures which may form during the spinodal decomposition of $YBa_2Cu_3O_{7-x}$. These transient phases provide the best kinetic accomodation of the local vacancy concentration, and have the stoichiometry $YBa_2Cu_3O_{7-n/(2n+1)}$ where n is an integer. The structure of the n phase has a diffraction maximum at the point [n/(2n+1) 00].

Measurement of Physical Properties

Extensive measurements of transport properties of superconductors are performed. These include measurements of resistivity as a function of crystallographic direction, pressure, frequency, etc., and measurements of thermoelectric power. Measurements of magnetic susceptibility are performed at low frequencies (for example, using SQUID magnetometers) and at radio frequencies (using pick-up coils). Measurement of electromagnetic properties is extended to higher frequencies through microwave and infrared absorption measurements. Other important physical properties measured include elastic properties (Young's modulus, etc.), the superconducting energy gap with photoemission and tunneling spectroscopies, specific heat, oxygen diffusion and the oxygen isotope effect. Work is also being initiated on nuclear magnetic resonance of ^{17}O.

Stress-dependent and anisotropic resistivity and thermoelectric power measurements in Y-Ba-Cu-O (Zettl) suggest metallic-like conduction in the Cu-O planes, but semiconducting behavior along the c-axis. For the normal state, increasing pressures up to 1 kbar cause the c-axis resistivity to decrease dramatically and tend toward a metallic-like temperature dependence. No change is observed in the ab plane resistivity. The pressure dependence of T_C in single crystal Bi-Ca-Sr-Cu-O compounds has been examined as well (Yu, Zettl), with the resulting relations showing a pronounced nonlinear behavior. In related work in progress, the temperature and pressure dependence of electrical resistance in high-quality single crystals of Cu_2O and CuO is under investigation.

Elastic measurements on Y-Ba-Cu-O and Bi-Sr-Ca-Cu-O crystals have shown that high T_C is not necessarily correlated with structural phase transitions (Zettl).

Ceramic samples of the high-T_C superconductors can exhibit highly-nonlinear electrodynamic behavior, due to the weak links between superconducting grains (Jeffries, Zettl). For bulk samples of $YBa_2Cu_3O_7$ in a

radio frequency magnetic field and in a dc magnetic field H, novel nonlinear behavior was observed, including high-order odd-harmonic generation induced in the pick-up coil if H=0. See Figure 2. If H 0, there is additional even-harmonic generation. The even-harmonic power displays a very sharp dip at H=0 of width ~100 mG. This and related behavior can be semiquantitatively understood by modeling the system as a suitably averaged collection of flux-quantized supercurrent loops containing Josephson junctions. The theoretical models are being broadened to take account of the sample geometry, critical state, and fluxon pinning and motion. This work has a bearing on the problem of high critical currents in high magnetic fields, as well as on the origin of the superconductivity.

Magnetically modulated microwave absorption measurements are proving valuable as a probe for granular superconductivity, with the complex behavior observed generally attributed to networks of Josephson junctions. Portis and Weber are investigating dispersive behavior associated with fluxon nucleation within Josephson junctions. Also, these investigators, together with Thomas, are correlating high-resolution transmission-electron microscopy (HRTEM) measurements with low-magnetic-field modulated microwave absorption, in samples of nominal composition $Bi_2Sr_2Ca_2Cu_3O_y$. Absorption onsets are associated with transitions at both 110 and 80 K. The addition of Pb eliminates the lower transition temperature. This observation is consistent with the HRTEM observations and supports the general view that microwave absorption arises primarily from grain boundaries and planar defects.

Microwave surface impedance studies are underway (Portis), in a collaboration with D.W. Cooke (Los Alamos) and H. Piel (Wuppertal, W. Germany). Films of YBCO deposited by laser-ablation yield the smallest microwave loss. Efforts are underway to achieve low surface resistance in other film compositions, and to examine the potential for low losses of various composite film structures.

Measurements of far-infrared absorptivity have the potential to reveal the role of the energy gap in the complicated electrodynamics of these superconductors. As materials improve, however, the reflectivity in the a-b plane becomes difficult to distinguish from unity. A novel calorimetric experiment has been developed to directly measure small absorptivities in these materials (Richards). Preliminary absorptivity measurements on c-axis films of $Er_1Ba_2Cu_3O_7$ produced at Stanford show that the absorptivity increases linearly with frequency from 30 to ~300 cm^{-1}, followed by a step increase between 400 to 600 cm^{-1}. The linear absorptivity is probably an extrinsic property of the films measured. The step increase is well known from reflectivity measurements of other groups. Higher quality films, for future measurements, have been acquired from Bellcore. In addition to the question of an energy gap, the results of these experiments will be used as an indicator of film quality and to predict the performance of high frequency thin film devices.

The superconducting energy gap in $Bi_2Sr_2CaCu_2O_8$ has been observed. The mechanism which causes the pairing of charge carriers in the high-T_C superconductors has not yet been identified. Since the magnitude of the ratio of the energy gap 2Δ to the thermal energy k_BT_C is a quantity which any physically correct theory must explain, it is particularly important to determine the value of the energy gap separating the lowest-lying (unpaired) excitations from the ground state. Previous optical spectroscopy and electron tunneling data have yielded proposed values for $2\Delta/k_BT_C$

ranging all the way from 2 to 18 for the La-Sr-Cu-O and Y-Ba-Cu-O systems. Now, for the first time, high resolution UV-photoemission spectroscopy has been used to determine a superconducting energy gap. The spectroscopy was performed by Y. Petroff's group at the Laboratoire pour l'Utilization du Rayonnement Electromagnetique in Orsay, using single crystals grown in A. Zettl's laboratory in Berkeley. The results on two samples (Figure 3) clearly show a redistribution of electronic states near the Fermi level in the superconducting phase. The displacement of states away from the Fermi level is direct evidence for the existence of an energy gap. The estimate for 2Δ has been made by assuming the (provisional) BCS form of the density of states. The results are Δ=30 5 meV, which, with T_C=88 K, yields $2\Delta/k_BT_C$=8 1.4. Tunneling measurements by G. Briceno and A. Zettl on similar crystals give supporting results, $2\Delta/k_BT_C$=7.9 2. Future refinements of these experiments are planned to determine the temperature dependence of the gap and to extend the results to other compounds. The BCS theory in the weak coupling limit gives $2\Delta/k_BT_C$=3.5. Thus, it is clear that a correct theoretical description of these experimental results will require either strong coupling, strong anisotropy, or a non-BCS type of pairing.

The specific heats of a number of new samples of YBCO, made at LBL and also in other laboratories, have been measured (Phillips). Evidence for an intrinsic "linear" term, $\gamma(0)T$, in the zero field specific heat has continued to accumulate, but $\gamma(0)$ may be closer to 4.5 or 5 than the 6 or 7 mJ/mole K^2 obtained in earlier measurements. There is no doubt that magnetic impurity phases contribute to the observed $\gamma(0)$, but it continues to appear that there is an intrinsic component that persists in the pure YBCO limit. This point is of considerable interest in connection with theory—the existence of a non-zero $\gamma(0)$ is an important prediction of one of the major theories.

By contrast, measurements on a number of samples of Bi-Cu oxides have shown that $\gamma(0)$ is an order of magnitude smaller than in YBCO, and zero within the experimental uncertainty. The reason for this difference is not clear at this time, but even if $\gamma(0)$ 0 is an intrinsic property of all high-T_c oxide superconductors, it seems quite possible that it might assume different values in different materials. The Tl-Cu and Bi-Pb-Cu oxides investigated showed linear terms comparable to those found in YBCO.

An analysis of high-temperature data for YBCO, in which the lattice specific heat is represented by an expansion in inverse powers of T, has been used to estimate γ (the normal-state value). The interesting result is that the value agrees

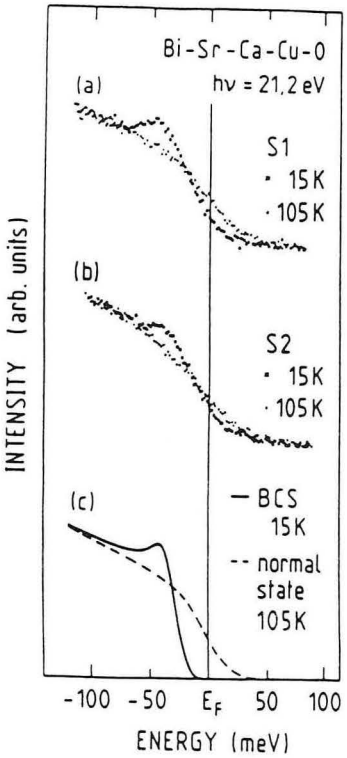


Figure 3
Intensity of photoelectrons versus energy, for two samples, S1 (a) and S2 (b), in the normal state (105 K) and in the superconducting state (15 K). Calculated spectrum (c) in the normal state (dashed line) and in the superconducting state with D=30 meV.

approximately with those estimated from the "jump" in C at T_C (using BCS relations) and that obtained from $\gamma(H)$ in the mixed state.

The magnetic field dependence of C near T_C for YBCO consistently shows a suppression of the *magnitude* of the specific heat anomaly, but the *onset* is unaffected by field. This result is qualitatively consistent with the importance of the fluctuation effects associated with the short coherence lengths.

The oxygen isotope effect studies were continued this year. It is hoped to clarify the role of phonons in forming the superconducting electron pairs. Extensive measurements of electrical resistance and magnetic susceptibility on $YBa_2Cu_3O_7$ and $La_{1.85}Sr_{0.15}CuO_4$ have yielded values of α of 0.019 0.004 and 0.14 0.008, respectively (Zettl, Cohen). Here α is determined from $T_C \sim M^{-\alpha}$ and M is the oxygen mass. The value of α for YBCO is in excellent agreement with the value 0.019 0.005 obtained earlier by D.E. Morris' group.

Another detailed study of the effect of ^{18}O substitution in $YBa_2Cu_3O_7$ was pursued by Michaels and Stacy, in collaboration with Dr. Krillov and D.T. Hodul (Varian) and R.H. Fleming (Charles Evans and Associates). Characterization of samples was performed by secondary ion mass spectroscopy (SIMS), temperature programmed desorption (TPD) and reduction (TRR), Raman spectroscopy, and magnetization measurements. The characterization measurements showed that even for temperatures as low as 400 °C and times as short as 2 h, ^{18}O is not substituted exclusively into the chain site in $YBa_2Cu_3O_7$. In addition, no consistent variation in the transition temperature with the degree of substitution was found. Therefore, it was not possible to extrapolate to 100% ^{18}O substitution based on samples with partial substitution.

While the variation of oxygen concentration by diffusion is important for isotope effect measurements, it is also of great importance to the other physical properties of the high-T_C superconductors. D.E. Morris' group has examined the reversible shift of T_C caused by annealing Bi-Ca-Sr-Cu-O samples at 600 °C in oxygen. The highest $T_C = 78.5$ K of the "80 K" phase is obtained with an O_2 pressure of 10^{-2} bar. T_C shifts down to 65.4 K after treatment at 137 bar. No structural change is observed in X-ray powder diffraction, and the original T_C is restored upon re-treatment in O_2 at low partial pressure. The 110 K phase showed a much smaller decrease in T_C (~4 K) after treatment at 134 bar.

Two NMR (nuclear magnetic resonance) studies of high-T_C superconductors have been initiated. J. Michaels plans to use ^{17}O NMR to clarify oxygen transport in oxide superconductors. A. Pines is working with two techniques, double axis rotation (DOR) and dynamic angle hopping (DAS), for removing second-order broadening from spectra of quadrupolar nuclei. These techniques afford the possibility for high-resolution solid-state NMR for an entirely new class of nuclei.

Synthesis

The synthesis research includes the synthesis of new materials and the growth of single crystals.

The group of D.E. Morris has focused on the synthesis of high-T_C compounds utilizing a high-pressure oxygen environment. For example, the 1-2-4 compound $YBa_2Cu_4O_8$, which had been discovered in the form of thin films, was successfully synthesized in bulk form using a new high pressure oxygen technique. It was also discovered that Y in this compound can be replaced by any of the rare earths Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm. The T_C's of this series of compounds range from 57 K to 81 K, in-

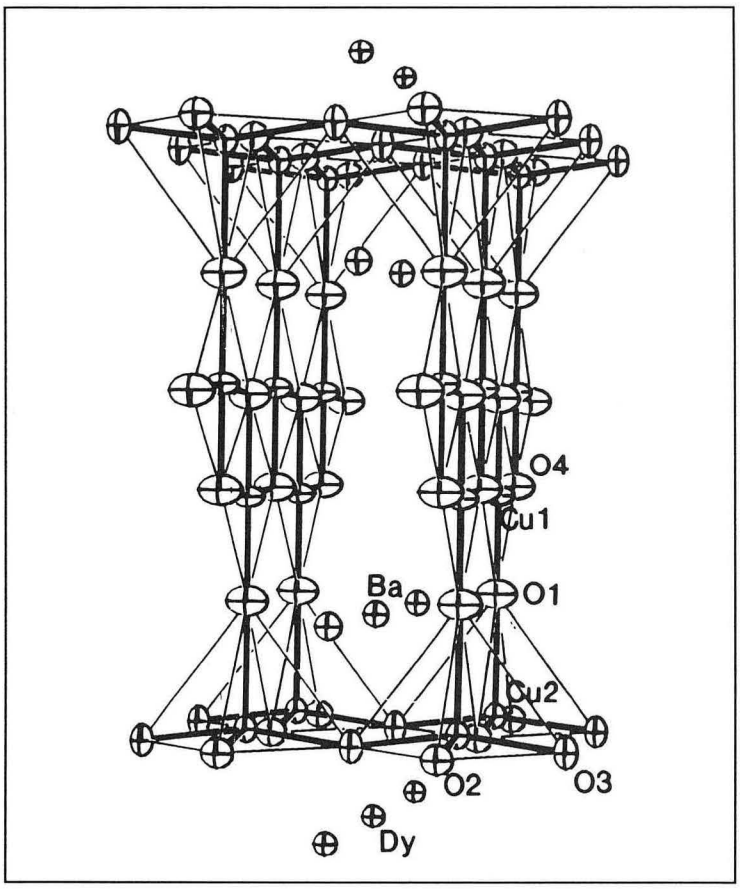


Figure 4
The crystal structure of $DyBa_2Cu_4O_8$ with 90% probability thermal ellipsoids. Planar-coordinated copper and oxygen atoms display prolate vibration ellipsoids with major to minor axial ratios exceeding 2:1.

versely with ion size. Single crystals of the Dy compound ($DyBa_2Cu_4O_8$) were analyzed by x-ray diffraction, in a collaboration with R.M. Hazen and L.W. Finger of the Carnegie Institution. The diffraction results confirmed the orthorhombic crystal structure shown in Figure 4. Copper-oxygen layers perpendicular to the c-axis are dimpled as in the 1-2-3 structure. Unique copper-oxygen strips between these layers have copper in a distorted square-planar configuration.

The stability of the 123, 124, and 247 superconductors has been investigated (D.E. Morris). The 247 phase ($Y_2Ba_4Cu_7O_{15-x}$) is composed of alternating layers of 123 and 124. As an aside we note that, surprisingly, it has a much lower T_C (40-50 K) than either 123 or 124. It has been found that the 124 superconductor has a more stable oxygen content than 123, and that for a wide range of starting stoichiometries, 124 is the only superconducting phase formed when the oxygen pressure is sufficient. The 123 phase is stable only up to a few atm.; the 247 phase is favored at intermediate pressures.

The new oxide superconductors generally have been prepared by reactions of intimate mixtures of the metal oxides, carbonates, oxalates, or nitrates at high temperatures (often up to 1100°C). Since this synthetic route often leads to impure, inhomogeneous products, there is a clear need to discover new synthetic routes. The Stacy group has isolated $La_{2-x}M_xCuO_4$ (M = Ca,Sr,Ba) and $Ba_{1-x}K_xBiO_3$ from fused NaOH/KOH melts at temperatures as low as 300°C. The oxides are dissolved in wet, molten NaOH/KOH. Heating between 300°C and 450°C results in slow loss of water and precipitation of the product. The route is a single-step process that leads to high-T_C superconductors at temperatures much lower than those used in previous syntheses. Because the products are precipitated directly from solution, it is possible to control the stoichiometry precisely, and also the particle size. Single crystals can be grown, as well as thin films.

Crystals of $Bi_2CaSr_2Cu_2O_8$ have been grown (Zettl, D.E. Morris) for use in experiments on electronic structure (e.g., photoemission), optical prop-

erties, tunneling, transport properties, and Raman spectroscopy.

Now that several copper oxide and bismuth oxide superconductors have been discovered, it is time to search for superconductivity in other metal oxides. Niobium is a particularly interesting choice because so many niobium compounds are superconducting. (In addition, there was a report from Japan on superconductivity at high temperatures (above about 150 K) in films containing a niobium oxide.) The Stacy group is exploring three areas: 1) intercalation of Li into NbO; 2) deintercalation of Li from $LiNbO_2$; and 3) synthesis of new niobium oxides containing alkaline earths and rare earths. While elemental Nb superconducts near 7K and NbO near 1 K, elemental niobium with a small amount of oxygen dissolved superconducts near 11 K. By tuning the oxidation state of NbO with Li it may be possible to raise T_C. $LiNbO_2$ has the NbS_2 structure; NbS_2 superconducts near 7 K. By removing Li from $LiNbO_2$ to prepare NbO_2 with the NbS_2 structure it may be possible to prepare a new superconductor. Work in these two areas is underway. In the third area, a new compound $BaNbO_3$ has been isolated and characterized.

THIN FILMS AND THIN FILM DEVICES

P. Berdahl, I. Brown, J. Clarke, E. Haller, A. Hunt, D. Olander, P. Richards, M. Rubin, R. Russo

The thin-film research includes film synthesis, film characterization, and the investigation of thin-film devices such as bolometers and Josephson junctions. A thin-film information service is supplied as well. President Reagan designated Lawrence Berkeley Laboratory as a Superconductivity Research Center for Thin-Film Applications in 1987.

Of the various film synthesis techniques, sputtering is under investigation by Clarke, Haller, and Rubin; laser ablation is being pursued by Clarke, Russo, and Olander; ion-implantation, by Brown and Rubin; and sol-gel chemical deposition by Hunt. Most of the film synthesis research was in a start-up phase in 1988. In particular, major new funding was received in May 1988 from Conservation and Renewable Energy at DOE, for film research relevant to electric power systems. Superconducting films have been synthesized by sputtering (Haller, Rubin) and laser ablation (Russo), and work is underway to improve superconducting properties, and to develop improved buffer layers, lithographic techniques, etc.

Various film characterization techniques are available to CAM researchers. Electrical resistance measurements are made in several laboratories (Berdahl, Haller, Zettl). Two commercial SQUID magnetometers are used for magnetization measurements. Chemical composition information is obtained from Rutherford backscattering, x-ray fluorescence spectroscopy, and Auger spectroscopy. Morphological information is obtained from x-ray diffraction and electron microscopy.

Sputtered YBCO films were deposited on $SrTiO_3$ buffer layers on Si and, simultaneously, on $SiTiO_3$ (100) crystals (Rubin). The transitions for the films on $SrTiO_3$ buffer layers were broad and reached zero resistivity around 20 K, as contrasted with films on single crystals, which had sharp transitions above 77 K. Buffer layers for deposition of YBCO on metal tape substrates will be investigated next, to pursue suitable configurations for conductors in power systems.

Film deposition by pulsed laser ablation is proving to be a highly

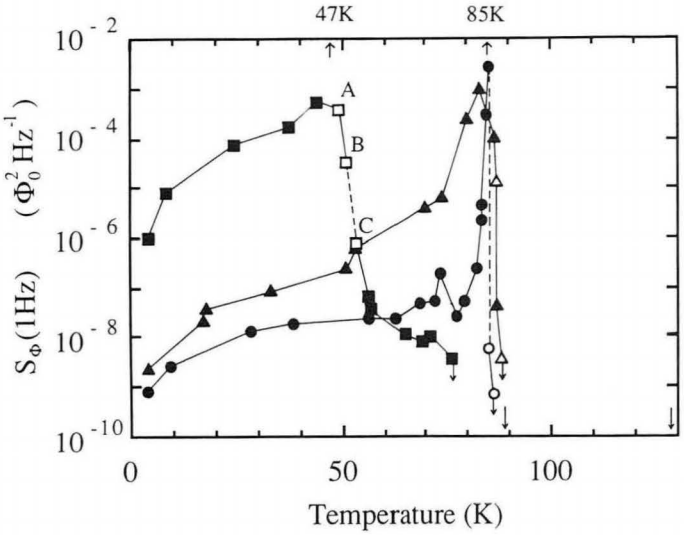


Figure 5
Spectral density of flux noise at 1 Hz vs. temperature for three YBCO films: squares, a sample with T_C = 47 K; triangles, a sample with mixed a- and c-axis orientation, circles, a sample with more than 90% c-axis orientation. Unfilled symbols show the occurrence of white, rather than 1/f, noise. Φ_o is the flux quantum (= 2.07 x 10^{-15} Wb).

promising technique for forming high-quality films of various high-T_C compounds. Russo's research in this area is in collaboration with B. Olsen and M. Fluss (Livermore). They have constructed a deposition system around a pulsed high-energy excimer laser (1.5 J per pulse at 308 nm). Superconducting films of YBCO are formed at a deposition rate of 5 angstroms per pulse. The use of noble metal buffer layers is also being explored. These buffer layers are expected to permit deposition of sperconducting YBCO films on metal substrates such as stainless steel. In 1989, two additional new laser ablation deposition chambers are planned to be operational (Clarke and Russo groups). Also, a collaboration between Russo and Olander will explore a laser vaporization technique for film deposition, using long (millisecond) laser pulses.

A detailed study of thin films of YBCO (Clarke) has shown that the low-frequency magnetic flux noise increases with temperature, while decreasing markedly as the microstructure of the films is improved. These results imply that SQUIDs and flux transformers involving high-temperature superconductors must be made from films with large grain size, with c-axis orientation and with high critical current density. Furthermore, there will be a considerable reduction in noise if the devices are operated at 28 K, the boiling point of liquid Ne, rather than at 77 K, the boiling of of liquid N_2. The measurements were made by patterning 1 mm square washers of the films, made at Stanford University, and mounting them close to, but not in contact with, an Nb-based SQUID. The SQUID was maintained at 4.2 K, while the temperature of the YBCO film could be raised to its transition temperature. The magnetic flux noise generated in the film was measured by the SQUID, and found to have an 1/f power spectrum. This technique enables one to screen different materials relatively quickly, to study the noise generated by the film independently of the noise generated by the junctions, and to study the temperature dependence of the noise. It is believed that the noise arises from the hopping of flux vortices from one site to another, possibly along grain boundaries. Thus, an increase in the grain size decreases the total length of grain boundary in a given area of film with a concomitant reduction in the level of flux noise. Figure 5 shows measured noise values for three difference YBCO films.

Detailed measurements have been made of the low-frequency voltage

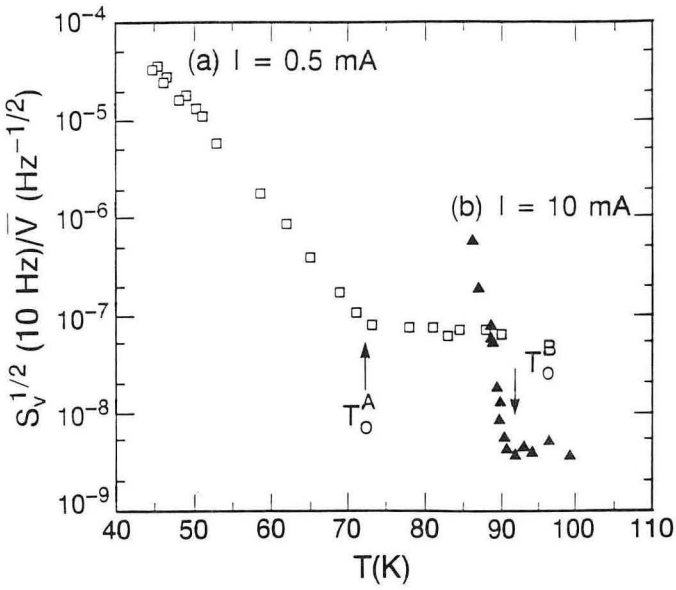


Figure 6
Normalized voltage noise vs. temperature for two films of YBCO.

noise at the resistive transition of films of YBCO (Clarke, Richards). The noise was found to decrease markedly as the microstructure of the films was improved, as was found in measurements of magnetic noise. These measurements have demonstrated that YBCO films can be used as a thermometer on a far infrared bolometer operated near 90K, which should be more sensitive than other liquid-nitrogen cooled detectors for wavelengths greater than 20 μm . The noise was determined by mounting the samples, made at Stanford University, on a temperature regulated block in a vacuum can and measuring the voltage noise at constant current bias. The spectral density of the noise, $S_V(f)$, scaled as 1/f and varied markedly across the resistive transition, as shown in Figure 6. This plot shows the square root of $S_V(f)$, normalized by the average voltage $\bar{V}$ across the sample. Sample A was a polycrystalline film with a semiconducting behavior at temperatures above the broad transition, while film B was epitaxially grown and showed a metallic behavior above a relatively narrow transition. For the better film, at the midpoint of transition, the 1/f noise was low enough to permit a temperature resolution of 10^{-8} K $Hz^{-1/2}$ at 10Hz. This result was used in an optimization procedure for a bolometer from which it was concluded that a noise equivalent power (NEP) of (1-20) x 10^{-12} $WHz^{-1/2}$ should be achievable with the incoming radiation chopped at 10 Hz. The NEP improves as the heat capacity of the substrate supporting the YBCO film and absorbing film is reduced. This projected value of the NEP represents a substantial improvement over than obtained with existing 77 K detectors for wavelengths greater than 20 μm.

Superconducting quasiparticle detectors and and mixers for infrared and millimeter waves are under development (Richards). These detectors and mixers are based on quasiparticle tunneling in superconductor-insulator-superconductor (SIS) tunnel junctions fabricated from low-T_c superconductors. Thin-film superconducting heterodyne mixers with planar lithographed antennas, RF impedance matching structures and tunnel junctions have been fabricated in collaboration with NBS Boulder

and tested at 90, 180 and 270 GHz. A review article has been written on the subject of superconducting components for infrared and millimeter wave receivers. The goals of this research are to reach the quantum limit to the performance of these devices and to prepare for similar applications of high-T_c superconductors.

The thin-film information service provides bibliographic and interpreted information to scientists who are investigating, or who wish to begin investigating, high-T_c thin films (Berdahl). An annotated bibliography on sputtered films was prepared and distributed to 250 scientists. It is also planned to distribute a comprehensive bibliography on thin films which is derived from the extensive Westinghouse bibliographic database. Further, a day-long short course of Introductory Reviews on Thin-Film Superconductors was presented to 100 attendees of the Conference on the Science and Technology of Thin-Film Superconductors (Colorado Springs, CO, November 1988).

CERAMIC PROCESSING

L. De Jonghe

The ceramic processing research investigates the chemical and physical processes occurring during the synthesis and sintering of the high-T_c ceramics. Activities include sintering studies, including the effects of temperature gradients; development of techniques for cladding and plating of high-T_c ceramics with ordinary metals; and investigations of microcracking during processing, utilizing acoustic emission techniques. This research addresses the key technological problem that critical current densities are too small. Cladding for mechanical strength and low-resistance electrical contacts will also facilitate technological development. Most of the ceramic processing research is funded by the Electric Power Research Institute (EPRI).

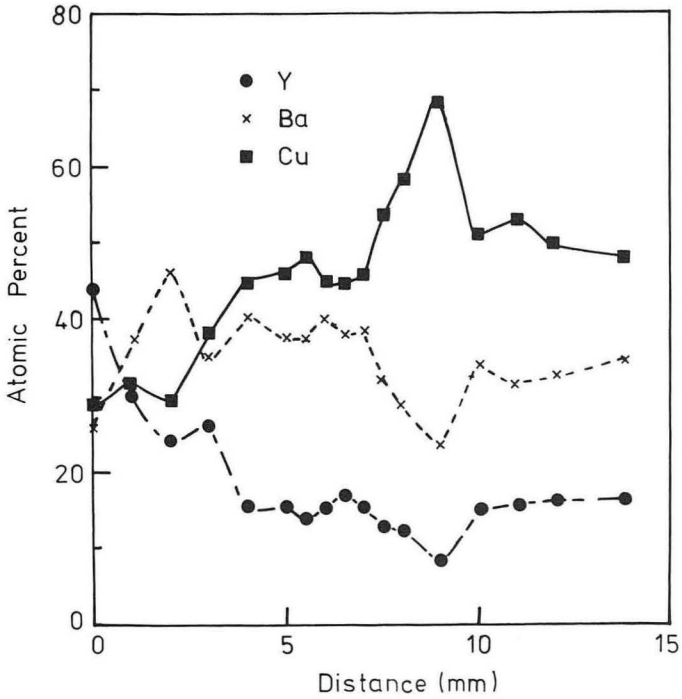


Figure 7
The formation and transport of a liquid phase during sintering of YBCO in a temperature gradient of 25°/mm results in chemical demixing as the copper-rich liquid moves to the right down the gradient. These curves display the normalized atomic percent of yttrium, barium, and copper in the sample as a function of distance from the hotter end (940°C).

Sintering of Ceramic Superconductors

Densification and shear deformation during sintering of $YBa_2Cu_3O_7$ compacts were studied using a loading dilatometer operating in the range of 910-940°C. The measured ratio of densification rate to creep rate under constant, small uniaxial stresses provides strong support for the presence of a liquid phase during sintering.

Mass transport and chemical demixing were observed along the length of a thin cylindrical compact of YBa_2Cu_3Ox which was sintered in a static temperature gradient of 25°/mm (max. 940°C) in air for 12 hours. The results (Figure 7) are consistent with formation of a copper-rich liquid phase in the hot region, transport of the liquid down the temperature gradient, and formation of different eutectic compositions along the length of the sample. Implications for sintering of Y-Ba-Cu-O powder compacts include the need for phase pure powders and careful temperature control during sintering.

Metal Cladding

For virtually every potential use of high-T_c oxide superconductors in the form of wires or tapes it is desirable to have the ceramic material encased in a normal metal sheath, or "cladding." Cladding provides improved current carrying capacity, enhanced fracture strength and toughness, environmental stability, and more efficient cooling. It also makes establishment of electrical contacts simpler and more reliable. Due to the physical dissimilarities between ceramics and metals in general, and to the instability and reactivity towards most metals exhibited by the superconducting oxides in particular, cladding of these novel materials presents a challenge in materials science.

A technique was developed for aluminum cladding of high-temperature superconductors by thermocompression bonding. A thin layer of silver (Figure 8) prevents chemical interaction between the highly oxidizing cuprate superconductor and the reducing normal metal, aluminum. The result is a composite with improved strength and environmental stability with specific interface resistivity at 77 K of less than 35 $\mu\Omega$-cm^2 at electrode current densities as high as 400 Acm^{-2}. This process, for which a patent application has been filed by EPRI, has been applied to small samples of YBCO. Efforts continue to expand the method to cladding of large and irregular surfaces and eventually to continuous cladding of superconductor wires and tapes.

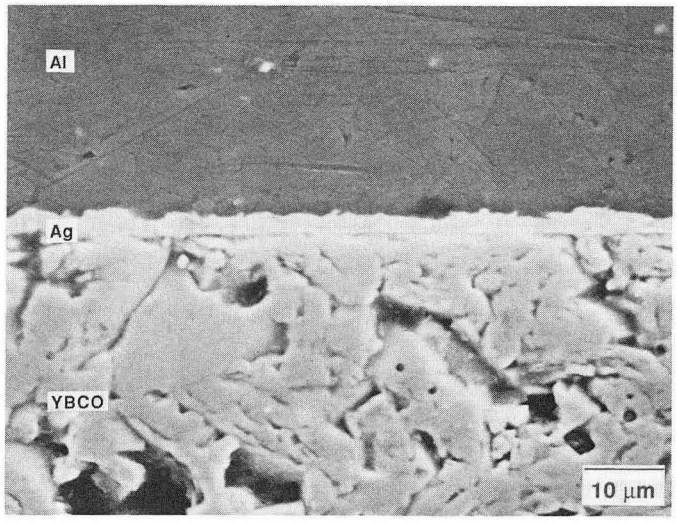


Figure 8
Reaction between the highly oxidizing ceramic superconductor and its readily oxidized aluminum cladding is avoided by the interposition of a thin barrier layer of silver, as seen in this scanning electron micrograph of the composite interface region. The silver is applied to the superconductor surface by evaporation in a vacuum chamber, after which high-purity aluminum is diffusion-bonded to the silver under applied pressure.

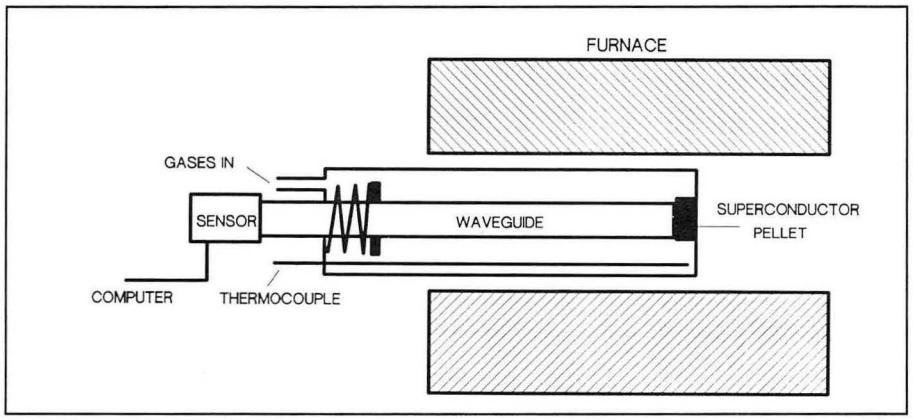


Figure 9
Acoustic emissions originating within a ceramic specimen as a result of microcracking are detected by a piezoelectric sensor and analyzed by a dedicated computer. The effects of changes in processing parameters (heating and cooling rates, gas composition and flow rate) and sample microstructure on cracking intensity assist in determining optimum processing conditions. This technique has provided the first direct evidence of oxygenation-induced cracking in $YBa_2Cu_3O_x$.

Electroplating of High-T_C Superconductors

A process has been developed for electroplating high-temperature superconductors with metallic aluminum using a non-aqueous electrolyte. The process can be used to create electrical contacts or for cladding. The thickness and surface distribution of the metal layer are controlled by coulometry and masking. The electrodeposited aluminum is continuous, uniform in thickness, fills surface pores in the ceramic and exhibits a thin oxide interface region whose specific interface resistivity is less than 40 $m\Omega\text{-}cm^2$ at 77 K. Efforts continue to create coherent thin films of silver on superconductor surfaces by electrodeposition. Grain size and porosity of silver films are strongly dependent upon electrolyte composition and deposition rates.

Microcracking

The anisotropic expansion and contraction of YBCO during thermal processing, oxygenation, and cryo-cooling result in intra- and intergranular stresses that are largely relieved by microcracking. While considerable effort has been devoted to investigation of grain boundary phases, orientation alignment and densification processes, only recently has attention

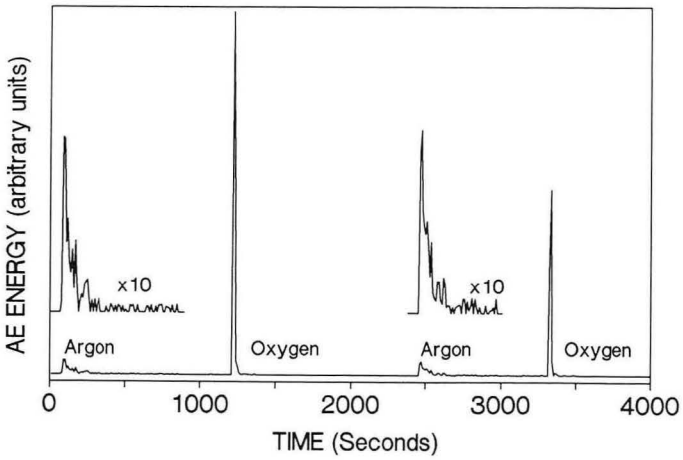


Figure 10
Oxygen uptake by $YBa_2Cu_3O_x$ is rapid at temperatures above 400 °C, while removal of oxygen takes place more slowly and produces less acoustic emission. The figure shows the acoustic emission response at 600 °C for a sintered YBCO pellet subjected to sudden increases and decreases in oxygen partial pressure. Through experiments such as these, processing routines for producing crack-free ceramics can be developed and tested.

been paid to the role of microcracking in limiting the critical current density in bulk YBCO samples.

Acoustic emission signals produced during microcracking are qualitative and quantitative measures of the degradation in connectivity developing in a sintered compact. The rate and intensity of cracking are correlated with processing parameters (heating/cooling rates, oxygen pressure), with the presence or absence of various additives, with microstructural characteristics (density, grain size, boundary phases) and with transport critical current densities. An understanding of the processes involved will lead to the development of processing schedules and/or formulations which minimize the deleterious effects of microcracking.

The apparatus, shown schematically in Figure 9, allows detection and analysis of acoustic emissions from ceramic samples under controlled conditions of temperature and ambient atmosphere. Experiments to date have demonstrated the direct connection between the phase transition from the oxygen-deficient, non-superconducting, tetragonal YBCO structure to the oxygen-rich, superconducting, orthorhombic phase and the occurrence of microcracking. The onset and duration of acoustic emission are temperature- and oxygen pressure-dependent. At temperatures above 400°C, YBCO responds rapidly to changes in oxygen partial pressure. The acoustic response to oxidation (increase in O_2 pressure) is both sharper and stronger than that for reduction (Figure 10).

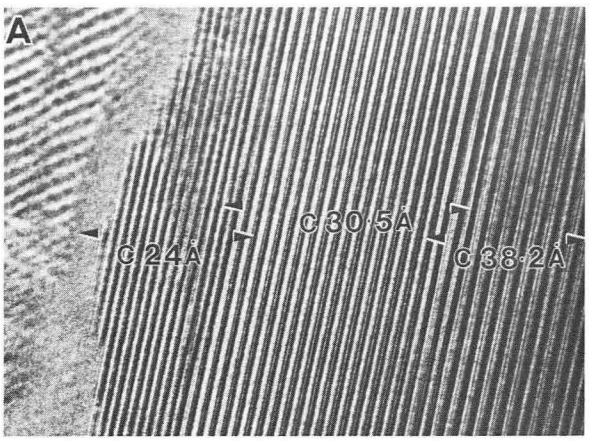
The possibility that very slow cooling through the tetragonal-orthorhombic transition at constant oxygen pressure will allow accommodation of the induced stresses and, thus, reduce the severity of cracking is currently being investigated. Fracture and microfracture during cryogenic cooling and cycling are also of great interest. The effects of texturing, cladding, and noble metal incorporation on thermally-induced acoustic emission will also be studied.

ELECTRON MICROSCOPY

J. Evans, R. Gronsky, G. Thomas, J. Washburn

Electron microscopy of the high-T_C superconductors is being used to investigate grain boundaries, twin boundaries and various other defect structures. Of particular interest are the nature of bonding arrangements and deviations from stoichometry which occur at grain boundaries, since the ability of the high-T_C compounds (in polycrystalline form) to carry electrical current is strongly limited at present by unknown features of grain boundaries. The state-of-the-art facilities of the National Center for Electron Microscopy, including the Atomic Resolution Microscope, are extensively utilized in this research.

Grain boundary engineering (doping with PbO) has been demonstrated to result in higher T_C for zero resistance in Bi-Ca-Sr-Cu-O superconductors (Thomas group). This work is a collaboration with S.M. Green and H.L. Luo at the University of California at San Diego. It is difficult to synthesize the 2223 phase of the Bi-Ca-Sr-Cu-O system in pure form. Detailed microstructural analysis, using advanced transmission electron microscopy techniques, has shown that while most of the material is a single phase, a lower T_C polytypoid $Bi_2Sr_2CaCu_2O_y$, (or $Bi_2Sr_2Ca_2CuO_y$) forms near the grain boundaries. Further, a direct correlation was found between the periodicity in the c-direction (polytypoids) and the T_C (Figure 11A). The material near the grain boundaries has structures of spacings



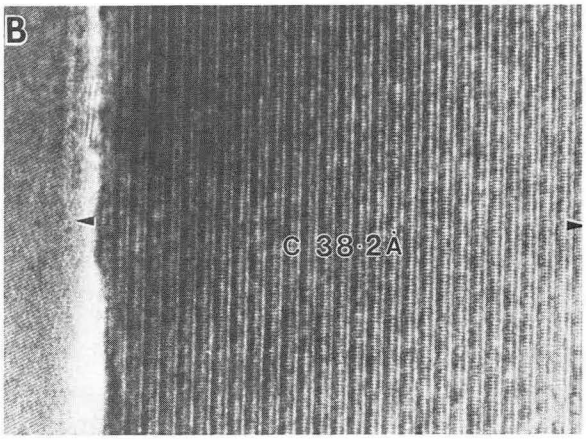
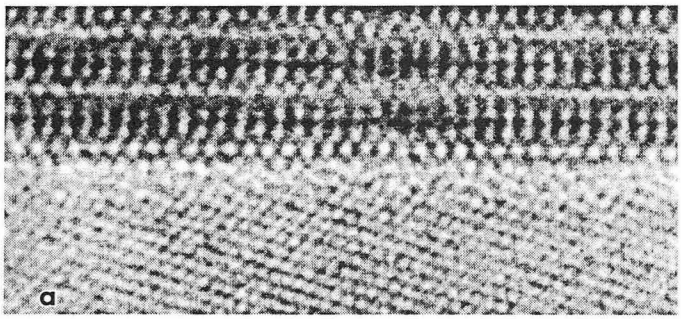


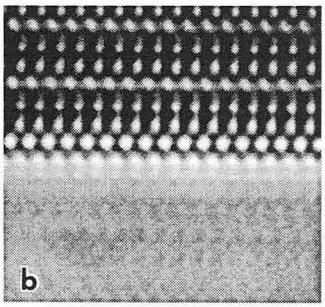
Figure 11A
High resolution lattice fringe electron micrograph of an unleaded sample showing the decrease in c-parameter close to the grain boundary. The 24 Å spacing polytypoid has a T_C of 20 K, the 30.5 Å polytypoid a T_C of 75 K, and the 38.2 Å polytypoid a T_C of 110 K.

Figure 11B
High resolution lattice fringe image from a leaded sample showing the uniform c-parameter of 38.2 Å up to the grain boundary.

c=24Å (T_C=20K) and c=30.5Å (T_C=75K) while that in the matrix has spacing c=38.2Å (T_C=110K). (This structural effect also occurs in other ceramics, e.g., sialons.) The grain boundary area is therefore not superconducting, due to the lower T_C polytypoid. Achievement of more uniform, higher T_C material requires therefore, that these structural compositional gradients be eliminated. It was found that this could be achieved using controlled additions of PbO to the ceramic. This addition leads to the formation of a low-melting eutectic which enables densification and homogenization of the composition of the superconducting phase (Figure 11B). Consequently, the temperature for zero resistance was increased from 75 to 104 K.

High resolution electron microscopy (HREM) studies of grain boundaries and fractured surfaces in both the tetragonal and orthorhombic phases of dense (> 90%) $YBa_2Cu_3O_{7-\delta}$ and tetragonal $LaBaCaCu_3O_{7-\delta}$ have been conducted. Grain boundaries in polycrystalline $YBa_2Cu_3O_{7-\delta}$ are found to be frequently parallel to a (001) plane of one of the adjacent grains, with a structure similar to that of the (001) surface of fractured $YBa_2Cu_3O_{7-\delta}$. Matching of experimental and calculated images shows the outermost surface layer in this compound is a deformed BaO layer (Figure 12) (Gronsky). Both grain boundaries and fractured surfaces in $LaBaCaCu_3O_{7-\delta}$ show no such tendency for preferential orientation of the interface plane. Results indicate that the low critical currents observed in sintered materials can be caused by textured grain growth in combination with the atomic structure of the grain boundary plane, and the intercalation of off-stoichiometric species near the grain boundary.





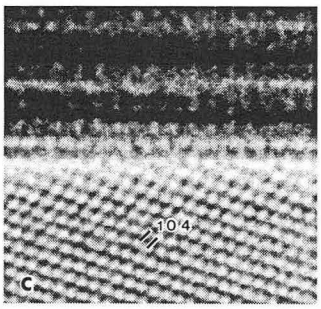


Figure 12
(a) Atomic-resolution micrograph of a grain boundary in YBCO, boundary plane parallel to (001) of the upper grain. (b) Processed version of the upper grain. (c) Processed version of the lower grain. Comparisons with calculated images reveal that the upper grain terminates on a BaO_x layer, leaving a partial unit cell at the grain boundary, which may act as an insulating layer.

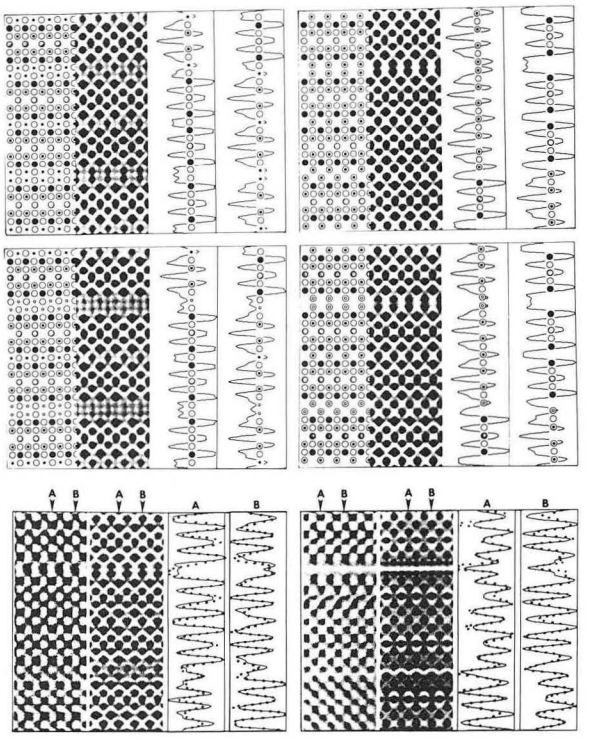


Figure 13
Comparisons of the atomic structure of the double CuO layer defect when viewed along (100) (left column) and (010) (right column) directions. The top two structures are those resulting from an a/2 shift of the crystal across the defect plane and the middle two structures from a b/2 shift. In the bottom two blocks, experimental and calculated images are compared. The line-scan intensity profiles are representative of a 0.075 nm wide line through positions A and B indicated in the bottom two blocks. Full lines give calculated data, dotted lines the observed intensity variations in the experimental images. The experimental parameters are: specimen thickness, 2nm; objective aperture 6 nm^{-1}; accelerating voltage, 1000 kV; spherical-aberration coefficient, 2.8 μm; beam-divergence angle, 0.6 mrad.

The structure of $(CuO)_2$ double layers in $YBa_2Cu_3O_{7-\delta}$ was investigated (Gronsky, Thomas). Detailed high-resolution electron-microscopy studies were applied to identify the atomic structure of planar defects formed as a result of exposure to oxygen. The analysis involved computer simulation of images and comparisons with experimental images, evaluated at the atomic level through side-by-side matching of intensity-line scans across image pairs (Figure 13). The best fit between experimental and calculated images was obtained for the model in which Cu-O-Cu-O chains occur in the direction of the displacement required to accommodate the extra CuO layer. This means that a shift along the b axis of the orthorhombic cell will leave the oxygen atoms at their original positions, whereas a shift along the a axis will lead to a rearrangement of the oxygen atoms in both CuO planes, such that the Cu atoms will occupy the originally vacant sites. Only in this way can the planar fourfold coordination of Cu be maintained. A secondary result of this study was that the presence of oxygen in the conduction planes could be detected directly in the images. Differences were observed at the location of oxygen-bearing columns of atoms along the beam direction when the specimen was imaged in a (100) direction as compared to a (010) direction. This was only possible because the performance of the microscope was sufficient to discriminate all cation positions, i.e., Ba, Y, and Cu.

An analysis of twin boundary structure and its effects in $YBa_2Cu_3O_{7-\delta}$ has been performed (Washburn). In this material the superconducting phase has a finely twinned microstructure arising from the solid state phase transformation, tetragonal to orthorhombic, which is associated with oxygen ordering on the basal plane. From neutron diffraction data it was concluded that dO_x/dT, the oxygen uptake as a function of temperature can be considered to be the ordering parameter. A nucleation and growth mechanism and an oxygen depleted twin boundary model were proposed which are consistent with observed oxygen uptake kinetics and with computer simulated and observed high resolution TEM images. Twin boundaries in this material were assumed to have one or more layers containing oxygen vacancies thus reducing the strong Coulomb repulsion between close oxygen ion pairs that would otherwise exist. While the oxygen content within the twin domains approaches the stoichiometric $YBa_2Cu_3O_7$ during the tetragonal to orthorhombic transformation it is thought that in the immediate vicinity of a twin boundary the composition will remain close to $YBa_2Cu_3O_6$. This structure is consistent with a number

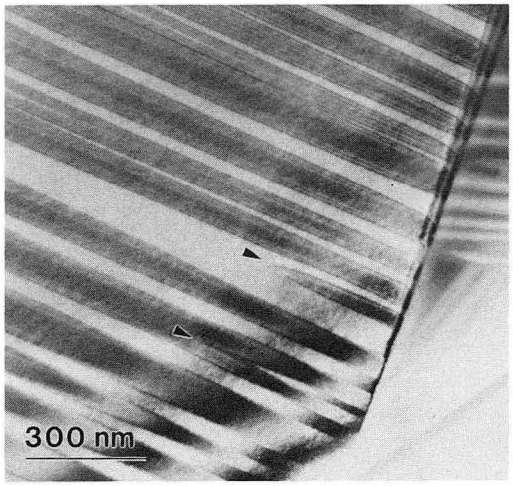


Figure 14
Advancement of two twin regions (tips indicated by arrows) from the grain boundary into an adjacent grain of the superconductor YBa2Cu3O7-d following two hours of annealing at 500°C in flowing oxygen at atmospheric pressure.

of experimental observations and also provides a faster diffusion path for oxygen during propagation of the phase change to interior parts of a grain. It could also explain the fact that the average equilibrium oxygen content only approaches the stoichiometric value 7 for high oxygen partial pressures.

A comparative analysis of structural features of the known high-T_C oxides has been conducted (Washburn), prompted by the fact that the correct explanation of superconductivity in these materials must be able to explain not only why they are superconductors but also why structurally very similar oxides are not. In this work a qualitative phenomenological description is proposed based on the observation that certain features of the bonding are common to all the known high-T_C oxide superconductors which are absent in closely related nonsuperconducting phases such as tetragonal YBCO. Some of the features considered in the model are: multiple charge states of the cations, structure of the boundary layers that separate the CuO_2 layers, oscillation of charge states and the possibility for macroresonance in the structures, and coupling of the resonance of the cation lattice through the boundary or capping layers.

TEM studies on the annealing of YBCO have clarified the formation of low-angle grain boundaries and planar faults (Evans). This research is a collaboration with S.M. Johnson of SRI International (Menlo Park). Annealing in oxygen-rich atmosphere at intermediate temperatures (400-600°C) has been proven necessary to provide the appropriate microstructure of superconducting YBCO. The symmetry of the orthorhombic phase requires that if domains that are (110) and (110) twin related are present within a grain, a distorted region should exist inside the multiple-twinned grain. This distorted region hinders the tetragonal-to-orthorhombic transformation and may account for some retained tetragonal phase inside an otherwise orthorhombic grain. Figure 14 shows the advancement of two twin regions (tips indicated by arrows) from the grain boundary into an adjacent grain of YBCO. A physical model describing the formation of such regions was formulated. Extended annealing at intermediate temperatures apparently leads to the formation of planar faults in off-stoichiometric samples. Transmission electron microscope image contrast and energy-dispersive x-ray analyses of highly defective regions suggested that these defects are extra CuO_x (x=1,2) layers that result from the slight copper enrichment in the $YBa_2Cu_3O_{7-\delta}$ used here. These extra layers tend to form near grain boundaries or free surfaces, where oxygen is readily available.

A major multi-laboratory technology assessment was performed in 1988, "Assessment of Energy Productivity Applications of High-Temperature Superconductivity." This study, funded by Conservation and Renewable Energy at DOE and by the Electric Power Research Institute, included analyses of various technology areas: motors, transportation, materials production, separations technology, electromagnetic pumping, magnetic heat pumping, materials fabrication, and power electronics. LBL's role in the Assessment was to participate on the management team for the study and to perform analyses of fundamental processes and emerging materials properties (Berdahl). An illustrative example of the analysis performed by LBL follows.

Magnetic pressure provides an important illustrative example of how physical principles constrain technology development. Most electrical applications of superconductivity utilize electromagnets. The design of any electromagnet requires that provision be made for structural support to contain the magnetic field. For an ordinary iron-core electromagnet with copper windings, with a field of 1 tesla, this pressure is only 400 kPa (60 psi). However, this pressure is proportional to the square of the field, so that for a high-field superconducting solenoid, containment of the magnetic pressure is a major problem. At 20 tesla, the record for a (very low temperature) superconducting solenoid, the pressure is larger than that at the bottom of the ocean, as illustrated in Figure 15. In principle, magnets with field strengths exceeding 100 tesla are possible with the high-T_c superconductors, due to the very large values of the upper critical H_{c2}. However, Figure 15 makes it clear that present-day materials are not strong enough to support the resulting magnetic pressure.

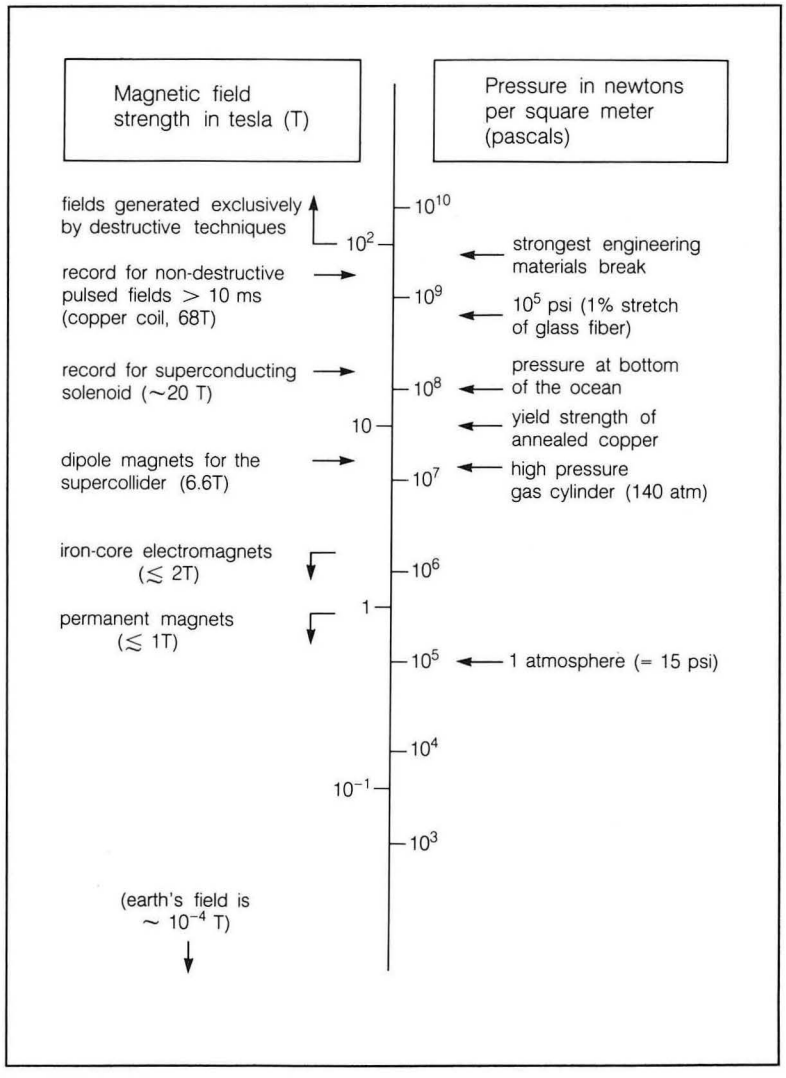


Figure 15
Illustration of the pressure of a magnetic field as a function of field strength.

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INDUSTRY INTERACTIONS

Technology Transfer

- A patent application was filed for the aluminum cladding of high-temperature superconductors by thermocompression bonding.
- A day of introductory reviews on thin-film superconductors was presented at the conference on the Science and Technology of Thin-Film Superconductors (Colorado Springs).

Research Contracts

- The Electric Power Research Institute supports much of the Ceramic Processing project research on improved superconducting ceramics for high current applications.

Industrial Collaborations

- H. Morawitz of IBM, Almaden collaborated with V. Kresin on an explanation of the observed high-superconducting temperatures which, in their view, is due to the exchange of both phonons and plasmons.
- A. Stacy collaborated with R. Fleming of Charles Evans and Associates and D. Krillov and D. Hodul of Varian Associates, in a detailed study of the effect of ^{18}O substitution in $YBa_2Cu_3O_7$.
- R. Gay of Rockwell International is collaborating with R. Russo on the fabrication of Tl-compound films by laser ablation.
- J. Clarke and P. Richards are collaborating with the new corporation Conductus to commercialize electronic devices utilizing high-T_c thin films.
- S.M. Johnson of SRI International collaborated with J. Evans on the TEM studies of the annealing of YBCO.
- H. Rosen of IBM, Almaden is collaborating with D.E. Morris on Raman spectroscopy of various high-T_c cuprates.

Industrial Fellow

- William Link of Raychem worked with John Clarke's group on the fabrication of thin films.

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Berdahl, P., *Future Applications of the New High-T_c Superconductors*, Fourth Annual Energy Research Conference, Jackson, Mississippi, April, 1988.

Clarke, J., *Small Scale Applications of Superconductivity*, President Reagan's Advisory Group on Superconductivity, New York, New York, April 1988.

Clarke, J., *Impact of High-T_c*, International Superconductor Applications Convention, Los Angeles, CA, February 1988.

Clarke, J., *The Impact of High Temperature Superconductivity on SQUIDs*, 5th International Workshop on Future Electron Devices: Topical Meeting on High-Temperature Superconductivity Electron Devices, Miyagi-Zao, Japan, June 1988.

Clarke, J., *SQUID-Magnetometers*, 1st Topsoe Summer School on Superconductivity, Riso, Roskilde, Denmark, June 1988.

Clarke, J., *High-T_c Superconductivity, SQUIDs and Brains*, Annual Scientific and Dinner Meeting, Gastroenterology Division, University of California at San Francisco, San Francisco, CA, March 1988.

Clarke, J., *The Impact of High-T_c Superconductivity on Superconducting Quantum Interference Devices*, American Physical Society, New Orleans, LA, March 1988.

Clarke, J., *Progress on High Transition Temperature SQUIDs*, International Superconductivity Technology Center, Tokyo, Japan, May 1988.

Clarke, J., *Research and Development of Superconductivity in the U.S.A.*, 25th Anniversary Meeting of the Metal Mining Agency, Tokyo, Japan, May 1988.

Clarke, J., *SQUIDs (Superconducting QUantum Interference Devices)*, Conference on the Science and Technology of Thin-Film Superconductors, Colorado Springs, CO, November 1988.

Cohen, M.L., *High Temperature Superconductivity: Current Theoretical Situation*, Institut de laVie International Conference, "De la Physique Theorique a la Biologie", Versailles, France, 1988.

de Fontaine, D., *Oxygen Ordering in* $YBa_2Cu_3O_x$, IBM Almaden Research Center, San Jose, California, April 1988.

de Fontaine, D., *Vacancy Ordering in Superconductors*, delivered at Materials Science Symposium, John Cahn 60th Birthday Celebration, National Bureau of Standards; and The Naval Research Laboratory, Washington, D.C., January 1988.

de Fontaine, D., *Vacancy Ordering in Superconductors*, Naval Research Laboratory, Washington, D.C., January 1988.

de Fontaine, D., *Order-disorder Transformations in* $YBa_2Cu_3O_z$, June 1988. Delivered in Japan at Fukuoka University; Osaka Unversity; Kyoto University; Nagoya University; Nagoya Institute of Technology; Japanese Committee for Alloy Phase Diagrams; Tohoku University; Hokkaido University; and the Institute for Solid State Physics, Tokyo University.

De Jonghe, L.C., *Superconductor Processing*, Los Alamos, New Mexico, August 1988.

Falicov, L.M., *Superconductivity: Phenomenology*, Topsoe Summer School, Denmark, June 1988. (To Be Published in Atomic Energy Commision Establishment of Denmark.)

Gronsky, R., *High Resolution Electron Microscopy Study of Grain Boundaries in Superconducting* $YBa_2CU_3O_{7-\delta}$, Materials Research Society Spring Meeting, Reno, NV, April 1988.

Gronsky, R., *Structural Properties and Twins*, Panel Discussion, DOE/BES/DMS Information Meeting on High Temperature Superdonductors, Sandia National Laboratories, Albuquerque, NM, January 1988.

Gronsky, R., *Low Temperature Ceramics, High Temperature Superconductors*, American Ceramics Society, Northern California Section Meeting, Hayward CA, March 1988.

Gronsky, R., *Atomic Level Characterization of High Temperature Superconductors: A Tutorial*, American Ceramics Socity, Pacific Coast Regional Meeting, San Francisco, CA, October 1988.

Hetherington, C.J.D., R. Ramesh, M.A. O'Keefe, R. Kilaas, and G. Thomas, *High Resolution Electron Microscopy and Image Simulation Studies of Superconducting Polytypoids in Bi-Ca-Sr-Cu-O Ceramics*, Fall MRS Meeting, Boston, MA, November, 1988.

Khachaturyan, A.G. and J.W. Morris, Jr., *Phase Diagram of the Superconducting Oxide* $YBa_2Cu_3O_{6+\delta}$, University of California at Los Angeles, Los Angeles, CA, February 1988.

Khachaturyan, A.G. and J.W. Morris, Jr., *Phase Equilibrium in* $YBa_2Cu_3O_{7-x}$ *Superconducting Oxides*, Rutgers University, New Jersey, February 1988.

Khachaturyan, A.G. and J.W. Morris, Jr., *On the Phase Diagram and Microstructure of the Superconducting* $YBa_2Cu_3O_{6+\delta}$ *Oxide*, 1988 American Physical Society, New Orleans, LA, March 1988.

Kresin, V., *High-*T_c *Superconductivity*, University of North Carolina, Charlotte, NC, April 1988.

Kresin, V., *Plasmons in Layered Crystals*, University of Maryland, College Park, MD, April 1988.

Kresin, V., *Proximity Effect and High-*T_c, Conference on Applications of Superconductivity, Los Angeles, CA, February 1988.

Kresin, V., *High-*T_c *Superconducting Films*, Gordon Conference on High-T_c, Santa Barbara, CA, January 1988.

Kresin, V., *Normal and Superconducting Properties of the High* T_c *Oxides*, Latin-American Conference on High Temperature Superconductivity, Rio de Janeiro, Brazil, May 1988.

Kresin, V.Z., G. Deutscher, and S.A. Wolf, *Exotic Normal and Superconducting Properties of High T_c Oxides and Small E_f*, Latin-American Conference on High Temperature Superconductivity, Rio de Janeiro, Brazil, May 1988.

Kresin, V.Z. and H. Morawitz, *Phonon-Plasmon Mechanism of High T_c Superconductivity*, Latin-American Conference on High Temperature Superconductivity, Rio de Janeiro, Brazil, May 1988.

Morris, D.E., *Oxygen Diffusion and Isotope Shift in High Temperature Superconductors*, DOE/BES/DMS Information Meeting on High Temperature Superconductors, Sandia National Laboratory, Albuquerque, New Mexico, January 1988.

Morris, Jr., J.W. and A.G. Khachaturyan, *The Structural Properties of $YBa_2Cu_3O_{6+\delta}$*. Presented at Hyundai Heavy Metals, Ulsan, Korea, June 1988; and the MRS International Meeting on Advanced Materials, Tokyo, Japan, June 1988.

Morris, Jr., J.W. and A.G. Khachaturyan, *The Structural Properties of $YBa_2Cu_3O_{6+\delta}$*, Seoul National University, Seoul, Korea, June 1988.

Phillips, N.E., *Specific Heat of High-T_c Superconductors*, CRTBT/CNRS, Grenoble, France, February 1988.

Phillips, N.E., *Specific Heat of High-T_c Superconductors and Specific Heat of $YBa_2Cu_3O_7$ Superconductors and Materials and Mechanisms of Superconductivity*, International Conference on High-T_c Superconductivity, Interlaken, Switzerland, February 1988.

Phillips, N.E., *Specific Heat of High-T_c Superconductors*, Conf. Theoretical Foundations of High-T_c Superconductivity, Aspen Inst. Phys., Aspen, Colorado, January 1988.

Ramesh, R., G. Thomas, S.M. Green, Y. Mein, C. Jiang, and H.L. Luo, *Liquid Phase Sintering and Zero Resistence above 100K in Bi-Ca-Sr-Cu-O Superconductors*, Fall MRS Meeting, Boston, MA, November-December 1988.

Ramesh, R., G. Thomas, G. van Tendeloo, S.M. Green, and H.L. Luo, *New Modulated Structure in Pb-Doped Bi-Ca-Sr-Cu-O Superconductor*, Fall MRS Meeting, Boston, MA, November-December 1988. (Appl. Phys. Lett., volume 53, p. 2220, 1988.)

Richards, P.L., *Superconducting Detectors for Infrared and Millimeter Waves*, Conference on Lasers and Electro-Optics (CLEO '88), Anaheim, California, April 1988.

Richards, P.L., *Far Infrared and Submillimeter Devices*, Seminar at the Radio Research Laboratory, Tokyo, Japan, February 1988.

Richards, P.L., *Far Infrared and Submillimeter Devices*, Advanced Telecommunications Research Institute International, Osaka, Japan, February 1988.

Richards, P.L., *Superconducting Detectors for Infrared and Millimeter Waves*, 1988 IEEE MTT-S International Microwave Symposium, New York, New York, May 1988.

Richards, P.L., *Superconducting Detectors for Infrared and Millimeter Waves*, Conference on the Science and Technology of Thin-Film Superconductors, Colorado Springs, CO, November 1988.

Scalapino, D.J., D.R. Clarke, J. Clarke, R.E. Schwall, A.F. Clark, and D.K. Finnemore, *New Research Opportunities in Superconductivity*, Workshop on Problems in Superconductivity, Copper Mountain, Colorado, April 1988. (D.R. Clarke and R.E. Schwall, IBM T.J. Watson Research Center.) (To be published in Cryogenics.)

Weber, E.R., *Microwave-Measurements of High-T_c Superconductors*, Seminar, Technical University of Aachen, Aachen, West Germany, October 1988.

Wille, L.T., A. Berera, and D. de Fontaine, *Phase Diagrams for the Basal Plane of $YBa_2Cu_3O_z$*, American Physical Society Meeting, New Orleans, Louisiana, March 1988.

Zandbergen, H.W., R. Gronsky, and G. Thomas, *High Resolution Electron Microscopy Study of Grain Boundaries in Superconducting $YBa_2Cu_3O_{7-\delta}$*, MRS 1988 Meeting, Reno, NV, April 1988.

Zandbergen, H.W., R. Gronsky, and G. Thomas, *High Resolution Electron Microscopy Study of Grain Boundaries in $YBa_2Cu_3O_{7-\delta}$*, International Conference on High-Temperature Superconductors and Materials and Mechanisms of Superconductivity, Interlaken, Switzerland, February-March 1988. (Physica C, vol. 153, p. 1002, 1988.)

Zandbergen, H.W., R. Gronsky, and G. Thomas, *The Atomic Structure at Grain Boundaries, the Cause of Low Critical Currents in Sintered $YBa_2Cu_3O_{7-\delta}$*, EUREM Congress, York, UK, September 1988. (Inst. Phys. Conf. Ser. vol. 2, p. 257, 1988.)

Zandbergen, H.W. and G. Thomas, *Defect Characterization in Sintered $YBa_2Cu_3O_{7-\delta}$ by HREM*, EUREM Congress, York, UK, September 1988. (Inst. Phys. Conf. Ser., vol. 2, p. 259, 1988.)

Contributed Papers

Fisher, R.A., N.E. Phillips, C. Marcenat, J. Flouquet, P. Haen, P. Lejay, and J.-M. Mignot, *Specific Heat of (Ce,La)Ru_2Si_2 in High Magnetic Fields*, International Conference of Magnetism, Paris, France, July 1988. (To be published in J. de Physique.)

Holland, G.F., S.L. Russek, A.M. Stacy, and J.N. Michaels, "Electrochemical Studies of the Mixed-Conductor System $YBa_2Cu_3O_{7-\delta}$," *Materials Research Society Fall Meeting*, November 1988.

Keuper, T. and L.C. De Jonghe, *Electrodeposition of Aluminum on $YBa_2Cu_3O_x$ Superconductors*, American Ceramic Society, Cincinnati, Ohio, May 1988.

Kresin, V.Z., G. Deustcher, and S.A. Wolf, *Properties of the New High T_c Materials: An Analysis Based on Fermiology*, March 1988 Meeting of the American Physical Society Meeting, New Orleans, LA, March 1988.

Kresin, V.Z. and S.A. Wolf, *Determination of the Geometry of the Fermi Suface and Its Unique Effects on the Properties of the High T_c Oxides Superconductors*, International Conference on High Temperature Superconductors, Materials, and Mechanisms of Superconductivity, Interlaken, Switzerland, March 1988.

Ramesh, R., G. Thomas, S.M. Green, C. Jiang, Y. Mei, and H.L. Luo, *Bi, Ct-Sr-Cu-O Superconductors: The Connectivity Issue*, 1988 Applied Superconductivity Conference, San Francisco, California, August 1988.

Richards, P.L., *Infrared Energy Gap Measurements in BCS CuO*, American Physical Society March Meeting, Special Session on "Triple Digit Superconductivity", New Orleans, Louisiana, March 1988.

Richards, P.L., S. Verghese, T.H. Geballe, and S.R. Spielman, *The High T_c Superconducting Bolometer*, IEEE 1988 Applied Superconductivity Conference, San Francisco, California, August 1988. (Submitted to Proceedings.)

Richardson, T.J. and L.C. De Jonghe, *Aluminum Cladding of Ceramic Superconductor by Thermocompression Bonding*, 41st Pacific Coast Regional Meeting of the American Ceramics Society, San Francisco, California, October 1988.

Rosenthal, P., R.H. Hammond, M.R. Beasley, R. Leoni, Ph. Lerch, and J. Clarke, *Low Frequency Resistance Fluctuations in Films of High Temperature Superconductors*, Applied Superconductivity Conference, San Francisco, California, August 1988. (To be published in a special issue of IEEE Trans. Mag.)

Sherwin, M.S., P.L. Richards, and A. Zettl, *Far Infrared Reflectance of La-(Sr,Ca)-Cu-O: BCS Electrodynamics but Uncertain Energy Gap*, American Physical Society March Meeting, New Orleans, Louisiana, March 1988.

Other LBL Reports (including journal articles submitted or in press)

Berdahl, P., "High Temperature Superconductors: Fundamentals and their Applications," in *Assessment of Energy Applications of High-Temperature Superconductivity*, EPRI. (In Press.)

Berdahl, P. and R.B. Buckius, LBL-25722, *Sputtering of High-Temperature Superconductors: A Bibliography.*

Berera, A. and D. de Fontaine, LBL-25449, "Oxygen-Vacancy Phase Equilibria in $YBa_2Cu_3O_z$ Calculated by the Cluster Variation Method," *Phys. Rev. B1: Condensed Matter.* (In Press.)

Chmelka, B.F., K.T. Mueller, A. Pines, Y. Wu, and J.W. Zwanziger, LBL-26607, "Oxygen-17 NMR in Solids by Dynamic Angle Spinning (DAS) and Double Rotation (DOR)," *Nature.* (Submitted.)

Crommie, M.F., A.Y. Liu, A. Zettl, M.L. Cohen, P. Parilla, M.F. Hundley, W.N. Creager, S. Hoen, and M.S. Sherwin, "c-Axis Stress Dependence of Normal and Superconducting State Properties of $YBa_2Cu_3O_7$," *Phys. Rev. B.* (In Press.)

de Fontaine, D., "Psuedo Binary Phase Diagram of the High-Temperature Superconductor $YBa_2Cu_3O_z$," *Special Lecture at the Fifth Meeting of the Japanese Committee for Alloy Phase Diagrams.* (In Press.)

Falicov, L.M., "Superconductivity, a Brief Introduction to its Phenomenology and Theories," *IEEE J. of Quantum Electronics.* (In Press.)

Ferrari, M.J., M. Johnson, F.C. Wellstood, J. Clarke, P.A. Rosenthal, R.H. Hammond, and M.R. Beasley, LBL-26237, "Flux Noise and Flux Creep in YBCO Thin Films," *IEEE Trans. Mag.* (In Press.)

Fisher, R.A., J.E. Gordon, and N.E. Phillips, "Specific Heat of the High-T_c Oxide Superconductors: A Review," *J. Superconductivity*. (In Press.)

Fisher, R.A., S. Kim, S.E. Lacy, N.E. Phillips, D.E. Morris, A.G. Markelz, J.Y.T. Wei, and D.S. Ginley, "Specific Heat Measurements on Superconducting Bi-Ca-Sr-Cu and Tl-Ca-Ba-Ca Oxides: Absence of a Linear Term in the Specific Heat of Bi-Ca-Sr-Cu Oxides," *Phys. Rev. B*. (Submitted.) (D.S. Ginley, Sandia National Laboratory.)

Goldstein, H.F., L.C. Bourne, P.Y. Yu, and A. Zettl, LBL-25595a, "Pressure Dependence of Superconductivity in Single-Crystal $Bi_2Sr_2CaCu_2O_8$," *Phys. Rev.* (Submitted.)

Gordon, J.E., M.L. Tan, R.A. Fisher, and N.E. Phillips, "Specific Heat Data of High-T_c Superconductors: Lattice and Electronic Contributions," *Solid State Communications*. (Submitted.)

Ham, W.K., S.W. Keller, J.N. Michaels, A.M. Stacy, D. Krillov, D.T. Hodul, and R.H. Fleming, "Partial Substitution of ^{18}O in $YBa_2Cu_3O_7$," *J. Mater. Res.* (Submitted.) (D. Krillov and D.T. Hodul, Varian Research Center; R.H. Fleming, Charles Evans and Assoiciates.)

Jou, C.J., R. Kilaas, and J. Washburn, LBL-25149, "Oxygen Vacancies and twin Boundaries in $YBa_2Cu_3O_{7-\delta}$ Superconductors," *J. Appl. Phys. Lett.* (Submitted.)

Jou, C.J. and J. Washburn, LBL-26065, "Formation of Coherent Twins in High-T_c $YBa_2Cu_3O_{7-\delta}$ Superconductors," *J. Mat. Res.* (In Press.)

Jou, C.J. and J. Washburn, LBL-26078, "A Macro-Resonance-Cell Model for High T_c Oxide Superconductors," *Applied Physics A*. (In Press.)

Jou, C.J. and J. Washburn, LBL-26108, "Twins in High T_c $YBa_2Cu_3O_{7-\delta}$ Superconductors," in *Studies of High Temperature Superconductors*, ed. A.V. Narlikar, Nova Science Publishers, Inc. (In Press.)

Kresin, V.Z., G. Deutscher, and S.A. Wolf, LBL-25483, "Exotic Normal and Superconducting Properties of High T_c Oxides and Small E_f," *Proc. for Latin-American Conference on High Temperature Superconductivity*. (In Press.)

Kresin, V.Z. and H. Morawitz, "Electron Energy Loss Spectroscopy of Layered Systems," *Phys. Rev. B*. (Submitted.)

Kresin, V.Z. and H. Morawitz, LBL-25482, "Phonon-Plasmon Mechanism of High T_c Superconductivity," *Proc. for Latin-American Conference on High Temperature Superconductivity*. (In Press.)

Kresin, V.Z. and H. Morawitz, "Spectroscopy of the Layered High-T_c Superconductors and Their Collective Plasmon Modes - A Pairing Model for Phonon and Plasmon Induced Pairing," *J. Opt. Soc.* (To be published in a special issue.)

Lam, Q.H. and C.D. Jeffries, LBL-26227, "Harmonic Generation and Flux Quantization in Granular Superconductors," *Phys. Rev. B1, Rapid Communications*. (Submitted.)

Liu, M. and L.C. De Jonghe, LBL-25498, "Effect of Geometry and Interfacial Resistance on Current Distribution and Energy Dissipation at Metal/Superconductor Junctions," *J. Mater. Sci.* (Submitted.)

Monteiro, O.R. and S. Johnson, LBL-26442, *TEM Studies on Annealing of $YBa_2Cu_3O_{7-\delta}$*.

Morris, D.E., C.T. Hultgren, A.M. Markelz, J.Y.T. Wei, N.G. Asmar, and J.H. Nickel, LBL-25907, "Large Shifts of T_c in the Bi-Ca-Sr-Cu-O Superconductor by Annealing in High Pressure Oxygen," *Phys. Rev. B*. (In Press.)

Morris, D.E., J.H. Nickel, J.Y.T. Wei, N.G. Asmar, J.S. Scott, U.M. Scheven, C.T. Hultgren, A.M. Markelz, J.E. Post, P.J. Veblen, and D.R. Hazen, LBL-26221, "Eight New High Temperature Superconductors," *Phys. Rev. B*. (In Press.)

Morris, D.E., J.Y.T. Wei, N.G. Asmar, and J.H. Nickel, LBL-26250, *Bulk Synthesis and Thermodynamic Stability of the 1-2-4 and 2-4-7 Superconductors in Oxygen below 30 atm Pressure.*

Morris, Jr., J.W. and A.G. Khachaturyan, LBL-25347, "The Structural Properties of $YBa_2Cu_3O_{6+\delta}$," *Proceedings from the Materials Research Society International Conference on Advanced Materials*. (In Press.)

Ramesh, R., G. Thomas, S.M. Green, Y. Mei, C. Jiang, and H.L. Luo, LBL-25557, "Microstructure of Pb Modified Bi-Ca-Sr-Cu-O Superconductor," *J. Appl. Phys.* (Submitted.)

Ramesh, R., G. Thomas, S. Green, C. Jiang, Y. Mei, M.L. Rudee, and H.L. Luo, LBL-25276, "Polytypoid Structure of Pb Modified Bi-Ca-Sr-Cu-O Superconductor," *Phys. Rev. Lett.* (In Press.)

Richards, P.L., J. Clarke, R. Leoni, Ph. Lerch, S. Verghese, M.R. Beasley, T.H. Geballe, R.H. Hammond, P. Rosenthal, and S.R. Spielman, LBL-26113, "Feasibility of the High T_c Superconducting Bolometer," *Appl. Phys. Lett.* (Submitted.)

Richards, P.L. and Q. Hu, LBL-26169, "Superconducting Components for Infrared and Millimeter Wave Receivers," *Proceedings of the IEEE.* (In Press.)

Richards, P.L., S. Verghese, T.H. Geballe, and S.R. Spielman, LBL-25812, "The High T_c Superconducting Bolometer," *IEEE Trans. Magn. MAG-25.* (In Press.)

Rosenthal, P., R.H. Hammond, M.R. Beasley, R. Leoni, Ph. Lerch, and J. Clarke, LBL-26235, "Low Frequency Resistance Fluctuations in Films of High Temperature Superconductors," *IEEE Trans. Mag.* (To be published in special ASC Conference issue.)

Scalapino, D.J., D.R. Clarke, J. Clarke, R.E. Schwall, A.F. Clark, and D.K. Finnemore, "New Research Opportunities in Superconductivity," *Cryogenics.* (In Press.) (D.R. Clarke, R.E. Schwall, IBM T.J. Watson Research Center.)

Sherwin, M.S., P.L. Richards, and A. Zettl, LBL-24502, "Far Infrared Reflectance of La-(Sr,Ca)-Cu-O: BCS Electrodynamics but Uncertain Energy Gap," *Bull. Am. Phys. Soc.*, vol. 33, p. 451, 1988.

Svensmark, H. and L.M. Falicov, "Ginzburg-Landau Theory of Deformable Superconductors," *Phys. Rev. B.* (In Press.)

Thomas, G., R. Ramesh, R.L. Meng, P.H. Hor, and C.W. Chu, LBL-25405, "Electron Microscopy of a Gd-Ba-Cu-O Superconductor," *J. Mat. Res.* (Submitted.)

Thompson, R.S. and V.Z. Kresin, LBL-25480, "Fluctuation Pairing and Heat Capacity of High T_c Superconductors," *J. Moder. Phys. Lett.* (In Press.)

Zandbergen, H.W., R. Gronsky, and G. Thomas, LBL-25800, "The Atomic Structure at Grain Boundaries, the Cause of Low Critical Currents in Sintered $YBa_2Cu_3O_{7-\delta}$," *Proc. EUREM Congress.* (In Press.)

Zandbergen, H.W., R. Gronsky, and G. Thomas, LBL-25800, "The Atomic Structure of (001) Grain Boundaries and (001) Surfaces in $YBa_2Cu_3O_{7-\delta}$," *J. Microsc. Spectrosc. Electron.* (Submitted.)

Zandbergen, H.W., R. Gronsky, and G. van Tendeloo, LBL-26397, "Atomic Structure of Grain Boudaries in $YBa_2Cu_3O_{7-\delta}$ and $LaBaCaCu_3O_{7-\delta}$," *J. Superconductivity.* (Submitted.)

Zandbergen, H.W., C.J.D. Hetherington, and R. Gronsky, LBL-24614, "Sample Preparation of $YBa_2Cu_3O_{7-\delta}$ for High Resolution Electron Microscopy," *J. Superconductivity.* (Submitted.)

Zandbergen, H.W. and G. Thomas, LBL-24603, "Grain Boundaries in Sintered $YBa_2Cu_3O_{7-\delta}$," *Acta Crystallogr. B.* (Submitted.)

Polymers and Composites

80 . . . . . Anisotropic Polymeric Materials
86 . . . . . Polymer/Substrate Interactions
89 . . . . . Enzymatic Synthesis of Materials

Anisotropic Polymeric Materials
Polymer/Substrate Interactions
Enzymatic Synthesis of Materials

Polymers and Composites Program

The CAM Polymers and Composites Program is concerned with the prediction and control of structure development in high-performance polymers and the synthesis of polymers through the use of enzymes. The program focuses on three areas:

- *ANISOTROPIC POLYMERIC MATERIALS*—the study of structure development in anisotropic materials, particularly liquid crystal polymers.
- *POLYMER/SUBSTRATE INTERACTIONS*—the study of interactions between solid surfaces and polymers in the liquid and glassy states.
- *ENZYMATIC SYNTHESIS OF MATERIALS*—the use of naturally occurring and engineered enzymes in the synthesis of novel materials.

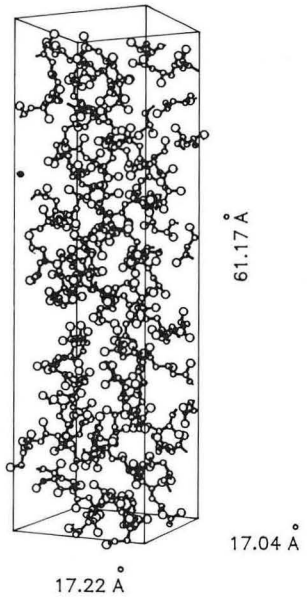
The development of computational tools for the prediction of structure development in complex shaping flows has been a major thrust of the program since its inception and is integrated into both of the first two primary program areas.

ANISOTROPIC POLYMERS, characterized by a "domain" structure in the melt, represent a major area of opportunity for significant advances in high performance polymers. The domains are micron-scale regions of high local order, interconnected by submicron regions within which rapid changes in local orientation occur. The orientation and flow of the molecules in a given domain (domain flow and orientation) have a major effect on the macroscopic properties of the polymer product.

CAM research in the Anisotropic Polymeric Materials project during the past year includes:

- Viscosity and nuclear magnetic resonance spectroscopy measurements demonstrating that the currently accepted theory of polymeric nematics is not applicable to liquid crystal polymers of possible commercial interest, probably because of the inhibition of cooperative chain motions by small crystallites present in the melt of the materials.
- Rheological measurements showing little gap dependence of properties, in contrast to literature reports, but a surprising effect of small amounts of submicron particulate additives.
- Theoretical work showing that regions of rapid in-plane orientation are likely to be unstable in nematic polymers, causing out-of-plane orientation and fully three-dimensional orientation distributions.

The *INTERACTION BETWEEN A POLYMER AND A SOLID SURFACE* (e.g., a die, or a



fiber of a composite) plays a significant role in the development of bulk structure during processing, and, through its effect on polymer conformation, is expected to be important in determining the mechanical properties—particularly failure and fatigue—of composite materials.

CAM research in the Polymer/Substrate Interactions project during the past year includes:

- Atomistic simulations of a free glassy atactic polypropylene surface which predict the internal energy contribution to surface tension and show variations in the density and bond orientation distribution over a 10 Å distance.
- Large-scale simulation of flow in a melt viscometer which showed that the free surface deviates from the profile assumed in conventional rheology. The free surface is believed to be the cause of an artifact leading to apparent gap-dependent viscosities.
- A new code which attempts to deal with the large stresses near a corner of the bounding surface has shown the presence of regions of large stress gradients transverse to the main flow.

ENZYMES CATALYZE REACTIONS with rate enhancements of up to twenty orders of magnitude while exerting exquisite control over the structure of the reaction products. Recent advances in molecular biology, enzymology and bioorganic chemistry now promise the ability to engineer enzymes to catalyze "non-biological" reactions leading to the synthesis of materials with enhanced properties. This new CAM project, supported by the Division of Materials Sciences and also by the Division of Energy Biosciences, seeks to explore ways that enzymes can be engineered to do materials synthesis, understand the reaction conditions that could lead to this synthesis, and examine the properties of the products produced and relate them to their structures. Recent results in the Enzymatic Synthesis of Materials project include:

- Synthesis of several fluorinated sugar monomers and use in the enzymatic polymerization of fluorinated polymers.
- Use of engineered enzymes in the *in vitro* synthesis of polyamides.
- Engineering of a polysaccharide synthesizing enzyme for thermal stability.
- Enzymatic modification of the surface of a doped semiconductor to alter its adhesive characteristics.
- Development of a method to insert unnatural amino acids site-specifically into enzymes to alter their active sites.

ANISOTROPIC POLYMERIC MATERIALS

Liquid crystal polymers contain rigid elements in their backbone which cause them to exist in a highly-oriented ("mesophase") state in the melt. Melt-processible nematic liquid crystalline polymers are currently molded for use as interconnects in electronics applications; their low resistance to flow enables easy filling of small, complex shapes. The rigid polymer backbone, which causes the high degree of local order in the liquid state, is also the cause of other properties of these materials that are considered to be exploitable in high-performance applications: high melting point, high modulus and strength, small in-plane coefficient of thermal expansion, and excellent resistance to chemical solvents.

The high degree of local order has stood in the way of the development of shaping processes which can exploit these other desirable properties, however, because it leads to poor transverse physical properties and poor adhesion (and self-adhesion). Prediction and control of orientation development during processing remain a major outstanding technical problem.

We have studied the rheology of several liquid crystalline polymers, including fully-nematic polymers and polymers which can be multiphasic and can undergo phase transitions. The rheology of these polymer melts is not described by any available theory. Nuclear magnetic resonance (NMR) spectroscopy experiments suggest that cooperative chain motions may be inhibited in the neighborhood of small crystallites present in the melt. The processing of a nematic liquid crystalline polymer introduced a significant gap dependence of viscosity that was not present in the unprocessed resin. The addition of submicron carbon black particles caused a slight viscosity reduction in the larger of two capillaries, but not in the smaller. Those effects are not understood, but may have considerable significance in applications. A theoretical analysis shows that nematic liquids will undergo orientation redistributions when flow induces large orientation gradients, generally leading to a three-dimensional orientation distribution.

Shear-Thinning Behavior

M.M. Denn, D. Kalika, D. Giles

We have obtained consistent viscosity data over more than eight decades of deformation rate, using three rheometers, for the wholly-nematic co-polymer of 80 mole percent p-hydroxybenzoic acid and 20 mole percent poly(ethylene terephthalate) (PET) manufactured by Tennessee Eastman (Figure 1). Power-law behavior is observed over the entire range, with a slope that is close to -0.5. This viscosity curve is inconsistent with any available theory for the rheology of liquid crystalline polymers. It is also inconsistent with the conventional "three-region" description of the viscosity curves of liquid crystalline polymers, but the three-region description is based on a generalization of

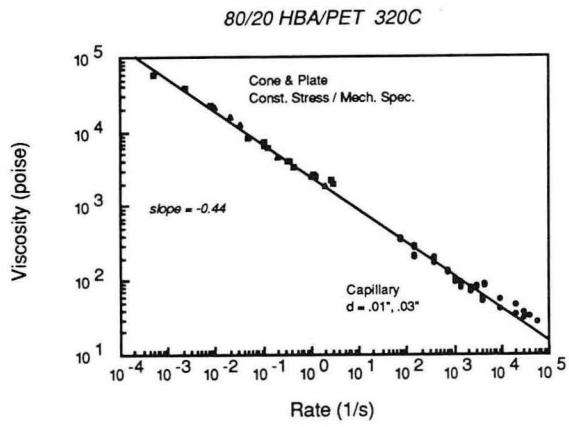


Figure 1
Viscosity of a wholly-nematic thermotropic liquid crystal polymer comprised of 80% p-hydroxybenzoic acid and 20% poly(ethylene terephthalate) (PET), over eight decades of shear rate, using a capillary rheometer, a constant stress rheometer, and a mechanical spectrometer. The power-law behavior over the entire range is inconsistent with any existing theory for liquid crystalline polymers, and is also inconsistent with the "three-region" viscosity functionality that is often described in the literature.

data obtained on liquid crystalline solutions ("lyotropic" systems), and is apparently not applicable to thermotropic (melt-processible) polymers.

NMR Spectroscopy

J. Reimer, K. Amundson

Rheological measurements on both the hydroxybenzoic acid/PET co-polymer and Hoechst-Celanese Vectra (a co-polymer of hydroxynaphthoic acid [HBA] and hydroxybenzoic acid in a 73/27 molar ratio) show evidence of significant growth of crystallites in the melt over times of the order of one-half to two hours. We have reported NMR observations of a separate crystalline phase of hydroxybenzoic acid in the solid state in the HBA/PET co-polymer. These observations agree with diffraction and microscopic work done in other laboratories. NMR relaxation measurements on the HBA/PET co-polyester system above the glass-transition temperature are sensitive to cooperative motion. In our case a quickly-relaxing component of the NMR excited state emanates from regions experiencing cooperative motion, while a slowly-decaying component emanates from regions not experiencing cooperative motion. Based upon our measurement of relative relaxation rate of aromatic and aliphatic protons, it appears that the dominant mechanism of relaxation is thermal fluctuations of the rigid segments of the polymer chain about the local nematic direction of alignment.

The slowing-decaying proton line shape of the component is not crystalline poly(hydroxybenzoic acid) domains, but is instead surprisingly similar to that of the polymer bulk (Figure 2). The inference is that cooperative motion in large fractions (about 15 to 25%) of the polymer bulk above the glass-transition temperature is not inhibited by local chain bonding, but by the inclusion of polymer chains in crystallites. One possible interpretation is that the small crystallites known to exist in the melt inhibit angular fluctuations of rigid polymer segments in the vicinity of the crystallite because of the packing problem of polymer chains leaving a crystal surface without reentry. A second possibility is that cooperative motion is suppressed in tie chains between crystallites. In either case it is clear that the very small fraction of crystallites existing in the melt has a major effect on the chain dynamics, and hence on processing.

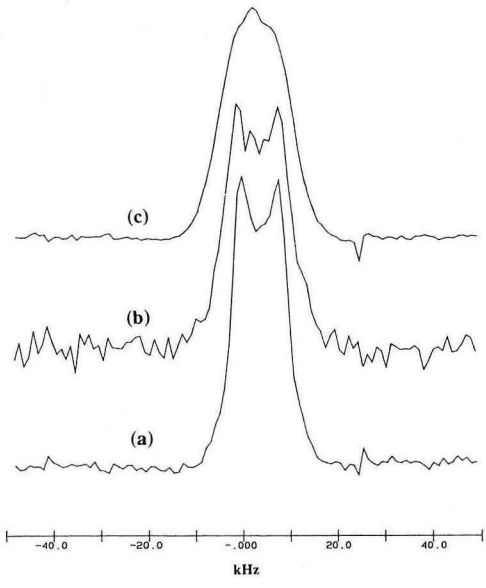


Figure 2
Proton NMR line shape of (a) the nematic HBA/PET copolymer at 240°C; (b) the slowly-relaxing component under the same conditions, comprising about one percent of the total signal; and (c) poly(hydroxybenzoic acid) at 260° C. The line shape of the slowly-relaxing component is nearly identical to that of the bulk, indicating that the suppression of cooperative motion is caused by the existence of small crystallites, but that the slowly-decaying component is not itself made up of a crystalline phase of poly(hydroxybenzoic acid).

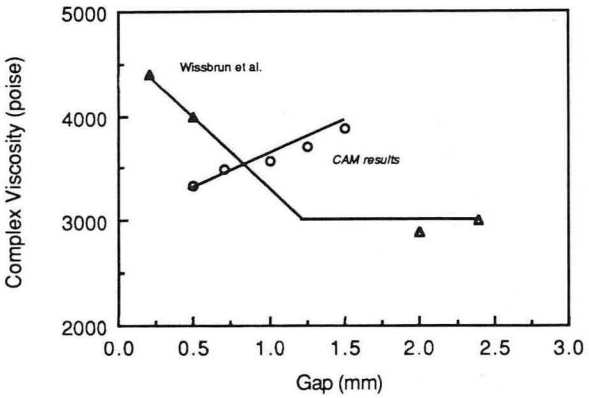


Figure 3
Magnitude of the complex viscosity, as measured in an oscillatory shearing experiment at 1.0 radian/second, as a function of spacing between parallel plates. The data of Wissbrun and coworkers, from a collaborative Hoechst-Celanese/ICI study, indicate an increase in resistance to flow at small gap spacings, and are consistent with their experiments in capillary flow as well. The CAM experiments indicate that there is no increase in flow resistance as the gap spacing is decreased, and there may in fact be some decrease; CAM capillary experiments show little or no gap effect. The polymers used have the same composition, and comparable experimental techniques were used. An increase in flow resistance in small spacings would reduce the effectiveness of these polymers in complex moldings for electronics applications.

Gap Effect

M.M. Denn, D. Kalika

The effect of the dimension of the flow geometry on the measured viscosity of a polymer with the chemical composition of Hoechst-Celanese Vectra was recently described in a joint publication from the Hoechst-Celanese and ICI Laboratories. The work reported that the measured viscosity of the polymer increases dramatically as the gap spacing is decreased to less than about 0.5mm. This result suggests that some of the advantage of using liquid crystalline polymers for the molding of small complex parts for electronics applications could be lost, since the ease of molding would be offset by the dramatically increasing viscosity in small sections of the mold. We have carried out a series of measurements at the same shear rates on the gap spacing dependence of the viscosity of Hoechst-Celanese Vectra A-900. Our capillary viscometer data show essentially no gap dependence over a capillary diameter range in which the Hoechst-Celanese/ICI work reported a three-fold increase in viscosity. Our data between parallel plates show little gap dependence beyond the likely experimental error, and the trend that we observe instead is the opposite of that reported in the Hoechst-Celanese/ICI work (Figure 3). The slight decrease that we observed with decreasing gap would enhance the moldability of these materials. (We reported last year on an anomalous gap dependence in flexible polymers at small gap spacings. We have since established that the apparent gap effect is a consequence of an edge-induced artifact in conventional rheometrical technique, and we are able to obtain consistent measurements over a wide range of gap spacings for rheological standard fluids and flexible polymers by paying special

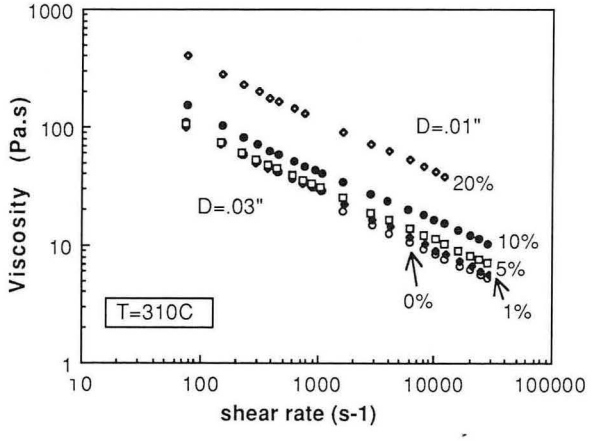


Figure 4
Viscosity of Hoechst-Celanese Vectra (a liquid crystalline polymer melt) filled with carbon black particles. The viscosity of the processed but unfilled (0%) polymer shows a substantial decrease with decreasing capillary diameter, in contrast to unprocessed polymer. The viscosity increases uniformly with carbon black concentration in the smaller (25mm) capillary, but the carbon black has little or no effect up to 5 volume percent in the larger (76mm) capillary. This effect cannot be explained on the basis of any known properties of the polymer or the filler. It is clearly not caused by segregation at the wall.

attention to the polymer/air free surface. The same technique has been used in these experiments, so the small decrease in viscosity with decreasing gap shown in figure 3 is unlikely to be associated with artifacts in the experiment).

We have discussed these experiments with the authors of the published work, and we are confident that consistent experimental techniques have been used. The gross qualitative differences in the two sets of measurements undoubtedly reflect subtle changes in the polymer properties which result from material changes that would not be evident in standard characterization experiments. This is consistent with results reported last year, in which we found that small changes in polymer preparation, and resulting small changes in the phase behavior, could result in qualitative changes in processing behavior for these liquid crystalline polyesters.

Filled Liquid Crystal Polymers

M.M. Denn, L. Nuel

Thermotropic (melt-processible) liquid crystalline polymers are often used with particulate fillers, in part because the fillers appear to improve the isotropy of properties in molded parts. We have studied the rheology of Hoechst-Celanese Vectra A950 with a variety of particulate fillers. The compounding was carried out for us by the Ferro Corporation. We also studied the rheology of unfilled polymer that had been subjected to the same processing history (two passes through a twin-screw extruder).

The unfilled, processed polymer showed a surprising gap dependence in capillary rheometry that was not observed in the unprocessed polymer. The viscosity in a 25mm capillary was less than that in a 76mm capillary, while any difference between the capillaries for the unprocessed polymer was within the probable experimental error. (This gap dependence is the opposite of that reported by the Hoechst-Celanese/ICI group, as described above.) The effect of large (order 10μm) particles, such as calcium carbonate, was as expected in each capillary: the viscosity increased uniformly with increasing particulate concentration. Submicron carbon black particles, however, had a dramatically different effect, perhaps because these particles are on the same size scale as the orientation defects in the polymer (Figure 4).

The viscosity increased uniformly with increasing particulate concentration in the 25mm capillary. In the 76mm capillary, however, there was essentially no change in the viscosity for concentrations between zero and five volume percent; indeed, the viscosity at one volume percent was very slightly below that of the unfilled polymer. At higher concentrations the dependence on filler composition was more usual. We do not have any explanation for this remarkable phenomenon. It is doubtful that it is associated with migration or wall effects, since such phenomena would be expected to have a greater effect in the smaller capillary. The implications for processing are undefined, but could be significant.

Phase Transitions in LCPs

M.M. Denn, R. Shen, P. Yu, D. Kalika

Most thermotropic liquid crystalline polymers exhibit only a nematic phase in the melt; decomposition occurs at temperatures before the transition to isotropic (non-liquid crystalline) behavior. Nematic polymers have local order about a single director; smectic liquid crystals have a layered two-dimensional order. Smectic melts are rare in polymers, but they are of interest in some side-chain systems which are being considered for possible nonlinear optical applications.

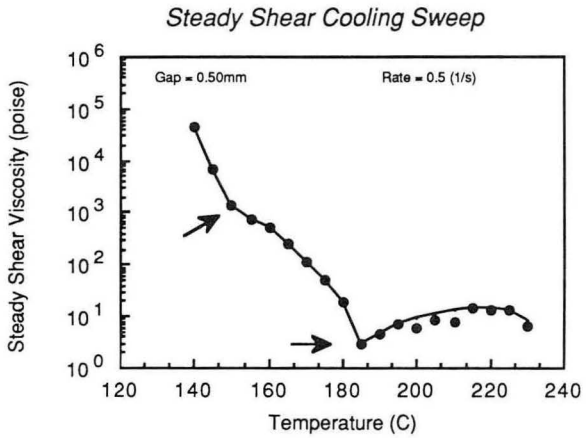


Figure 5
Steady shear viscosity at 0.5 sec-1 as a function of temperature.

We have synthesized sufficient quantities of a polymer consisting of a tri-aromatic rigid segment separated by flexible poly(ethylene oxide) (PEO) units for complete thermal and rheological characterization. This polymer, which was first synthesized by Lenz and co-workers, melts to a smectic liquid crystalline state, and then undergoes subsequent transitions to a nematic liquid crystal and an isotropic melt with increasing temperature. All transitions are at temperatures that are readily accessible, and decomposition is not a problem, so the effect of the phase transitions on rheology can be studied. Our thermal and optical analysis confirms the existence of the several transitions, although our NMR measurements indicate that the nematic region is biphasic, with an isotropic component. The steady shear viscosity at 0.5 sec-1 can be seen as a function of temperature (Figure 5). The arrows indicate differential scanning calorimetry transitions. The transition at about 185 °C is from the nematic to the fully-isotropic melt; the increase in viscosity with increasing temperature in this region is indicative of the increased resistance to flow in the non-aligned liquid. The transition shown at 145 °C is from the smectic to the nematic mesophase. The smectic material shows an unusually high viscosity activation energy, at a level that is far more typical of chemical reaction than of physical rate processes.

Banded Structures

M.M. Denn, A. Rey

Liquid crystalline polymers exhibit a characteristic banded texture during relaxation following shear. A similar banded texture is observed in lyotropic liquid crystalline systems when a sample is oriented in a strong magnetic field, and the field is then rotated 90° in the plane. In both cases the formation and relaxation of bands is likely to be associated with the orientational elasticity in the liquid crystal. We have used the Leslie-Ericksen theory of nematic liquids to analyze the kinetics of formation and decay of banded structures following orientation in a magnetic field. A banded structure is predicted to form because of in-plane rotation of the nematic director. The bands will not decay if the director remains in the plane. We have been able to show analytically, however, that under certain circumstances (which we believe correspond to parameters characteristic of high molar mass nematics) the banded structure will be unstable to perturbations orthogonal to the plane of the director. In that case the banded structure represents a metastable state and will decay as the director experiences thermal fluctuations and moves into a lower-energy "twist wall." The connection to the formation and relaxation of banded structures in shear flow, which is of more interest in processing applications, has not yet been made.

"Molecular composites" of rigid-rod polymers in an amorphous polymer matrix are of considerable interest as a possible means of achieving high performance properties. True molecular dispersion of the rigid molecule can be achieved only if kinetic processes are sufficiently slow to prevent attainment of thermodynamic equilibrium, which will otherwise cause phase separation between the rigid and flexible molecules.

We reported last year on a mathematical model giving the scaling dependence of the rotational diffusivity on rigid-rod length and amorphous polymer concentration. Knowledge of the rotational diffusivity of the rods is essential for understanding and modeling both the isotropic-nematic phase transition kinetics and the rheology of the blends. We have now conducted electro-optic (birefringence relaxation) experiments to measure the rotational diffusion coefficient of rod-like molecules in concentrated amorphous polymer solutions. The experiments were conducted on a well characterized model system consisting of collagen molecules in semi-concentrated (i.e., interacting) PEO solutions. The collagen samples consisted of two species of well-defined molecular lengths to enable testing of both the amorphous polymer concentration and the rod-length dependence of the orientation relaxation times.

The experimental results are seen as normalized birefringence relaxation times (reciprocal of the normalized rotational diffusivity) versus the square of PEO weight fraction (Figure 6). The excellent linear superposition of the data for both molecular species confirms the theoretically-predicted inverse seventh power dependence of the rotational diffusivity on rod length and the inverse second power dependence on amorphous polymer concentration. The coefficient, however, is of order 10^{-4}, while scaling based on "reptation" theories assumes a coefficient of order unity. This finding has obvious implications on the practical preparation and processing of molecular composites, since very fast rotational diffusion (as compared to typical processing time scales) indicates that it may be extremely difficult to obtain dispersed molecular composites. The difficulties may be overcome by introducing molecular "architectures" which will retard diffusion.

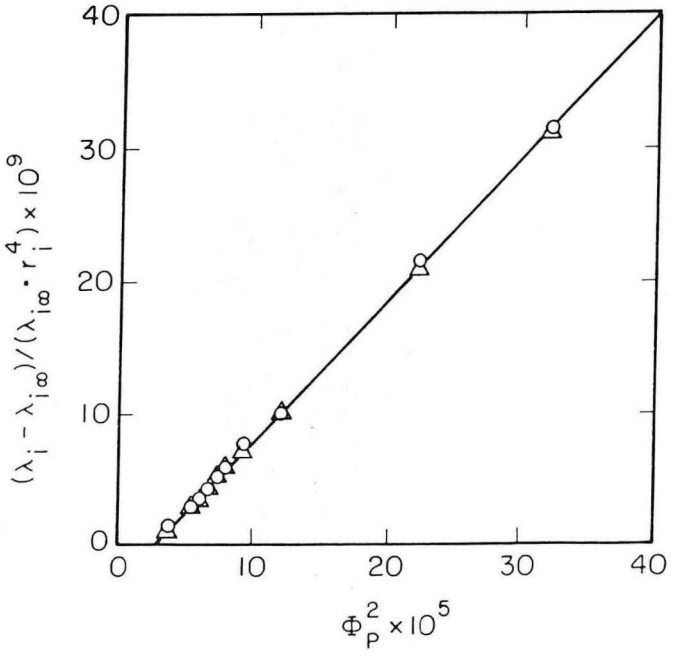


Figure 6
Normalized time of birefringence relaxation for collagen rods in poly(ethylene oxide) solutions as a function of the square of poly(ethylene oxide) weight fraction. The superposition of data for collagen species of different molecular lengths confirms the predictions of the scaling theory: rotational diffusivity is a function of the seventh power of rod length and the inverse second power of amorphous matrix polymer concentration. This measure of polymer mobility establishes the maximum processing time available for preventing phase segregation in the formation of "molecular composites" of rigid molecules in an amorphous matrix.

POLYMER/SUBSTRATE INTERACTIONS

The physical or chemical interaction between a polymer and a non-polymeric surface results in conformational changes of the polymer in the neighborhood of the interface, making it different from that in the bulk. Interaction during melt processing between the melt and the metal shaping surface is known to affect interface adhesion and the onset of flow instabilities, and hence the throughput and bulk material properties. The properties of polymer composites are determined by the nature of the interaction between the matrix and the particulate or fiber filler; the interaction affects not only interface adhesion, but such properties as failure and fatigue as well. The interaction of a polymer with a surface is also of significance in other areas, including tribology and such biomedical applications as implant wear.

Because of the industrial significance of polymer/surface interactions we initiated research in this area in 1987. Our theoretical work has been very successful in moving towards the goal of predicting macroscopic thermodynamic and mechanical behavior at interfaces from the chemical constitution of chains and solid surfaces. Experimental studies using nuclear magnetic resonance spectroscopy, attenuated total reflection Fourier transform infrared spectroscopy, and scanning tunneling microscopy were initiated during the past year with support from the LBL Directors Exploratory Research and Development Fund. The studies using NMR and FTIR spectroscopy are being continued and should produce useful results during the coming year.

Molecular Modeling

D. Theodorou, K. Mansfield

Our theoretical efforts on polymers at interfaces aim at understanding molecular organization in the region between a bulk polymer and a gaseous or solid phase, and at predicting macroscopic thermodynamic and mechanical behavior at interfaces from the chemical constitution of chains and solid surfaces. A long-term goal is to formulate methods for the rational, "molecular engineering" design of multiphase materials containing polymers, such as composites, adhesives, and coatings.

In our initial investigations we have focused on free glassy polymer surfaces (i.e., surfaces exposed to vacuum). We have undertaken detailed atomistic simulations of a very thin film of glassy atactic polypropylene. Our model film is an ensemble of

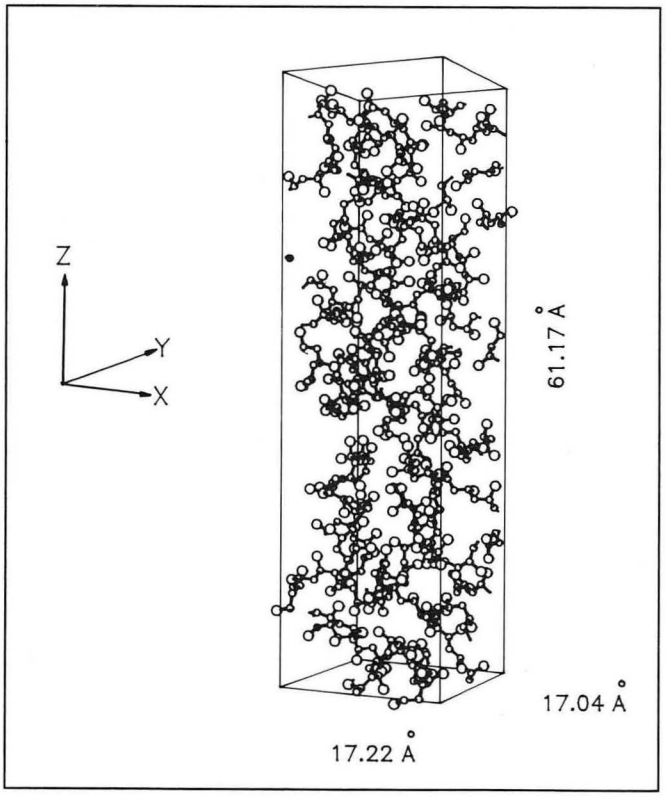


Figure 7
Model microstructure of glassy atactic polypropylene. An ensemble of such microstructures constitutes our atomistic model of a thin film of the polymer at -40°C and 1 atm. The structure is at a local minimum of total potential energy in configuration space. It is characterized by periodic boundary conditions in the x- and y- directions; it can thus be considered as part of a film extending infinitely in these two directions. The top and bottom faces are exposed to vacuum. The box contains segments of three polymer chains, each of molecular weight 3,214.

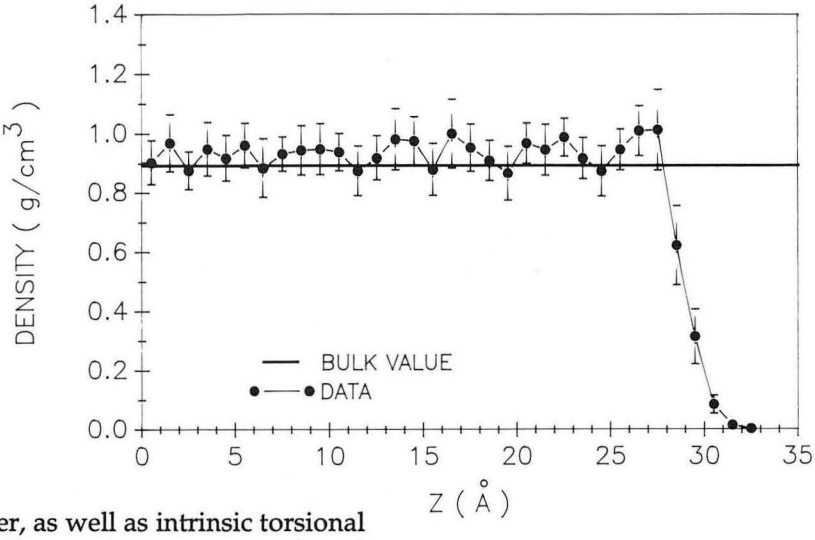


Figure 8
Local mass density profile of the surface of glassy atactic polypropylene, as obtained by averaging over 15 model microstructures. Error bars denote 95% confidence limits. The film midplane lies at z=0. In the middle region the density is indistinguishable from that of the bulk polymer. At the free (vacuum) surface the density drops to zero along a sigmoidal profile, which spans a distance less than 10 Å thick.

microstates, each in detailed mechanical equilibrium (Figure 7). A microstate is generated by a combination of Monte Carlo and potential energy minimization techniques. The total potential energy is calculated by summing Lennard-Jones interactions between all pairs of atoms in the polymer, as well as intrinsic torsional potentials associated with skeletal bonds. Potential parameters are based on Flory's recommendations and are not adjusted in the simulations.

From our ensemble of microscopic model structures and statistical mechanical principles we were able to predict the internal energy contribution to surface tension to within fifteen percent of experimental values. In addition, we have elucidated structure at the level of individual segments and bonds, and at the level of entire chains. As one traverses a free glassy polymer surface, density falls from its bulk value to zero along a sigmoidal profile, which spans a distance of less than 10 Å (Figure 8). There is a weak tendency for skeletal bonds to orient parallel to the surface. An examination of the spatial disposition of the segment clouds of individual chains has revealed that chains tend to lie flat on the surface, with their longest dimensions parallel to it. Perturbations in overall chain orientation persist over a distance from the surface that is roughly equal to two unperturbed radii of gyration.

Scanning Tunneling Microscopy

J.N. Michaels, A. Calahore

Surface properties of carbon fibers are likely to have a major effect on the macroscopic behavior of carbon-fiber/polymer composites, particularly on failure mechanisms. In most applications, surface characteristics are induced by pretreatment of the carbon. Pretreatment methods are typically empirically derived, and little is known at a molecular level about the structural and chemical changes brought about by these procedures. Systematic study of these changes is confounded by the complex morphology, heterogeneity, and the small sample size. It is therefore preferable to use a well-characterized carbon surface, such as that of highly-oriented pyrolytic graphite, as a model substrate. We have explored the use of scanning tunneling microscopy as a means of studying the effect of pretreating well-characterized carbon surfaces in order to understand in detail the changes to the carbon surface and to provide a means for controlled modification.

Three surface modification procedures were investigated: thermal oxidation in air, reactive oxygen-ion etching, and application of a localized electrical pulse between the scanning tunneling microscope tip and the pyrolytic graphite surface. The procedures yielded significantly different surfaces. Thermal oxidation produced large hexagonal pits in the

surface but left large areas of the surface undisturbed. In contrast, reactive ion etching caused no gross defects in the surface, but rather produced a uniform, atomically-rough surface. Application of a voltage pulse produced a single ring-like structure on the surface which was about 6 to 8 Å in diameter. The latter resembled images reported of adsorbates on carbon surfaces which had been prepared in this fashion, and it is likely that those images were of the modified carbon surface itself.

Adhesion

M.M. Denn, T. Hasegawa

We have carried out a series of adhesion "peel" experiments of cast polyethylene films on a variety of metal and metal-oxide substrates. This work was motivated by the observed failure of melt adhesion at high stresses when polyethylene is extruded through dies fabricated of various metals. The critical stress depends on the construction materials of the surface.

Peel rates were found to depend exponentially on applied force; adhesion strength depended on the nature of the material and the extent to which it had been pre-oxidized. A correlation was found between peel strength and the critical stress for "slip-stick" flow in the melt.

LARGE SCALE COMPUTATION

The focus of the CAM computational research is on the use of advanced techniques to predict structure development during shaping in the liquid state. Much of the work involves the development and implementation of state-of-the-art finite-element algorithms, some of which have been implemented on the National Magnetic Fusion Energy Computer Center CRAY-XMP at Lawrence Livermore National Laboratory. Research during the past year focused on two areas: development and testing of a finite-element technique for time-dependent free surface flows, with emphasis on free surface stability, and development and testing of hyperbolic numerical techniques for computing confined viscoelastic flows with stress singularities. The motivation for the first area is the observation that liquid/gas and liquid/liquid interfaces exist in many complex shaping operations, and the flow and flow-induced orientation in the neighborhood of the free surface is a critical factor in determining bulk morphology. Our concern with stress singularities arises from the fact that exceedingly high stresses occur when a polymeric liquid flows near a corner or a lip; numerical resolution of the stress singularities under conditions of processing interest is not possible with currently-available techniques, and the errors propagate throughout the flow. Major progress is required for both of these computational problems if numerical methods are to be extended to the prediction of flow-induced structure in high-performance materials of current interest.

Transient Free-Surface Flows

R. Keunings, R. Shipman

Our research on free-surface flows has resulted in the development of a fully-implicit finite-element code for solving transient free-surface flows of inelastic non-Newtonian fluids. This code has shown significant supercomputer time savings over previous codes for surface tension driven problems, and has been extended to solve three-dimensional axisymmetric problems. We have studied the shape of the free surface in the parallel plate viscometer, which we use for characterizing flexible and liquid

crystal polymers; free-surface effects appear to be the cause of the artifact leading to apparent gap-dependent viscosities for flexible polymers. The code predicts significant changes from the flat profile assumed in analyses for situations with high Reynolds numbers and low rotational Bond numbers (i.e., low surface tension). We have also examined the effect of pressure taps in the stationary plate of the rheometer on the flow. Multiple recirculation zones in the rheometer are induced when cylindrical regions of slip are introduced to simulate the effect of the pressure taps, in qualitative agreement with flow visualization studies reported some years ago by Savins and Metzner.

Hyperbolic Numerical Techniques

R. Keunings, J. Rosenberg

The numerical simulation of viscoelastic flows in confined geometries remains a challenging task, in part because of stress singularities and boundary layers predicted with currently available stress constitutive equations. Our previous work has shown that the hyperbolic character of viscoelastic constitutive models must be taken into account in any numerical scheme aimed at computing flows with high stress gradients. We have compared various streamline-upwind finite-element schemes and the method of characteristics in the numerical integration of viscoelastic constitutive models in a model extrusion flow. Our work has shown that the method of characteristics is vastly superior as far as numerical accuracy and stability are concerned. A general-purpose computer code consisting of decoupled iterations between a standard Galerkin/finite-element solution of the conservation laws and the integration of the viscoelastic constitutive model by means of the method of characteristics has been developed. Accurate results have been obtained at moderate values of the Weissenberg (elasticity) number for a model extrusion flow of dilute polymeric solutions. Significant stress boundary layers transverse to the main flow direction are predicted downstream of the exit section.

ENZYMATIC SYNTHESIS OF MATERIALS

Research in the enzymatic synthesis of materials project is focused on:

- Engineering of enzyme structure and activity to allow the synthesis of materials from novel substrates.
- Design of reaction conditions to allow synthesis of materials using enzymes.
- Structure/function relationships of enzyme-synthesized materials, prediction of properties from structure, design of structure to achieve target properties.

GENE CLONING AND EXPRESSION

J.F. Kirsch, B. Malcolm, J. Petithory

The availability of large amounts of genetically engineered enzymes for reactor synthesis requires the isolation (cloning) of the gene for that enzyme. It is also dependent on the development of an expression system in a "factory" organism that can use that clone to overproduce large quantities of the enzyme. Last year we reported the successful cloning and

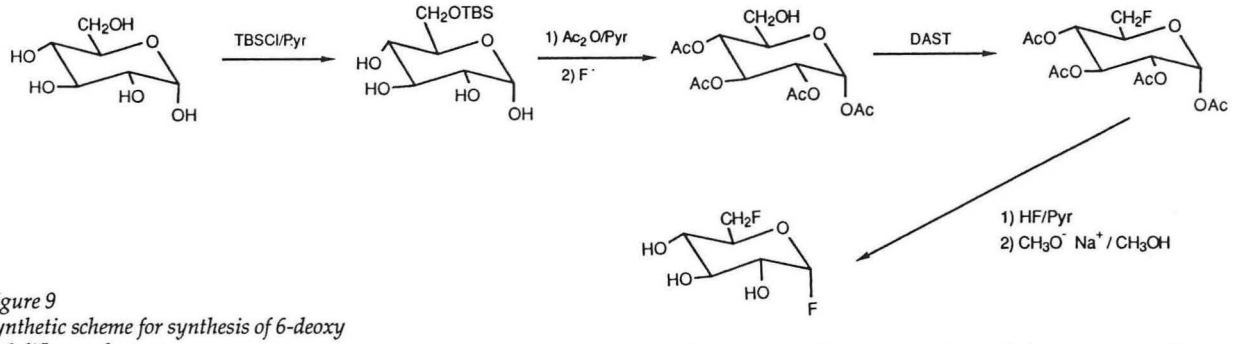


Figure 9
Synthetic scheme for synthesis of 6-deoxy 1, 6 diflouro glucose.

expression of the gene for the enzyme lysozyme, in collaboration with S. Rosenberg from Chiron Corporation, for use in the synthesis of polysaccharide-like polymers. Another enzyme, papain, is of interest because of its ability to synthesize oligopeptides (polyamides) from amino acids. It can bind up to seven monomers, and thus presents the possibility of controlled synthesis of a wide variety of copolymers. Polysomal RNA coding for this enzyme has been successfully isolated from papaya fruit. This RNA will be used to synthesize the DNA clone for the enzyme, which will then be expressed in an appropriate organism to produce sufficient quantities of the enzyme for further study and polyamide synthesis.

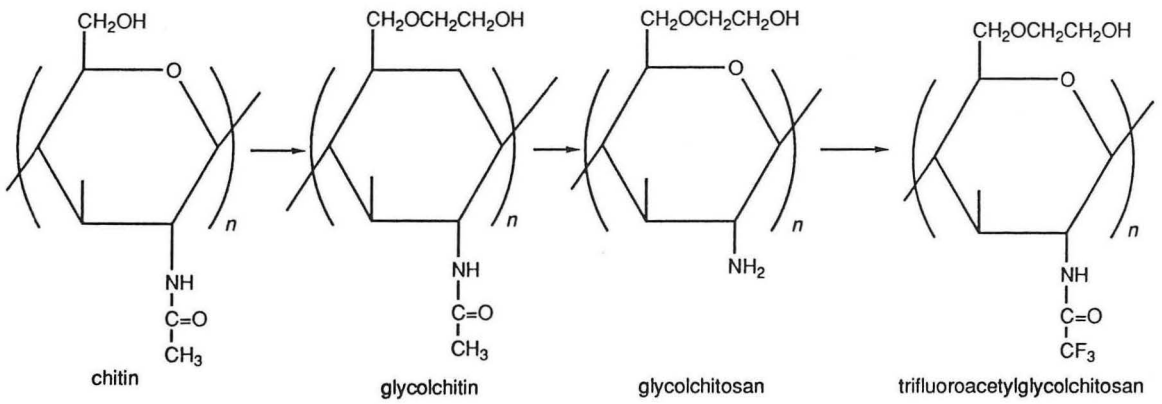
FLUORINATED MONOMER SYNTHESIS

M. Bednarski, D. Weitz, J.F. Kirsch, S. Edwards, A. Michiels, L. Oehler

Synthesis of novel polymers requires the synthesis of novel monomeric units for those polymers. This can be accomplished either enzymatically or chemically or through a combination of the two. Work in this area is now focused on fluorinated sugar derivatives, although some of the synthetic routes designed are adaptable for the synthesis of acetylated or sulfonated derivatives. Acetylenic and olefinic derivatives of α-amino acids are also being synthesized.

Fluorinated sugars are of particular interest because the one-position fluorine has been shown to act as a good leaving group in several polymerization reactions and these 1-fluoro compounds are relatively easy to derivatize further as monomers for the synthesis of novel polymers. The syntheses of the monomers glucose-1-fluoride, 1-fluoro-2-deoxy glucose and glucose 1,2 difluoride have been achieved through chemoenzymatic routes. Glucose, for example, was differentially protected at the C_6 hydroxyl group, flourinated using diethylaminosulfur triflouride and pyridium-hydrofluoride and deprotected to give a 6-

Figure 10
Synthesis of water soluble flourinated chitin derivatives.



deoxy-1,6-difluoroglucose (Figure 9). (M. Bednarski and D. Weitz)

A major technical barrier to the employment of the enzyme lysozyme in the synthesis of novel polymers is the water insolubility of its substrates, for example, short oligomers of chitin (poly N-acetyl glucosamine). Chitin can however be derivatized to a water soluble form by treatment with ethylene chlorohydrin to give "glycol chitin." This derivative has been deacetylated with strong base to yield a new compound "glycol chitosan." This material is soluble in water and can also serve as a starting point for the synthesis of a variety of potentially interesting chitin derivatives. Its exposed amino groups can, for example, be reacylated with a variety of agents to generate novel water soluble carbohydrate oligomers such as trifluroglycolchitosan which should be substrates for lysozyme in the synthesis of new fluorinated polymers (Figure 10). (J.F. Kirsch and S. Edwards)

ENZYMATIC POLYMER SYNTHESIS

Enzymatic synthesis of both polysaccharide and polyamide polymers has been achieved as has the synthesis of a fluorinated polysaccharide. A major problem that needed to be overcome in both types of reactions is the fact that the enzyme catalyzed degradative reaction competes strongly with the enzyme catalyzed synthetic reaction.

Polymers Synthesized Through the Use of a Multi-Enzyme System

M. Bednarski, D. Weitz

Glycogen phosphorylase is an enzyme which catalyzes the reversible polymerization of glucose-1-phosphate to form α1->4 linked glucose polymers

$$(\text{glucose})_n + \text{glucose-1-P} \rightarrow (\text{glucose})_{n+1} + P_i$$

The equilibrium constant for the addition of glucose is however, only 3.6. As a result, the second reaction product, inorganic phosphate, quickly reaches a high enough level to increase the rate of the reverse, degradative reaction, severely limiting the production of polymer. Therefore, to synthesize high molecular weight materials, methodology needed to be developed to drive the equilibrium towards the synthesis of polymers. One solution to this problem was found to be the use of a dual enzyme system.

The enzyme sucrose phosphorylase consumes inorganic phosphate in its splitting of sucrose to its constituent sugars fructose and glucose (in the form of glucose phosphate).

$$P_i + \text{sucrose} \rightarrow \text{glucose-1-P} + \text{fructose}$$

The addition of sucrose phosphorylase to the glycogen phosphorylase system consumes the phosphate as it is produced in that reaction and as a result, significantly affects the equilibrium, pulling it towards the synthesis of polymer.

Synthesis of Polyamides In Organic Solvents

C.H. Wong, J.A. Bibbs, H. Blanch, D. Clark, M. Fernandez

The amidase activity of virtually all serine and cysteine proteases can be selectively abolished by addition of an appropriate amount of a water-miscible organic solvent such as dimethyl formamide. Under these conditions, the enzyme will not degrade polyamides. Esterase activity is re-

tained however, and the enzyme can be used to link amino acid or peptide esters in long chain, stable polymers. Using this technique, homopolymers of methionine containing in excess of 50 residues were prepared using the enzyme subtilisin and the monomer methionine methyl ester. The reaction was carried out in a mixture of water and dimethylformide (1:1 to 1:5). (C.H. Wong, J.A. Bibbs)

The amidase activity of papain in water-dimethyl formamide (DMF) mixtures also decreases as the concentration of DMF is increased, going to zero at 60% DMF. Polymerization of the amino acids phenylalanine, leucine and methionine was achieved. NMR and mass spectroscopy data suggest that polymers of at least 10 monomers were synthesized. (H. Blanch, D. Clark, M. Fernandez)

Enzyme Engineering for Polymer Synthesis

C.H. Wong, J. Bibbs

Another strategy that may be effective in favoring polymer synthesis over degradation involves the modification of one or more of the essential groups in the enzyme active site in a manner that destroys degradative activity. An initial effort toward this goal was the selective methylation of the enzyme at one of the ring nitrogens of the histidine residue in the active site, subtilisin. This resulted in the loss of amidase activity. The enzyme retained esterase activity and thus was still able to polymerize amino acid esters to polyamides but it could not degrade those polymers.

Synthesis of a Fluorinated Polysaccharide Polymer

M. Bednarski, L. Oehler

Sucrose phosphorylase has been shown to accept glucose-1-fluoride as a substrate for catalysis at a rate similar to that for sucrose, its natural substrate. (As mentioned above, the use of glucose-1-fluoride has significant advantages over the use of sucrose in that this monomer is far easier to derivatize to produce unusual substrates for the enzyme.) The dual enzyme system described above was successfully used to polymerize glucose-1,6 difluoride to produce a uniform 6-fluoro polysaccharide polymer (Figure 11). Scale-up of the procedure is in progress to produce enough material for materials properties characterization and evaluation.

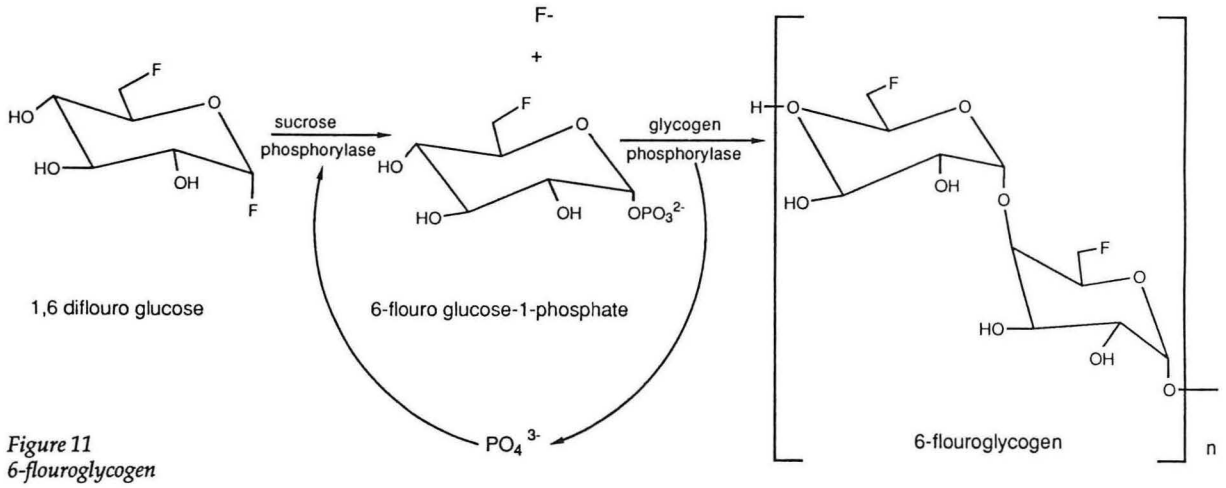


Figure 11
6-flouroglycogen

ALTERATION OF THE SUBSTRATE SPECIFICITY OF ENZYMES

One of the advantages of the use of enzymes in materials synthesis, the enzyme's specificity for a particular substrate, is, at the same time a disadvantage. If a particular target material requires a reaction with a nonnatural substrate, it is likely that no naturally occurring enzyme will be able to extend its specificity to catalyze that reaction. For this reason, a variety of methods are being applied or developed to alter enzyme specificity in defined, rational ways. Success here will allow reactions with novel substrates and would be expected to produce interesting materials.

Site-Directed Mutagenesis

Site-directed mutagenesis involves the substitution of one natural amino acid for another at a predetermined position in an enzyme's linear chain of amino acids. Substitutions using this method could alter the shape, charge localization, or functionality of an enzyme's active site and thus change its substrate specificity. Work was reported last year on the site-directed mutagenesis of the enzyme lysozyme. Catalytic amino acids were replaced by residues that were chemically inactive, and other active site residues that bound the substrate were altered. This allowed a detailed study of enzyme-substrate binding and should lead to a rational path for enzyme alteration for the binding of unusual monomers.

Semi-Synthetic Enzymes

P. Schultz, C. Noren

Site-directed mutagenesis is however restricted to the use of the 20 naturally occurring amino acids, limiting the fine tuning of geometry and functionality. This problem has been overcome by the development of a technique that allows the site-specific substitution of virtually any alpha amino acid that can be synthesized in the laboratory. This provides a vastly increased potential for specific modification of enzymes to tailor their activities for desired reactions and is being pursued with enzymes of interest in materials sysnthesis.

Catalytic Antibodies

P. Schultz

Substitution of nonnatural amino acids, although far less restrictive than site-directed mutagenesis, does share a limitation with it; the field of protein engineering has not yet progressed to the point where the effect of any given alteration in amino acid sequence can be accurately predicted. This limitation has been attacked through the synthesis of "catalytic antibodies." With the advent of technologies to produce monoclonal antibodies, it has become possible to generate proteins that selectively recognize virtually any given target substrate. Since a major aspect of

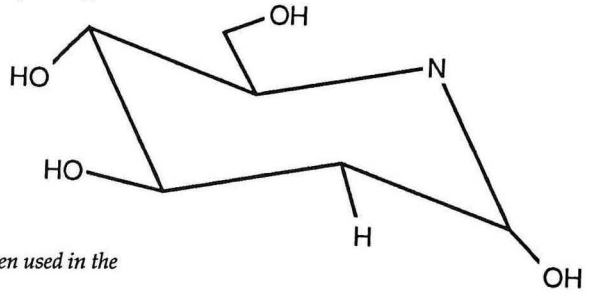


Figure 12
2-deoxynojirimycin, a transition state analog for monosaccharides, that has been used in the selection of catalytic antibodies for polysaccharide synthesis.

enzyme catalysis is the lowering of the activation energy of a reaction, the selection of antibody combining sites on the basis of their binding to a transition state analog of the reaction of interest can be a general route to the design of enzyme-like catalysts with tailored specificity. This ability to design catalysts with predetermined specificities for reactions such as the selective cleavage, condensation, or modification of natural and synthetic polymers is being applied to the development of a catalytic antibody capable of the catalysis of the glycosidic bonds between sugars in polysaccharides. The antibody was raised against deoxynojirimycin derivatives and it and related catalytic antibodies are being studied for polymer synthesis (Figure 12). The development of antibodies capable of the synthesis of a number of "non-biological" polymers is also in progress.

Thermostability of Enzymes

J.F. Kirsch, B. Malcolm

Since reaction rates rise steeply with increased temperature, the stabilization of enzymes so that they can function effectively at elevated temperatures will be an important advantage in bioreactors. Site-directed mutagenesis technology offers the opportunity to deal with this problem by explicit protein design, even though much remains to be learned about the relationship between protein structure and thermostability.

In collaboration with evolutionary biochemist Allan Wilson at Berkeley, it was noticed that among the tens of species of birds examined, a particular set of three amino acids at the base of the active site of lysozyme is found in only two forms: TIS—threonine, isoleucine, serine; or SVT—serine, valine, threonine. No intermediate forms with one or two of these amino acids in common are known to occur naturally. Since the probability of a simultaneous triple mutation (from TIS to SVT) is infinitesimal, at least two intermediates had to have occurred in evolutionary history but then disappeared. Lysozymes were then synthesized with these intermediate forms using site-directed mutagenesis and examined their thermostability.

All six enzymes were found to be equally active catalytically but their transition temperatures for thermodenaturation were found to vary considerably and to be approximately linearly related to the sum of the side chain volumes of the amino acids (Figure 13). (Crystal structures of these mutant proteins are being determined in collaboration with Brian Matthews, University of Oregon.)

What may be truly important from the point of view of enzyme design are the very large differences in thermostability realized at high tempera-

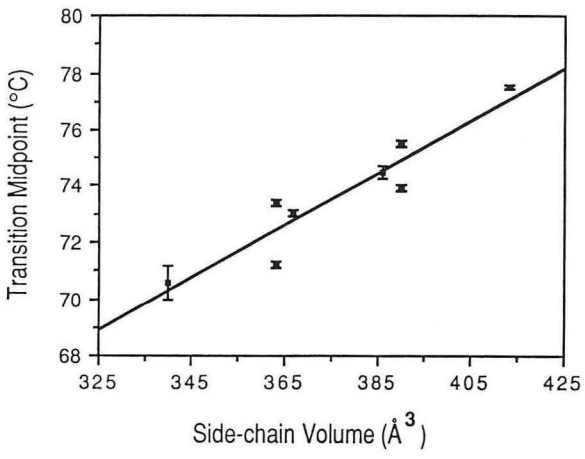


Figure 13
The correlation of thermal denaturation temperature with the sum of the side chain volumes of the amino acids in posititons 40, 55, and 91 of naturally occurring and genetically engineered lysozyme variants.

tures by the extremely small perturbations in structure seen from one mutant to another. The observed difference in T_m between the most stable and least stable mutants, which differ by just two methyl and one methylene group, is 6.9 C, and the rate constant for denaturation at 80°, a desirable bioreactor temperature, ranges from 9 hours to 24 hours. The conclusion is that substantial increases in thermostability can be engineered once the structural basis of this stability is well understood.

ENZYMATIC MODIFICATION OF METAL OR SEMICONDUCTOR SURFACES

M. Bednarski, M. Mastandrea

The ability to specifically modify the interfacial properties of materials without disrupting their existing structures is an important goal in materials science. Enzyme specificity and activity at room temperature and pressure are ideal characteristics of a system to achieve such modifications. The enzyme phosphorylase has been shown to be capable of grafting polymers onto a variety of primers and this methodology has been applied to the enzymatic grafting of polymers onto semiconductor surfaces to allow the exploration of applications of these methods to electronic and bio-compatible materials.

Chemo-enzymatic modification of the surface of a boron doped silicon wafer has been achieved. Alteration of the hydrophobic/hydrophilic nature of the surface of the wafer, through the attachment of lipid groups, altered the nonspecific binding of a population of bacterial cells which were used as a model for adhesion. Enzymatic addition of sugars allowed control of specific binding, depending on the presence or absence of receptors on the bacterial cell surface. Although microorganism binding to metal is used here as a model system, it is, in fact an important issue in the fouling of ship hulls. The ability to control the surface of a semiconductor suggests applications in sensors and also in promoting binding of other materials such as gold that would not otherwise adhere (Figure 14).

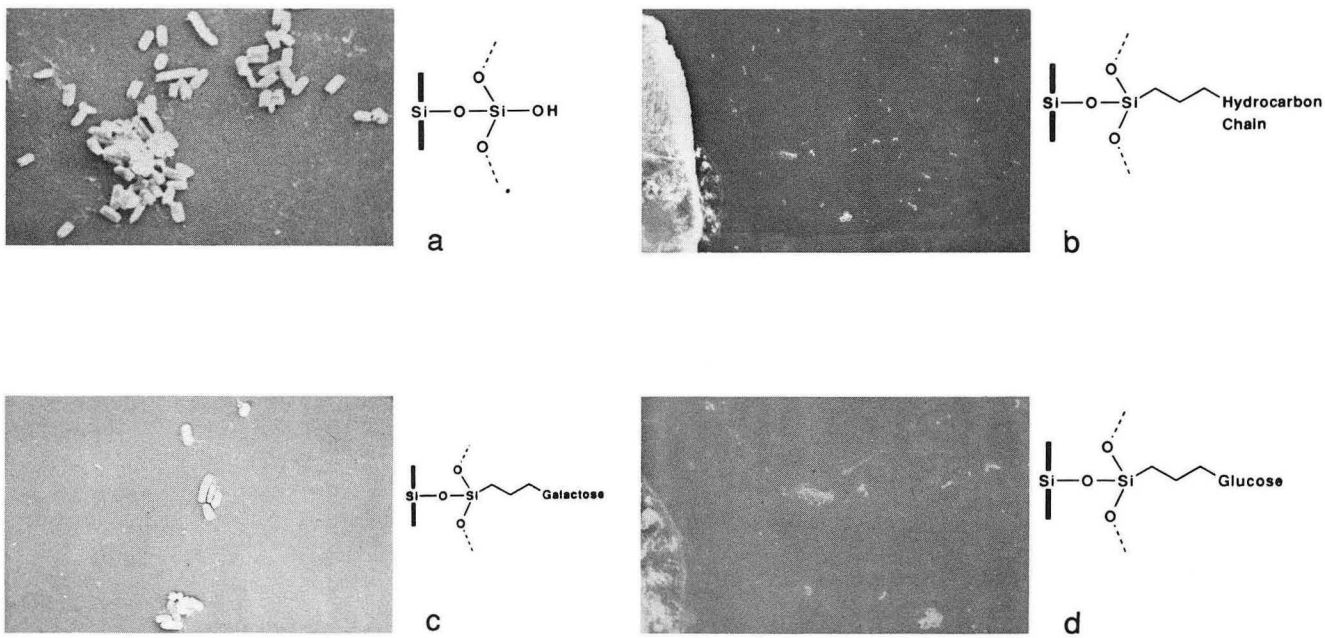
Figure 14

a.) The large number of free-OH groups on the surface of a silicon wafer creates a hydrophillic surface that allows non-specific binding of bacterial cells.

b.) Attachment of nonpolar hydrocarbon chains makes the surface hydrophobic; bacterial cells are unable to adhere.

c.) Enzymatic attachment of the sugar galactose (or mannose) to the hydrocarbon chain presents a surface to which the bacteria, with specific galactose (or mannose) binding sites (receptors), can adhere.

d.) Enzymatic attachment of the similar sugar glucose eliminates binding since the bacteria have no glucose receptors.



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AWARDS

- Alexis T. Bell was named B.F. Dodge Lecturer, Department of Chemical Engineering at Yale University.
- Alexis T. Bell was elected Fellow by the American Association for the Advancement of Science.
- Mark Bednarski was named an American Cancer Society Young Faculty Fellow.
- Mark Mastandrea was awarded an NSF Predoctoral Fellowship.
- Jeffrey Reimer was awarded a Camille and Henry Dreyfus Foundation Teacher-Scholar grant.
- Peter Schultz was awarded the National Science Foundation Alan T. Waterman Award.
- Doros Theodorou received the National Science Foundation Presidental Young Investigator Award.

INDUSTRY INTERACTIONS

Research Contracts

- The Union Carbide Corporation gave support to the polymer research on Physico-Chemical Aspects of Flowing Polymer Melt/Metal Interfaces.
- The Cargill Corporation is working with the Enzymatic Synthesis of Materials project on the study of new carbohydrate-based polymers.

Advisory Board

James Economy (Chairman)	IBM Research Laboratory
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Industrial Collaborations

- Patrick Gruber of the Cargill Corporation is collaborating with the Enzymatic Synthesis of Materials project on the development of a new class of carbohydrate-based polymers derived for monosaccharides or oliosaccharides functionalized with polymerizable side groups.
- Steven Rosenberg of Chiron Corporation is continuing his work on cloning and gene expression with the Enzymatic Synthesis of Materials project.

Industrial Fellow

- A.E. Zacharriades of IBM Corporation worked with M.M. Denn and D. Giles on the use of rheo-optics to study the development of structure in liquid crystalline polymers.

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Structural Materials

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116 . . . . . Mechanical Behavior of Materials
129 . . . . . Ceramic Processing

Structural Metals and Alloys
Mechanical Behavior of Materials
Ceramic Processing

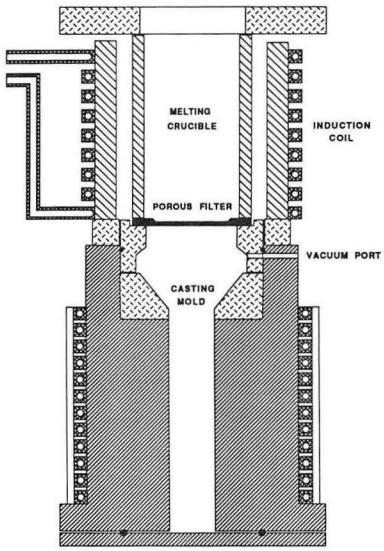
Structural Materials

The CAM program on Structural Materials is intended to further develop the fundamental materials science of metals, alloys and ceramics to the solution of basic structural problems that affect U.S. industry. Research is carried out in three areas:

- ***STRUCTURAL METALS AND ALLOYS***—the development and performance analysis of selected classes of stuctural materials critical to U.S. industry. The classes under investigation include light alloys for advanced aerospace systems, sheet metal fabricated for forming in advanced manufacturing applications, and structural alloys for high field superconducting magnets.
- ***MECHANICAL BEHAVIOR OF MATERIALS***—the study, from both macroscopic and microscopic perspectives, of the mechanics and micro-mechanisms of subcritical and critical crack growth in engineering ceramics, metals, and the interfaces separating them.
- ***CERAMIC PROCESSING***—the development of predictive, quantitative theories of densification and microstructure development in ceramics formed from powder compacts, and the application of these theories in the production of advanced structural ceramics with improved mechanical performance at elevated temperatures.

The ***STRUCTURAL METALS AND ALLOYS PROJECT*** develops and applies fundamental research in the materials science of metal alloys to the solution of generic problems that affect American industry. The research is conducted in close collaboration with industrial or national laboratory groups—the potential users of the research. Research on light alloys is done in collaboration with several aluminum and aerospace companies and has received support from Alcoa, Lockheed, Northrop, Allied Chemical and NASA. Research on sheet metal forming is conducted with and receives collaboration from Ford Motor Company, Rouge Steel and LTV steel. Research highlights of the past year include:

- The application of alloy design techniques to the development of the highest strength aluminum alloy known on a per atom of alloying element basis—Al-0.3Sc-0.3Gd (atomic%).
- The development of a mechanistic model and experimental techniques to study the effect of zinc crystallographic texture on formability of electrogalvanized steel sheet for automotive applications.
- The measurement and interpretation of increased fracture toughness in a high magnetic field of 304 stainless steel for high field magnet structures.



The aim of the ***MECHANICAL BEHAVIOR OF MATERIALS*** project is to develop a fundamental mechanistic understanding of fracture processes in order to provide guidelines for improved life prediction and the design of superior fracture-critical materials. Work during the past year includes:

- Characterization of cyclic fatigue-crack propagation behavior in ceramics under variable-amplitude loading.
- The first reported documentation of cyclic fatigue-crack growth rate behavior along glass/copper and alumina/aluminum ceramic/metal interfaces.
- The identification of the mechanisms underlying the unique fracture-toughness and fatigue-crack growth behavior of advanced aluminum-lithium alloys scheduled for aerospace and cryogenic applications.
- The development of extrinsic methods for toughening ceramic/metal interfaces, and identifying mechanisms of cyclic fatigue and environmentally-assisted crack growth along such interfaces (in collaboration with R.M. Cannon of the CAM Electronic Materials Program), with specific emphasis of microelectronic packaging applications.

Research in the ***CERAMIC PROCESSING*** project involves the development of processing methods for preparing ceramic bodies of improved uniformity from single phase commercial powders, powder-particulate mixtures, and novel, coated ceramic powders. The constitutive relationships that have been developed for densification and microstructural evolution are formulated in terms of a minimum of experimental parameters, and aim to quantify the deleterious effects of the heterogeneous nature of real powder compacts on sintering rates and microstructure development. The role of uniformity in the high temperature mechanical properties of the materials that have been produced is evaluated systematically. Recent research has produced a number of results:

- The measurement of the sintering stress for a wide range of sintered densities of a number of ceramics including alumina, magnesia, and zinc oxide.
- The first documentation of the constancy of the sintering stress under non-isothermal sintering conditions.
- The development of a 2-step sintering process that improves the performance of technical powders (i.e. the typical commercial powder) in producing more homogeneous ceramics.
- The development of a slurry process for coating ceramic powders.
- The production of alumina-coated silicon carbide whiskers and the forming of a nearly dense composite thereof with a whisker content of nearly 50 volume percent.

STRUCTURAL METALS AND ALLOYS

LIGHT ALLOYS

The light alloys program is focused on low density aluminum alloys for weight-limited structures such as aircraft and spacecraft. The main emphasis is on lithium-containing aluminum (Al-Li) alloys that can reduce weight by providing lower densities and higher elastic stiffnesses than competing aluminum alloys with similar combinations of mechanical properties. Although the development of these alloys was primarily aimed at the commercial aircraft market, their advantages over conventional alloys are even greater for spacecraft. This investigation primarily addresses the requirements of a specialized application, cryogenic fuel tankage for space vehicles. Much of the work is done in collaboration with industrial partners who participate in the experiments or who contribute to its funding. To complement this work on commercial and semi-commercial alloys, the program has a second, related thrust aimed at exploring the low density alloy system, aluminum-scandium (Al-Sc-X). Although these alloys are experimental, they are promising because they offer good performance at both high and low temperatures in addition to manufacturing advantages.

Aluminum-Lithium Alloys for Cryogenic Fuel Tankage

J.W. Morris, Jr.

The principal application of aluminum alloys at cryogenic temperatures is for large tanks used to hold cryogenic fuel (e.g. liquid hydrogen [20 K] or oxygen [100 K]) to power modern space vehicles such as the space shuttle and unmanned heavy launch vehicles now in development. LBL expertise and facilities for cryogenic mechanical properties evaluation allow CAM to make a unique research contribution in this important area. Aluminum-lithium alloys are highly attractive for this application because of the premium on reducing structural weight to maximize payload. In addition, previous LBL research (in collaboration with LLNL) showed that under some conditions Al-Li alloys display a dramatic improvement with decreasing temperature of an important design parameter, the strength-toughness combination. The combination of light weight, increased stiffness, and good low temperature mechanical properties, has stimulated the aerospace community to consider aluminum-lithium alloys as cryogenic tankage materials.

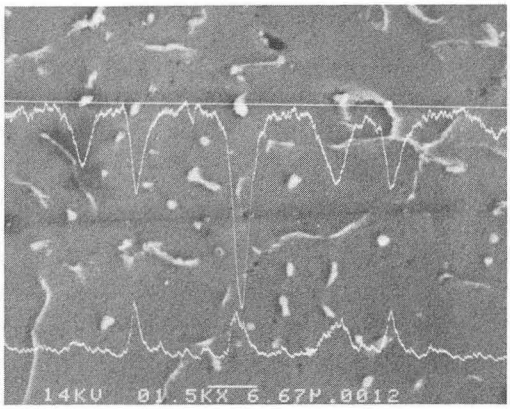
CAM research supports efforts to use Al-Li alloys for cryogenic tankage by studying the fundamental mechanisms that determine cryogenic mechanical properties, possible environmental effects such as hydrogen embrittlement, and related manufacturing issues such as welding and superplastic forming.

Cryogenic Mechanical Properties

D. Chu, J. Glazer

Studies of underlying mechanisms of cryogenic properties have focused on elucidating the sources of the good cryogenic properties measured in commercial alloys such as 2090, an Al-Cu-Li alloy. In plate form these alloys have a highly anisotropic microstructure that has a strong effect on their mechanical properties. Recent work has concentrated on separating these geometric effects from the influence of intragranular behavior.

Figure 1
Weldability of Al-Li alloys depends on careful preparation of the surfaces to be joined and proper selection of welding parameters. Shown here is a scanning electron micrograph of a gas-tungsten arc (GTA) weld of 2090, Al-2.7Cu-2.2Li (weight %). Even in a sound weld, Cu segregates and forms Cu-rich phase (white islands in the figure) during solidification of the weld pool. The profiles show the Cu peaks and Al valleys associated with the particles along the horizontal scan line. These phases provide fracture initiation sites because they are hard and brittle, and lower the strength of the matrix by concentrating the Cu solute atoms added for strengthening.



Weldability

A. Sunwoo

Although aluminum alloys are often joined by rivets, liquid fuel tanks must be of welded construction so that they do not leak. Unlike many aluminum alloys, Al-Li alloys are weldable; however, the mechanical properties of the welds are generally not as good as those of the base metal. To minimize their detrimental influence on the tank design it is important that the welds be as strong, tough, and durable as possible. Our program investigates the effects of welding and thermal processing on weld properties at low temperatures (Figure 1). The results indicate that with proper procedures and post-weld heat treatments, 2090 weldments with acceptable cryogenic properties can be produced. However, these properties are still inferior to those of the base metal and work to address the underlying causes continues. A collaborative program has been initiated with Alcoa to study the heat-affected zone that surrounds the weld.

Hydrogen Embrittlement

D. Chu

If a reusable fuel tank design is selected then the tank material will be exposed to warm hydrogen gas during reentry. Although aluminum alloys are not especially sensitive to hydrogen embrittlement, the reactive nature of Li has prompted concern. A preliminary investigation of the mechanical behavior of 2090 sheet before and after hydrogen charging did not reveal effects of engineering significance.

Superplasticity

T. Bradley, J. Glazer, P. Kramer, S. Verzasconi

Superplastic forming utilizes the extremely high ductility and low resistance to plastic flow of suitably processed alloys to form complex shapes with a minimum expenditure of energy and material. This technology is particularly appealing for Al-Li alloys because they are more costly than conventional aluminum alloys. An initial cooperative project with Lockheed Palo Alto Research Center suggested that the improvement in tensile properties at low temperature seen in plate persists in superplastic modifications. However, superplastic aluminum-lithium products are usually of lower strength than comparable non-superplastic sheet or plate. A much larger cooperative program with NASA Langley Research Center and Northrop Corporation investigated composition and process-

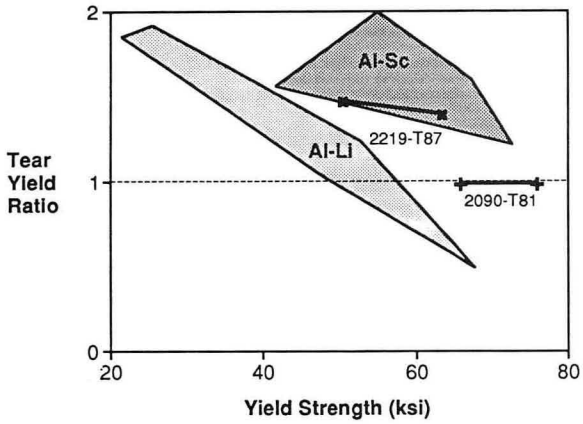


Figure 2
Superplastic aluminum sheet offers new design possibilities as well as savings in materials and manufacturing costs. Candidate alloys may be compared by their strength and toughness combination. One way to estimate sheet toughness is with the tear-yield ratio measured using a sharp-notched Kahn specimen; ratios over 1 indicate ductilite behavior. The figure summarizes data for a variety of superplastic Al-Li (-Cu/Mg) and Al-Sc (-Mg) alloys tested at room and liquid nitrogen (77 K) temperatures. Data for competing alloys that are not superplastic are shown for comparison. (Room temperature Al-Sc(-Mg) data obtained by Alcoa Research Laboratories.)

ing modifications of existing alloys that would increase the attractiveness of these alloys for cryogenic fuel tankage. Results to date indicate that while it is possible to increase strength, it is difficult to retain good low temperature toughness (Figure 2). In a related project with Alcoa, we have also investigated the low temperature properties of Al-Sc(-Mg) sheet. The extremely good strength-toughness combinations measured suggest that these materials are also promising candidates for cryogenic tankage applications.

Exploratory Studies of Aluminum-Scandium Alloys

R. Emigh, R. Sawtell

Although the unique properties of Al alloys containing scandium have been known for many years, this system has received relatively little attention because of the cost and scarcity of Sc and its limited solubility in aluminum. However, on a per atom basis, Sc is the most potent strengthener known for Al-based systems. When combined with ternary additions such as Mg, these alloys can reach strength levels of commercial interest and offer low density, good high temperature stability and superplastic formability as potential benefits (R.R. Sawtell, US Patent 4,684,090, 1987). As described above, these alloys may also have promise for use at cryogenic temperatures. We have investigated the possibility of increasing the strength of the alloy, while reducing the amount of scandium by adding rare earth elements, whose chemical interactions with Al are similar to those of Sc. The maximum tensile strength obtained to date in experimental Al-Sc alloys with rare earth additions is 310 MPa (45 ksi) in an Al-0.5Sc-1.8Gd (weight %) alloy (Figure 3).

Research on Al-Li-Sc alloys is now underway following the design, construction and refinement of a specialized melting facility for lithium-containing aluminum alloys (Figure 4). This alloy system has not been extensively studied, but is especially attractive because it may be possible to combine the advantages of Al-Sc alloys with the low density and increased stiffness offered by Al-Li alloys.

Evolution of Microstructure in Al-Li Based Alloys

S. Miyasato, G. Thomas

The formation mechanism of δ' (Al_3Li) in age-hardenable aluminum-lithium alloys has been the subject of considerable controversy. Clarification of the evolution of δ' will contribute to improvements in aluminum-lithium alloy design. High resolution electron microscopy results show a large volume fraction of off-stoichiometric ordered δ' regions in the aluminum matrix, which supports the theory by Khachaturyan, Lindsay and Morris that (under certain conditions) ordered phases form by decomposition on the ordered lattice. The tensile properties of this microstructure have also been investigated. The presence of the off-stoichiometric ordered regions results in a large increase, from 10 to 33%, in total elongation to failure as test temperature is reduced from room temperature to 77 K. Slow cooling after solution heat treatments result in heterogeneous nucleation of δ', which leads to an improvement in tensile properties in high Zr-content alloys. Research is continuing on the effect of δ' formation mechanisms on mechanical properties, as well as the study of the kinetics of δ' formation.

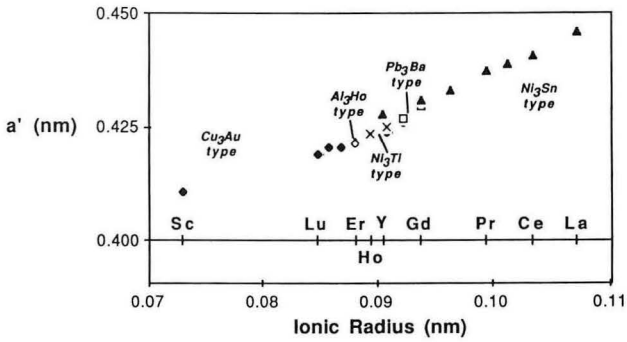


Figure 3 (above)
Aluminum-scandium-rare earth alloys are strengthened by $Al_3Sc_xRE_{1-x}$ (RE = rare earth) precipitates. The crystal structure of the Al_3X phase minimizes the atomic volume, which closely correlates with the ionic radius of the rare earth element. This chart shows the structure type and average lattice parameter of known Al_3X phases. The ionic radii of the rare earth elements are shown for comparison. For good mechanical properties, the most desirable phase is the cubic Cu_3Au type of Al_3Sc and Al_3Lu. Because of its small ionic radius, scandium can be combined with other rare earths to form this structure.

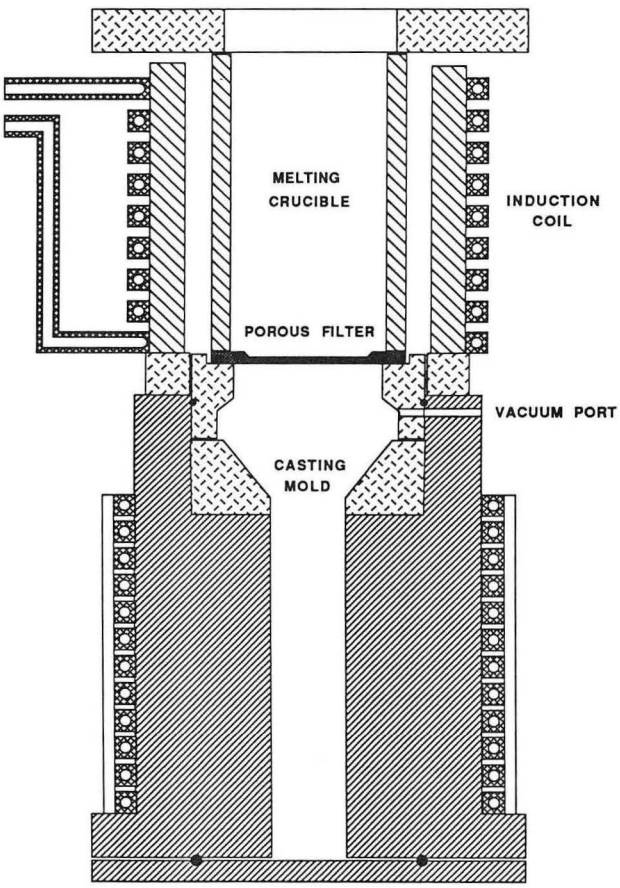


Figure 4
Melting and casting aluminum-lithium alloys requires specialized facilities because of the extreme reactivity of lithium. The furnace must be constructed of chemically resistant materials and limit the uptake of oxygen and hydrogen, which can combine with Li and cause severe grain boundary embrittlement. It must be able to produce sufficiently large ingots that thermal and mechanical processing can be performed prior to mechanical testing. The diagram shows the main features of the furnace designed at LBL for this application.The entire structure is enclosed in a containment vessel that can be evacuated and filled with inert gas. The melting and casting regions are separated by a porous filter that allows inert gas and molten Al to pass in response to a gas pressure differential.

SHEET METAL FORMING

The forming of metal sheet is central to a wide variety of critical manufacturing processes, yet remains among the least understood problem areas in materials science. Typical metal forming is accomplished through the interaction of a metal sheet and a tool piece. Its success depends on the plastic ductility of the sheet and the effective coefficient of friction between the sheet and the tool piece. One part of this investigation is concerned with the plastic behavior of common formable metals under large strains and addresses that subject at a fundamental level. A second part is concerned with the metallurgical interpretation and control of the effective coefficient of friction of electrogalvanized steel, which is the material of primary interest for the vehicle bodies of the future.

The Effect of Dislocation Substructure on the Plasticity of Low Carbon Steel Sheet

P. Johnson, A. Philip, J.-H. Schmitt, J.W. Morris, Jr.

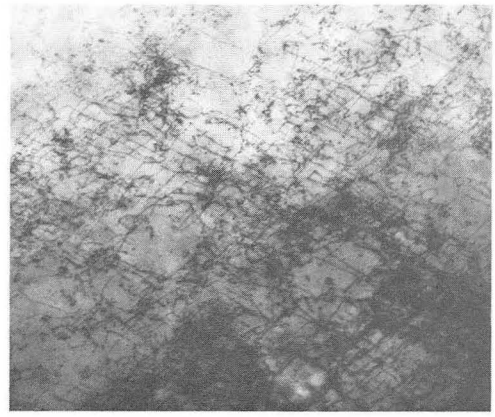
Accurate prediction of successful stamping processes requires constitutive equations which will adequately predict the flow stress during large deformations. It is therefore necessary to determine which features of the deformation structure govern the plastic behavior.

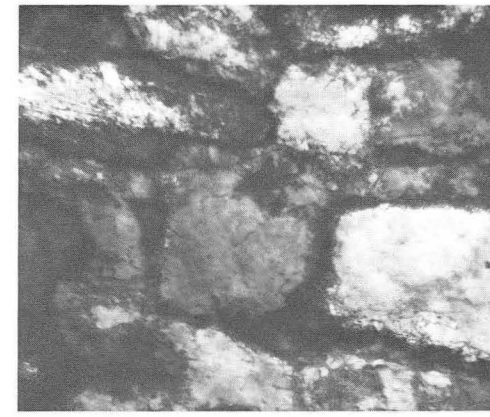
In Aluminum-Killed Drawing Quality Steel sheet deformed at room temperature, dislocations in the material tend to arrange themselves into regions of extremely high dislocation density (known as cell walls), surrounding virtually dislocation-free cell interiors. This tendency for cell formation is substantially suppressed when the deformation temperature is lowered. Since dislocation motion tends to be inhibited by dislocation-dislocation interactions, the flow stress at any point is expected to depend in part on the current arrangement of the dislocations.

The dependence of the flow stress on the dislocation substructure is being studied in a series of interrupted-temperature tensile tests, and in High Voltage TEM in-situ tensile tests. Specimens are prestrained at a particular temperature and strain rate. The tests are then continued at a "reference" temperature and strain rate. The behavior of the prestrained specimens is then compared to the behavior seen in uninterrupted tests at the reference conditions. For example, a specimen may be prestrained to 10% at -72 °C, after which the dislocations are homogeneously distributed throughout the grain interior (Figure 5). The subsequent room temperature behavior is then compared to a specimen without the low temperature prestrain, in which a well-developed cell structure exists (Figure 6).

Figure 5 (bottom left)
TEM observation of the dislocation distribution in a grain after a 10% tensile strain at low temperature (-72ºC). The thin foil plane is parallel to the sheet plane.

Figure 6 (bottom right)
TEM observation of the dislocation substructure developed after a 10% tensile strain at room temperature. (Note that the magnifications of the two pictures are similar).





Results to date show that the work hardening behavior is unaltered by the prestrain if the curves are compared from the same initial stress level. This suggests that for the range of conditions studied thus far, the dominant effect of the current structure on the subsequent behavior can be adequately described by a single parameter, and that this parameter is not determined by dramatic alterations in the dislocation arrangements. The implications of this are two-fold. First, it may be possible to write rather simple constitutive equations that accurately predict complex plastic behavior during forming processes. Secondly, if the arrangements of the dislocations are not controlling the flow stress, there is apparently some other controlling feature of the deformation structure, described by an single parameter, which needs to be determined.

A mapping of this scalar parameter as a function of the prestrain and reference conditions is being performed. In an ongoing collaborative project with Professor Baudelet's group at the Institut National Polytechnique de Grenoble (GPM2) in France, a study is planned which incorporates the results of this work with changes in the strain path.

Formable Electrogalvanized Steel

W. Nojima, S. Shaffer, J.W. Morris, Jr.

The effort by the automotive industry to increase the lifetime of vehicle bodies requires the use of corrosion-resistant steels, and has led to the selection of two-side electrogalvanized steels for many applications. These have a coating of 5-10 m of relatively soft zinc on either surface. The formability of electrogalvanized steel is under investigation in a joint program between LBL and the Ford Motor Company, LTV Steel, and Rouge Steel.

One of the limitations of the formability of electrogalvanized steels (EGS) originates in its highly variable frictional characteristics. As yet there is a lack of understanding of the micromechanisms of friction during strip drawing of EGS. During strip drawing, the frictional forces result from a complicated interaction between the sheet, the lubricant(s), and the tooling. Despite the presence of lubricant, much of the zinc layer is plastically deformed by the tooling (Figure 7). As such, the current thrust of our investigation is focused on the mechanical properties of the zinc layer.

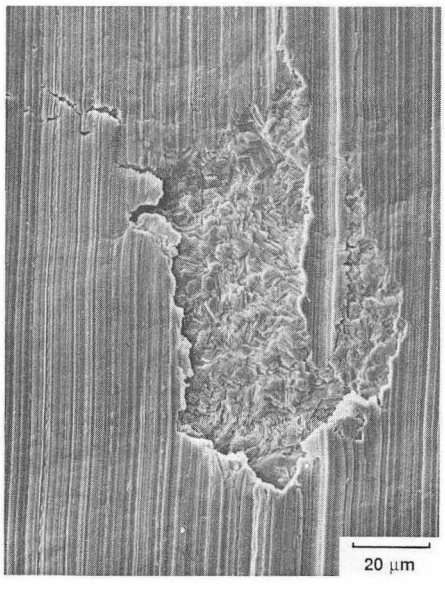


Figure 7
During drawing of electrogalvanized steel sheet, the soft zinc layer is plastically deformed where contact is made with the tooling. Shown here is an SEM micrograph of the zinc surface after simulative friction testing. Deformation of the zinc occurs at the asperities (due to the intentional roughness of the underling steel), while the valleys are left rather unaltered.

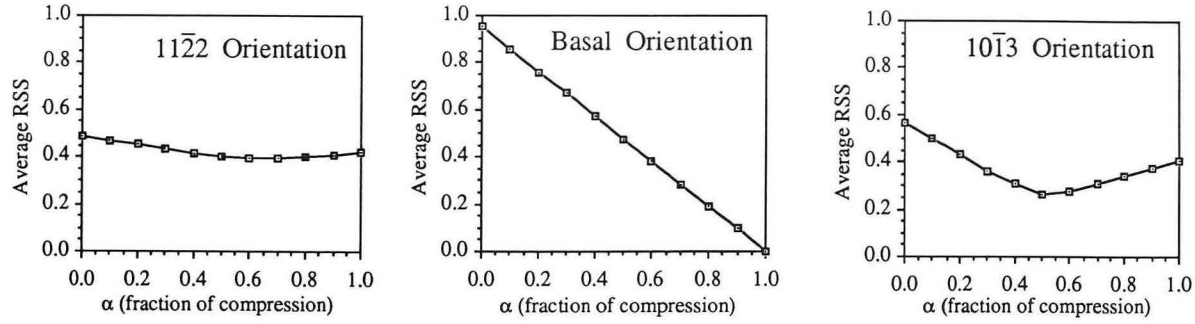


Figure 8
The resistance to deformation of the softer of two materials in frictional contact (or of a third, interfacial compound) gives rise to the frictional force. As measured by the resolved shear stress (RSS), three model textures of zinc will exhibit different resistances to deformation. This resistance to deformation is inversely proportional to the RSS. For the loading conditions typically found in sheet forming (defined by α=0.8), predict that electrodeposited zinc of basal orientation will have a higher resistance to deformation, hence give rise to a higher coefficient of friction, compared with either of the two pyramid orientations shown.

Zinc has very anisotropic slip characteristics due to the hexagonal close packed structure of the atoms. Hence its response to applied loads will vary strongly with texture (preferred crystallographic orientation). Texture can be controlled during the plating process by varying the electrodeposition conditions. A simple model, making use of the critical resolved shear stress for slip on the basal plane of zinc, allows prediction of "resistance to deformation" (i.e. friction) for different textures. Contrary to intuition, under the loading conditions encountered during strip drawing, electrodeposited zinc of basal orientation is predicted to give higher friction than either $10\bar{1}3$ or $11\bar{2}2$ textures (Figure 8). Experiments on steels with controlled texture are in progress. Research on the effect of microroughness (due to the zinc crystallite morphology) in support of the load by the lubricant has also begun.

STRUCTURAL ALLOYS FOR HIGH FIELD SUPERCONDUCTING MAGNETS

Current magnetic confinement fusion reactor concepts subject the magnet structure to very high cyclic stresses at cryogenic temperature. These service conditions require structural alloys that have high strength, good fracture toughness and good fatigue properties at cryogenic temperatures. Some of the candidate alloys are only marginally stable with respect to martensitic transformation in the proposed service environment, and transform to martensite at cryogenic temperatures when subjected to sufficient stress or strain. An understanding of the various mechanisms affecting fracture toughness and fatigue in the presence of martensitic transformation at the proposed operating conditions is required for effective alloy selection and design.

The alloys that are the leading current candidates for the magnet structure are the 300 series austenitic stainless steels. The particular alloys, 304L, 304, 304LN, are metastable to varying degrees (304L is the least stable and 304LN is the most stable) and are thus good for modeling the property changes that can occur with transformation at low temperatures and in a high strength magnetic field. The primary objective of this program is to determine and to develop an understanding of the mechanisms that are important in determining mechanical properties at the expected service conditions of these magnets.

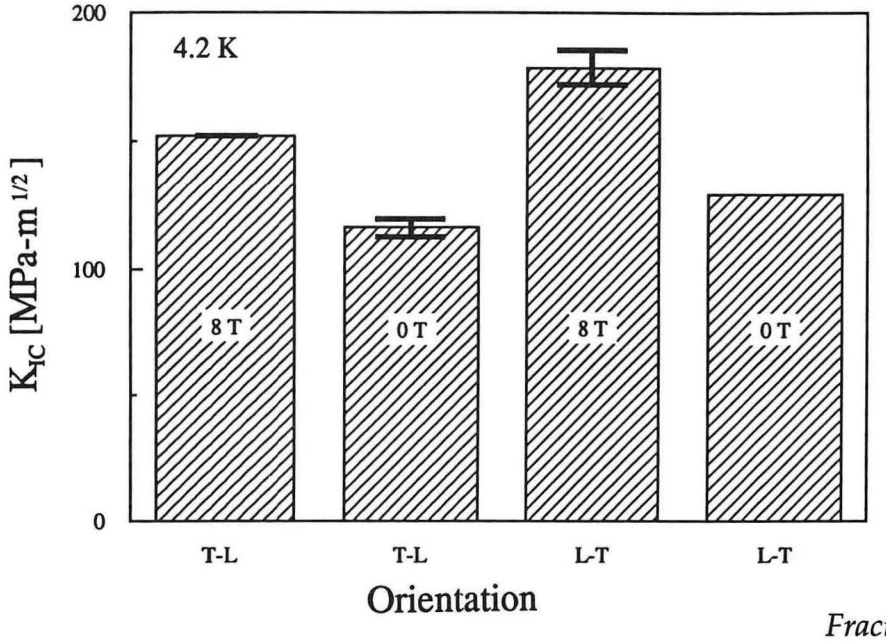


Figure 9
Fracture toughness of 304 at 4.2 K in 0 and 8 Tesla magnetic fields for both L-T and T-L compact specimen orientations. The higher fracture toughness obtained in the 8 Tesla magnetic field is associated with martensite formation during deformation.

Fracture Toughness

J. Chan, Z. Mei, J.W. Morris, Jr.

The magnet structure of a Tokamak reactor is highly stressed during operation. Thus the fracture toughness behavior at the operating conditions, 4.2 K in a strong magnetic field, is an important consideration for the design of the structural components. Using a unique testing facility, LBL research has shown that the effective fracture toughness of 304 stainless steel in an 8 Tesla magnetic field at 4.2 K is higher than that of 304 tested at 4.2 K without an applied magnetic field (Figure 9). Several mechanisms, all related to the martensitic transformation, have been identified as contributing to the increase in effective fracture toughness of 304 in a magnetic field. In an applied magnetic field, the extent of martensitic transformation during deformation is greater than that without an applied field (Figure 10). The higher strain hardening rate and the volume

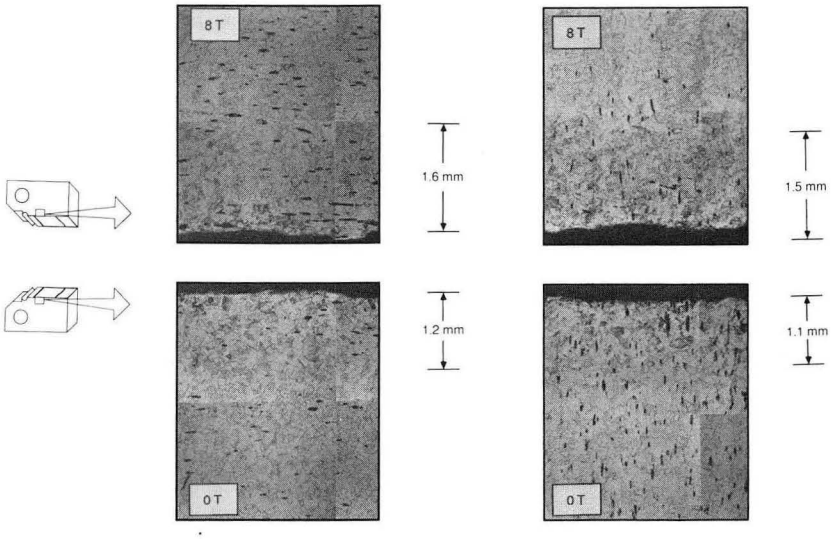


Figure 10
Optical crack profiles of T-L (left) and L-T (right) compact specimens tested in the two magnetic fields (0 and 8 Tesla). Differences in the extent of the martensite-containing zones are indicated. The dark parallel features within the grains are the martensite phase and the large dark stringers are sulfide particles deformed in the rolling direction.

expansion accompanying the transformation around the crack tip both act to reduce the local stress intensity and thus improve effective fracture toughness. The presence of the ferromagnetic material on both sides of the crack interface in a magnetic field also serves to reduce local stress intensity since it tends to resist interface separation.

Fatigue

Z. Mei, J.W. Morris, Jr.

Martensite that is produced at low temperature in the strain field of a fatigue crack can improve the fatigue crack propagation behavior by slowing the crack growth rate and increasing the threshold stress intensity for crack growth (Figure 11). The fatigue crack growth rates at room and at liquid nitrogen temperatures (RT and LNT) of metastable 304L and more stable 304LN stainless steels are plotted in figure 12. Under fatigue loads, 304LN remains austenitic at RT and transforms to martensite only when ΔK (the cyclic stress intensity) exceeds about 30MPa-m$^{1/2}$; 304L remains austenitic at RT but transforms at LNT even with ΔK approaching the threshold stress intensity range for crack growth. The mechanically induced martensitic transformation shifts the crack growth rate curve to higher stress intensity ranges. The magnitude of the transformation-induced shift decreases as the average stress (denoted by the stress intensity ratio or R-ratio) increases.

Theoretical calculations and experimental observations indicate that there are two major mechanisms, each dominant in different ΔK regimes. When ΔK is small, close to the threshold ΔK, the volume expansion due to the transformation induces a compressive residual stress field that reduces the nominal ΔK to a smaller effective ΔK. When the nominal ΔK is large, the material in the front of the fatigue crack is hardened by the martensite particles and thus reduces the crack growth rate.

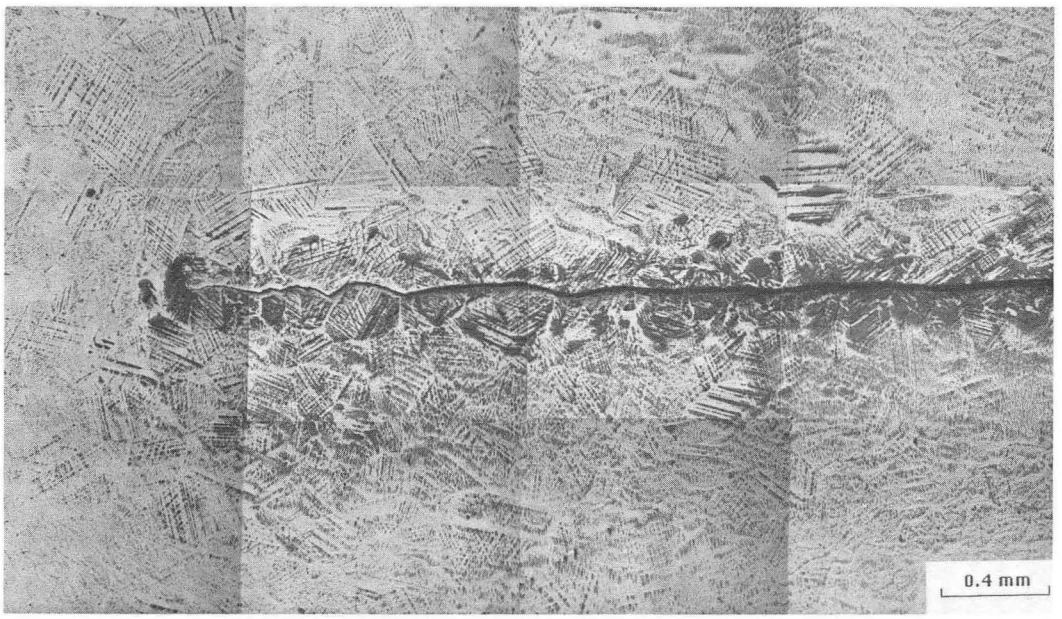


Figure 11
Fatigue crack profile of 304L stainless steel tested at liquid nitrogen temperature (77K) with a stress intensity range of 25 MPa-m$^{1/2}$. The dark ferromagnetic martensite laths in the light paramagnetic austenite matrix are revealed by a ferrofluid.

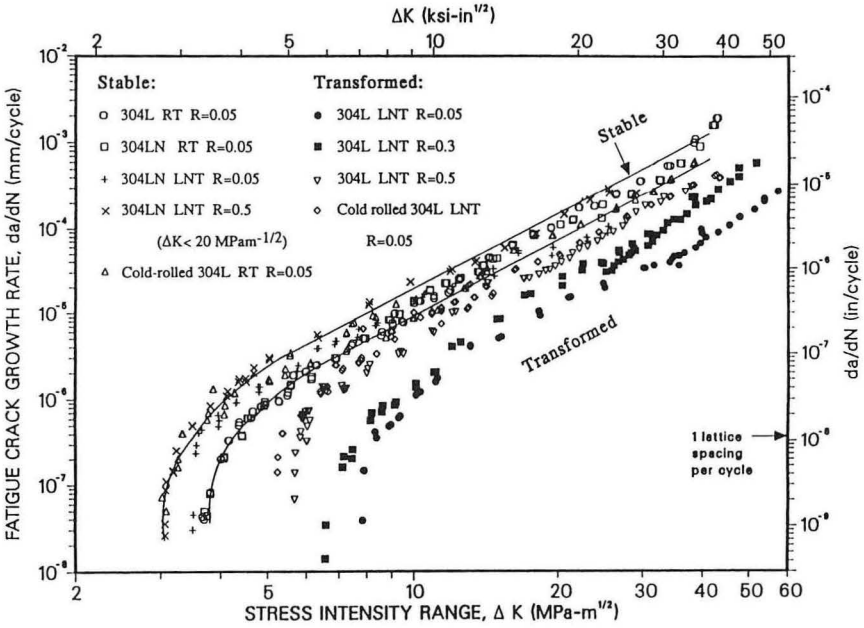


Figure 12
Fatigue crack growth rate for annealed 304L, cold-rolled 304L, and annealed 304LN stainless steel at room and at liquid nitrogen temperatures (RT, LNT) with various load ratios (R). The mechanically induced martensitic transformation improves the fatigue crack growth bahavior by increasing the threshold stress intensity and reducing crack growth rate at a given cyclic stress intensity.

THEORETICAL STUDIES OF STRUCTURE AND PHASE TRANSFORMATIONS

The theoretical studies done as part of this program are intended to exploit theoretical advances in materials science that offer immediate, useful insight into the microstructure and engineering properties of materials. Two current investigations concern the use of concentration-wave analyses to understand the structures of complex ordered intermetallics and oxides, and the use of elastic theory to understand the coarsening of solid-state precipitates and the interactions of deformed grains in solids undergoing plastic deformation.

Concentration-Wave Analyses of Ordered Intermetallics and Oxides

A.G. Khatchaturyan, T. Lindsey, J.W. Morris, Jr.

It has been shown that the ordering wave formalism can be used to predict the structures of ceramic crystals. During the last year, this formalism was applied to study phase relationships in the superconducting oxide $YBa_2Cu_3O_{7-x}$. The results included a prediction of the phase relationships and metastable ordering transformations as a function of the oxygen content. The model correctly predicted the low-temperature decomposition of the oxide, and correctly predicted the appearance of metastable Magneli phases, which differ from the stable phase in the period of oxygen order in the basal plane.

In other work we have shown that the concentration wave method can be used to describe ordering in complex intermetallic phases when the atoms and/or vacancies are distributed over the substitutional sites and interstitial voids of FCC or BCC parent structures. The substitutional-interstitial special point superstructures (Lifshitz structures) are an important class of structures. We have developed a systematic method to derive and enumerate all the special point superstructures for a given parent structure and applied this method to identify the substitutional

special point superstructures for the FCC and BCC structures. We are now applying the method to enumerate the superstructures for the more general case of substitutional and/or interstitial ordering.

The thermodynamic and ordering properties of the special point structures are investigated using the Khachaturyan ground state analysis, to gain insight into the ordered structures and transition paths for complex intermetallics and oxides. The ability to predict transition paths is particularly useful for the development of new materials containing intermetallic or ceramic phases.

Microstructural Development due to Strain-Induced Coarsening

M. McCormack, A.G. Khachaturyan, J.W. Morris, Jr.

A new type of coarsening has been recently observed in Ni-Al-X alloy systems. Initially spherical γ' precipitates coarsen into cuboidal shapes which subsequently split into smaller precipitates upon further coarsening. According to classical nucleation theory, the coarsening should lead to a coalescence of precipitates. This type of coarsening is the opposite of the observed splitting of cuboidal precipitates in Ni-Al-X alloys. Using analytic models, it was recently shown that the competition between elastic and surface energy can explain reverse coarsening. This approach successfully predicted some features of the coarsening sequence of the γ' precipitates, but considered only the behavior of isolated particles.

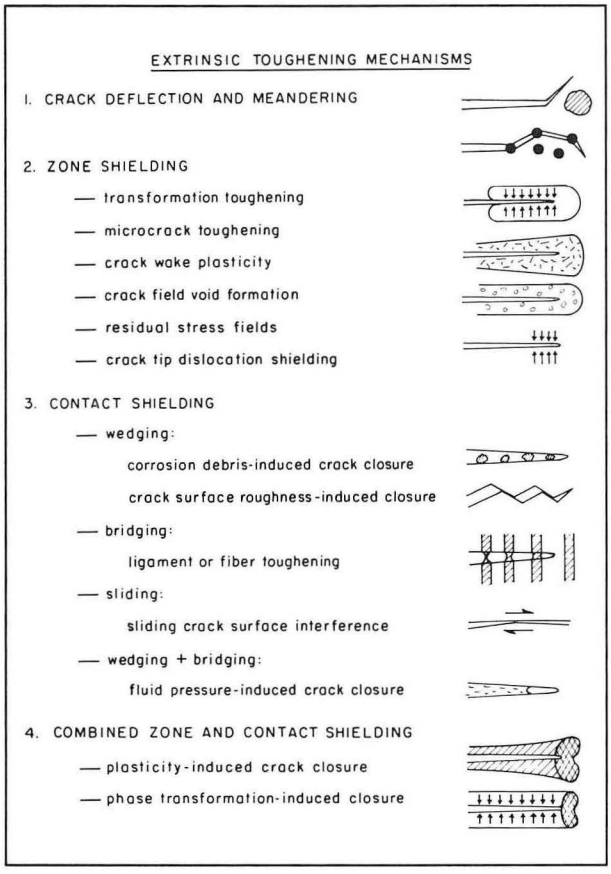
The elastic theory has since been used to create a computer simulation model that treats the evolution of systems of arbitrary two-dimensional distributions of interacting precipitates. Using a Monte Carlo simulation we have reproduced the results of the analytic solution. In addition, the simulation reproduces the experimentally observed hollowing of the cuboidal precipitates prior to splitting into plate doublets and the morphology of plate arrays in Al-Li-X alloys.

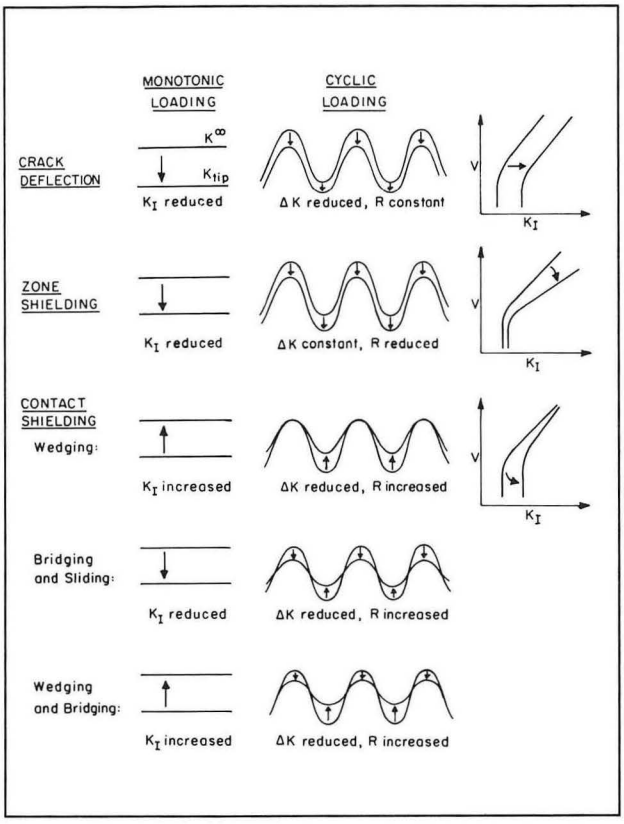
The stable configurations produced by the Monte Carlo simulations often correspond to metastable states. These states are of particular interest since the optimum precipitate distributions for mechanical properties are metastable. The simulation calculations will lead to a better understanding of the reverse coarsening microstructural development and, therefore, will contribute to the development of improved alloy designs for Al-Li-X type systems.

MECHANICAL BEHAVIOR OF MATERIALS PROJECT

CRACK-TIP SHIELDING: AN EXTRINSIC APPROACH TO TOUGHENING

Crack-tip shielding phenomena, whereby the "effective crack driving force" actually experienced at the crack tip is locally reduced, have been examined with reference to fatigue-crack propagation behavior in metals and ceramics. Sources of shielding were analyzed in terms of mechanisms relying on the production of elastically constrained zones which envelop the crack (zone shielding), on the generation of wedging, bridging or sliding forces between the crack surfaces (contact shielding), and on crack-path deflection and meandering (Figures 13, 14). These concepts have been applied to problems of the fatigue behavior of high-strength lithium-containing aluminum alloys, the fracture and fatigue behavior of transforming and nontransforming ceramics, and the toughening of ceramic/metal interfaces. It was found that whereas crack-tip





shielding can provide a potent means to enhance "resistance" to crack growth, such extrinsic toughening mechanisms can result in the apparently anomalous behavior of "small cracks" and the susceptibility of brittle materials to fatigue failure.

FATIGUE AND FRACTURE OF ALUMINUM-LITHIUM ALLOYS

Potential pay-offs from weight and fuel cost savings using materials with lower density and high stiffness have largely motivated the development of lithium-containing aluminum alloys. Compared to existing high-strength aluminum alloys, these advanced materials (containing 1-3 wt.% Li), offer 7 to 10% reductions in density, 7 to 12% improvements in stiffness, with energy savings of up to 30%. Moreover, although Li additions may lead to low ductility and fracture-toughness properties, most studies on Al-Li-X alloys to date have reported generally improved fatigue resistance compared to traditional 2000- and 7000-series aluminum alloys.

Such conclusions regarding the improved fatigue properties, however, are largely based on long (> 10 μm) crack results from fracture mechanics type specimens, cycled under constant amplitude loading conditions; results pertaining to small (< 500 μm) cracks, which are often more relevant in lifetime calculations, are known to propagate faster than long cracks at comparable (applied) stress-intensity levels.

Figure 13 (above, left)
Schematic representation of the classes and mechanisms of crack-tip shielding in metals, ceramics, polymers and composites. Such mechanisms act to toughen, or more generally to impede crack advance, by locally reducing the crack driving force ("extrinsic" toughening), rather than by increasing the "intrinsic" microstructural resistance.

Figure 14 (above, right)
Schematic illustration of the effect of specific crack-tip shielding mechanisms on the crack driving force, e.g., the stress intensity K_I and crack velocity under monotonic and cyclic loading.

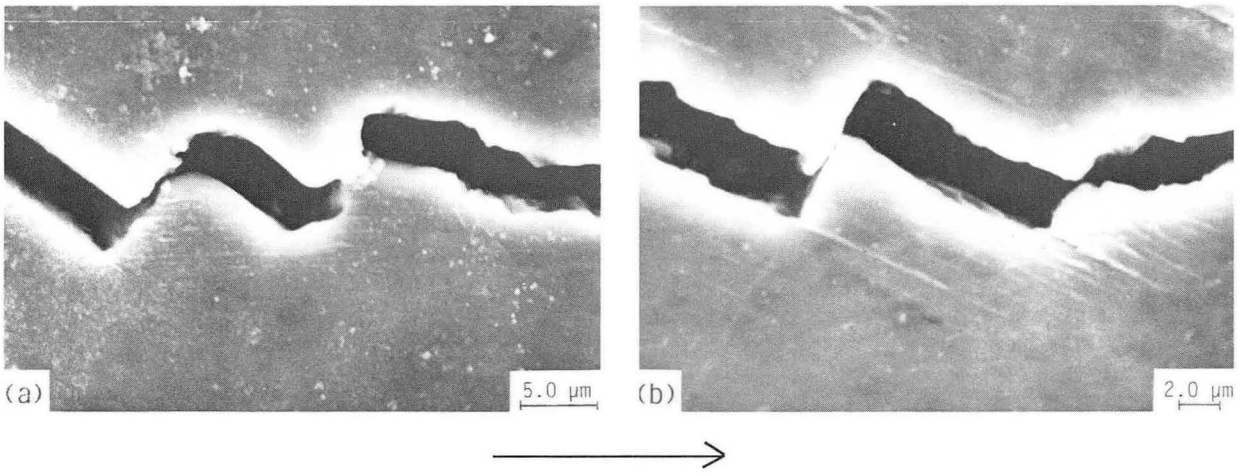


Figure 15
Example of deflected and faceted fatigue-crack paths in commercial aluminum-lithium alloys and the resultant wedging of fracture-surface asperities, which induces significant crack-closure forces (termed roughness-induced crack closure). Micrographs obtained on the specimen surface of the 2090-T8E41 alloy at a ΔK of 8 MPa$\sqrt{m}$. Arrow indicates general direction of crack growth.

Research at CAM during the past year has focused on obtaining a mechanistic understanding of cyclic crack advance in aluminum-lithium alloys. Comprehensive experimental programs, involving examination of the fatigue and fracture properties of commercial aluminum-lithium alloys including 2090, 2091, 8090, and 8091, have been conducted as a function of plate-orientation, crack size, loading sequence, microstructure and test temperature.

Fatigue Crack Growth—Long Cracks

R.O. Ritchie, K.T. Venkateswara Rao

Rates of (long) fatigue-crack extension in Alcoa alloy 2090-T8E41 in general, were found to be significantly slower (at a given stress-intensity level) than those in traditional aluminum alloys 2124 and 7150, although behavior was strongly anisotropic. Differences in growth rates of up to 4 orders of magnitude were observed between the L-T, T-L and T-S orientations, which show the best crack-growth resistance, and S-L, S-T, and L+45, which show the worst. Such behavior was attributed to the development of crack-tip shielding (which *locally* reduces the crack driving force), resulting from the role of the tortuous crack-path morphology in inducing crack deflection and crack closure from consequent asperity wedging (Figure 15). For example, crack advance was the slowest far orientations perpendicular to the rolling plane (L-T, T-L, T-S), owing to marked crack-path deflection and branching which produced high levels of shielding; conversely, fatigue fractures parallel to the rolling plane (S-L, S-T) occurred through an intergranular, delamination-type separation, with far less deflection, lower shielding levels and thus, faster crack-growth rates.

Fatigue Crack Growth—Small Cracks

R.O. Ritchie, K.T. Venkateswara Rao

As such crack-tip shielding mechanisms act primarily on the wake of the crack, their effect is very sensitive to crack size. Primarily for this reason, near-threshold fatigue-crack growth rates of naturally-occurring, microstructurally-small (2-500 μm) surface cracks in aluminum-lithium

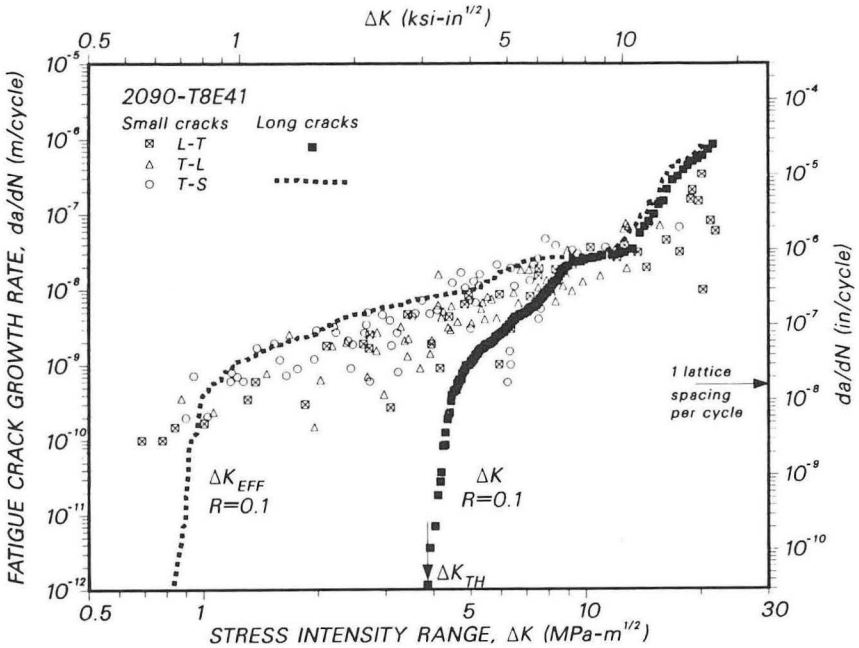


Figure 16
Comparison of the growth-rate behavior of naturally-occurring, microstructurally-small (2-1000 μm) surface cracks and long (5 mm) through-thickness fatigue cracks in aluminum-lithium alloy 2090-T8E41 (L-T, T-L, T-S orientations), as a function of the nominal stress-intensity range ΔK at a load ratio R of 0.1. Note that when long-crack data are plotted as a function of ΔK_{eff} (dashed line) after allowing for the effect of measured crack-closure loads, the discrepencies between long- and small-crack results are significantly reduced.

alloys, such as 2090-T8E41, can be 1 to 3 orders of magnitude faster than long cracks, subjected to the same nominal stress-intensity range. Closer correspondence between small and long-crack fatigue results can be obtained, however, after correcting long-crack data to account for the measured role of shielding from crack closure (Figure 16). When crack-growth rate data for Al-Li alloys are presented in this fashion, small differences are apparent in small-crack results with respect to plate-orientation and microstructure, in contrast to conventional long-crack data. Based on these data, it is apparent that due to the very high levels of crack-tip shielding developed in Al-Li alloys, they show the best long-crack fatigue properties of any high-strength aluminum-lithium; however, for the same reason, it is the limitation of such shielding inherent with cracks of restricted wake that leads to their less impressive small-crack properties.

Variable Amplitude Loading

R.O. Ritchie, K.T. Venkateswara Rao

Mechanistic studies on the Al-Li 2090-T8E41 alloy have shown that application of single tensile overloads on fatigue-crack growth at a given constant-amplitude baseline ΔK level, causes an immediate acceleration in crack-growth rate, resulting from crack advance during the overload cycle and a reduction in crack closure due to crack-tip blunting. Subsequent post-overload under growth becomes retarded, however, as the crack penetrates the overload plastic zone, due to the residual stress field in this zone and the resulting enhanced crack-tip shielding. Such delayed retardation is particularly potent in aluminum-lithium alloys, because of the generally high shielding levels due to their highly textured and planar-slip microstructures which promote meandering crack paths; moreover, extensive crack deflection (at the surface) often accompanies the overload,

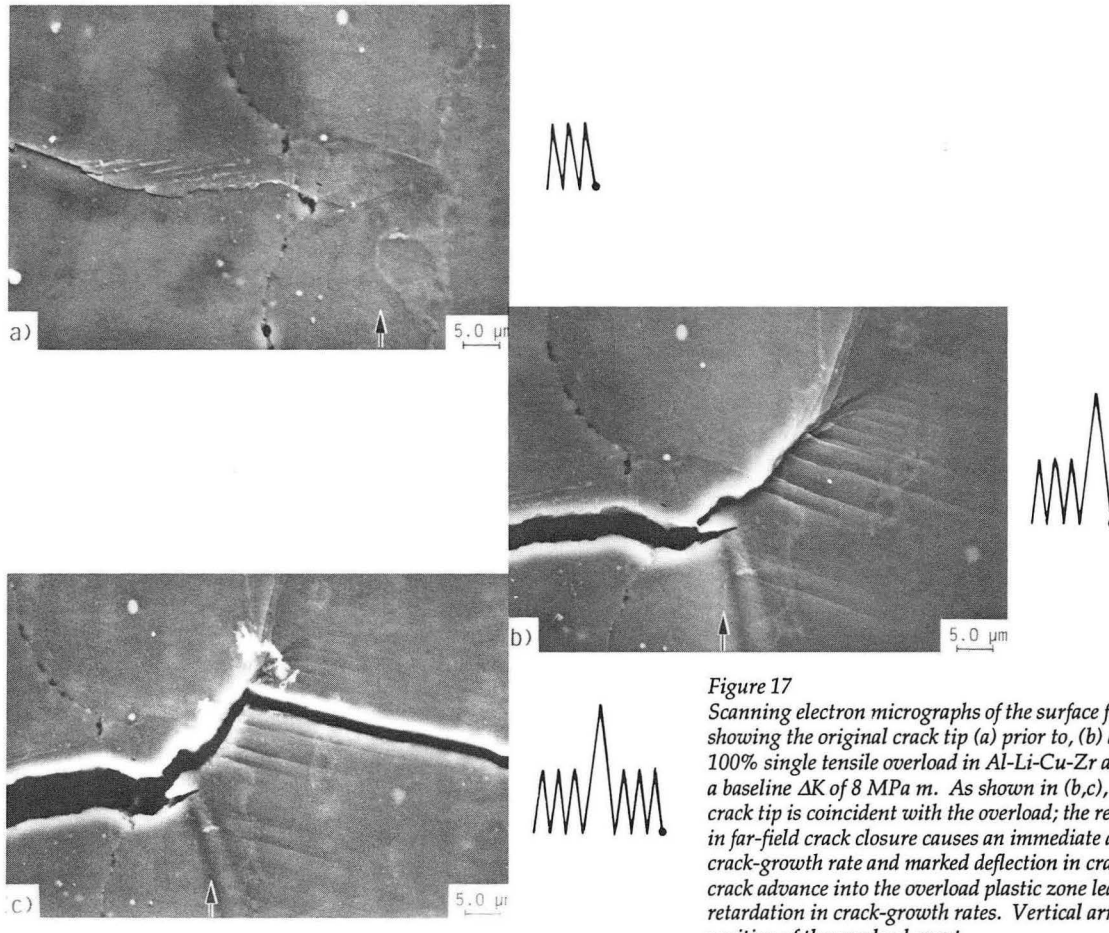


Figure 17
Scanning electron micrographs of the surface fatigue-crack profile, showing the original crack tip (a) prior to, (b) at, and (c) after a 100% single tensile overload in Al-Li-Cu-Zr alloy 2090-T8E41 at a baseline ΔK of 8 MPa m. As shown in (b,c), blunting of the crack tip is coincident with the overload; the resulting reduction in far-field crack closure causes an immediate acceleration in crack-growth rate and marked deflection in crack path. Further crack advance into the overload plastic zone leads to a transient retardation in crack-growth rates. Vertical arrows indicate the position of the overload event.

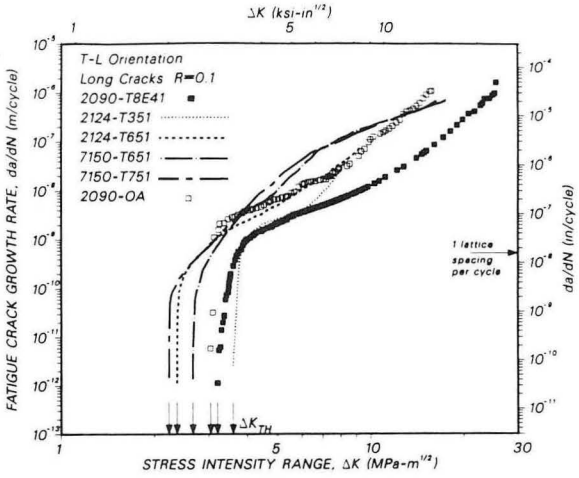
which further enhances shielding levels (Figure 17). For this reason, aluminum-lithium alloys offer perhaps the best resistance of any high-strength aluminum alloy to tension-dominated variable-amplitude loading spectra; under compressive-dominated spectra, however, they are less impressive, as the compression cycles tend to crush fracture-surface asperities, leading to a significant reduction in crack-closure levels.

Influence of Prolonged High Temperature Exposure

R.O. Ritchie, K.T. Venkateswara Rao

Aluminum-lithium alloys have recently been targeted for use in advanced aerospace vehicles, such as the Advanced Tactical Fighter and the National Aerospace Plane; with certain components, such applications involve periodic exposures to high temperatures (<260 C) for prolonged time periods during service. The high-temperature exposure has been shown to lead to overaging in Al/Li alloys, i.e., reductions in strength and toughness through the formation of plate-like, Cu-rich grain-boundary precipitates and associated Cu-depleted and δ′-precipitate-free zones. Similarly, resistance to fatigue-crack propagation was diminished (at least above ~10^{-9} m/cycle), resulting mechanistically from lower crack-closure loads due to more linear crack paths; near-threshold growth rates, conversely, were less affected. Despite this degradation in fatigue properties with prolonged high-temperature exposure, crack-growth rates in overaged Al-Li alloy 2090 were still comparable to traditional high-strength aluminum alloys, such as 2124-T351 and 7150-T651 (Figure 18).

Figure 18
Comparison of the fatigue-crack propagation behavior (at a load ratio R of 0.1) of peak-aged (T8E41) and overaged (1000 h at 163 C) 2090 Al-Li alloy with published results for 2124-T351, 7150-T651 and 7150-T751 alloys. It is evident that the lithium-containing 2090 alloy retains its superior fatigue-crack growth properties over traditional high-strength aluminum alloys, even after prolonged overaging exposures at high temperatures.



Cryogenic Fracture Toughness

R.O. Ritchie, K.T. Venkateswara Rao

One major attribute of many aluminum-lithium alloys is their excellent strength, ductility and toughness properties at liquid nitrogen and liquid helium temperatures. In fact, previous studies with J.W. Morris, Jr., showed that the fracture toughness of the 2090-T8E41 alloy *increases* from 35 to over 65MPa√(m) with a *decrease* in temperature from ambient to 4 K. In the present work, such toughness increases in 2090 were confirmed, for all but the short-transverse orientations, which conversely showed a toughness decrease. Moreover, the elevation in toughness with decrease in temperature was not universally displayed by all commercial aluminum-lithium alloys and aging conditions (Figure 19). The cryogenic toughening was attributed primarily to loss of through-thickness constraint resulting

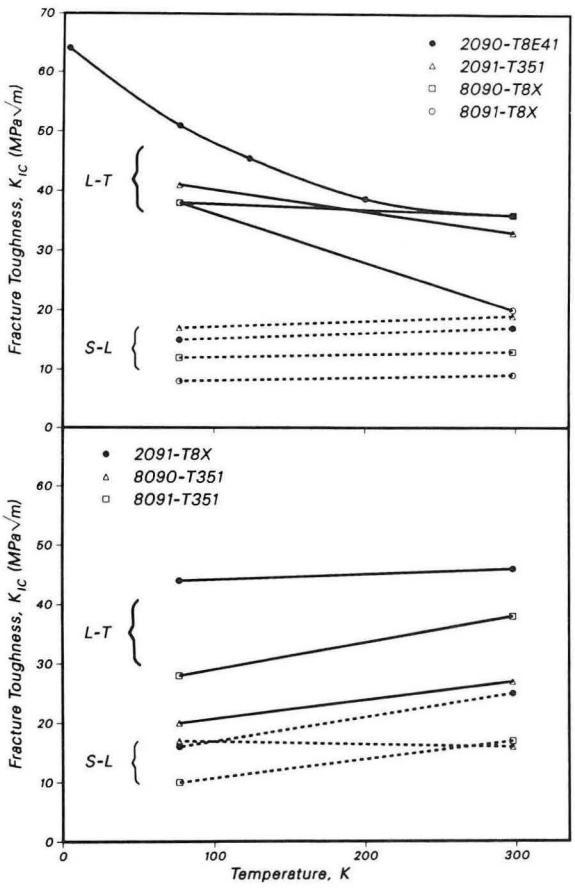


Figure 19
Variation in fracture toughness K_{Ic} with test temperature for commercial aluminum-lithium alloys in both in-plane (L-T) and short-transverse (S-L) orientations. Note that only certain alloys, namely 2090-T8E41, 2091-T351, 8090-T8X and 8091-T8X, show an increase in L-T toughness with decrease in temperature, whereas the remainder (2091-T8X, 8090-T351, 8091-T351) show a decrease. It is also apparent that increases in K_{Ic} with decreasing temperature are not observed in any alloy in the S-L orientation.

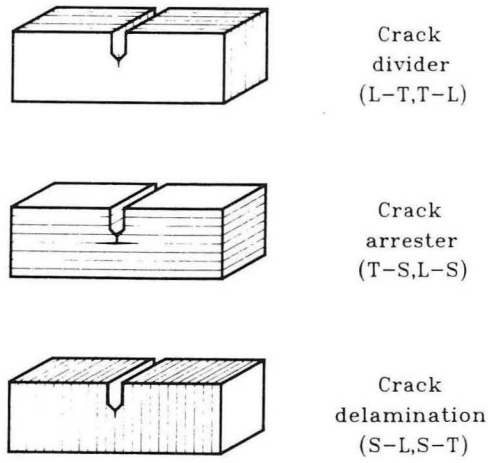


Figure 20
Mechanisms of toughening in microstructures containing weak short-transverse properties, showing a) crack-divider toughening due to loss of through-thickness constraint from fracture-surface splitting (delamination) (e.g., in the L-T orientation), b) crack-arrester toughening due to marked crack deflection and blunting (e.g., in the T-S orientation), and c) showing crack propagation by delamination in the short-transverse orientations (e.g., S-L orientation).

from enhanced short-transverse delamination (termed crack-divider delamination toughening), consistent with an observed reduction in short-transverse (S-L, S-T) toughness (Figure 20). Conversely, in the alloys which displayed a decrease in toughness with decreasing temperature, behavior was associated with a fracture-mode transition from ductile void coalescence to primarily transgranular shear.

CYCLIC FATIGUE IN CERAMICS

Cyclic Fatigue-Crack Growth in MgO-PSZ Transforming Ceramics

R.H. Dauskardt, R.O. Ritchie

The subcritical growth of fatigue cracks under (tension-tension) cyclic loading can occur in ceramic materials. The work, done in collaboration with D.B. Marshall of Rockwell International, involved experiments using compact tension specimens of a MgO partially-stabilized zirconia (PSZ), heat treated to vary the fracture toughness K_c from ~3MPa√(m) (overaged condition) to 16MPa√(m) (peak-toughness condition) and tested in inert and moist environments. Analogous to behavior in metals, cyclic fatigue-crack growth rates (over the range 10^{-11} to 10^{-5} m/cycle) were found to be a function of the stress-intensity range, environment, fracture toughness

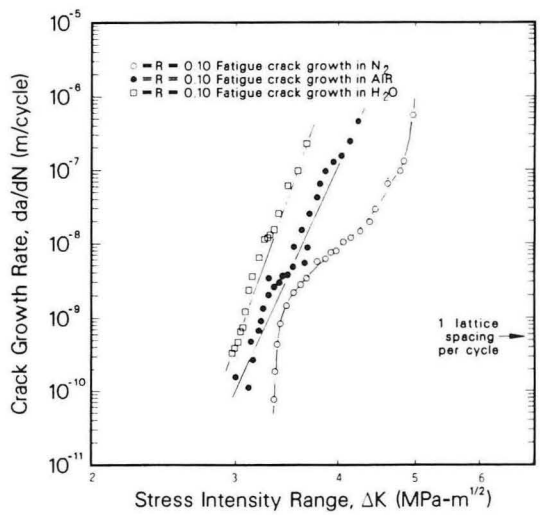
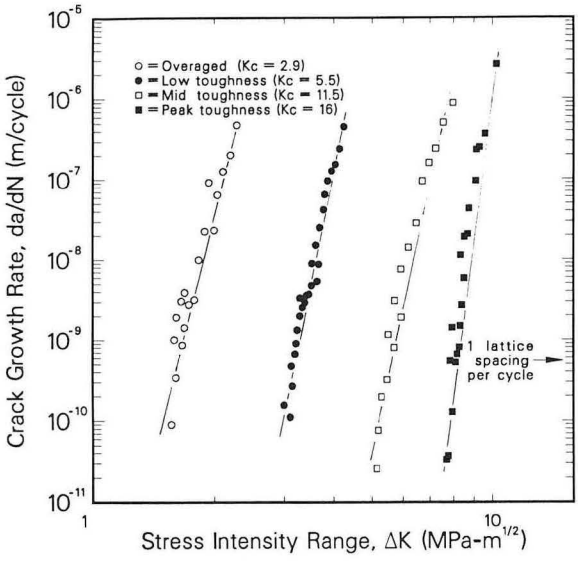


Figure 21
Effect of environment on the cyclic fatigue of ceramics, showing cyclic fatigue-crack growth rates, da/dN, as a function of the applied stress-intensity range, ΔK, in low-toughness (AF) MgO-PSZ in dry nitrogen gas, room air and distilled water environments, showing an acceleration in growth rates due to water vapor. Compact tension tests were performed at 50 Hz frequency with a load ratio R of 0.1.

Figure 22
Cyclic fatigue-crack growth behavior, in terms of growth rates per cycle, da/dN, as a function of the stress-intensity range, ΔK, for MgO-PSZ ceramic, subeutectoid aged to a range of K_c toughnesses from 2.9 to 16 MPa/m. Data were obtained on compact tension samples in a room-air environment at 50 Hz frequency with a load ratio ($R = K_{min}/K_{max}$) of 0.1, and show increasing fatigue-crack growth resistance with increasing fracture toughness.



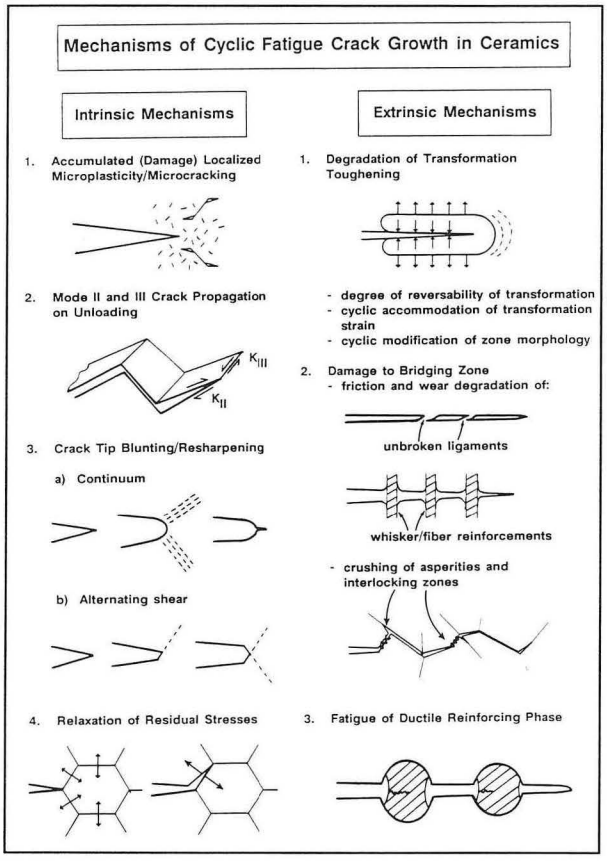


Figure 23
Schematic illustration of possible micro-mechanisms for cyclic fatigue-crack growth in ceramic materials. Processes are categorized in terms of a) intrinsic *mechanisms, where cyclic loads result in intrinsic microstructural "damage" ahead of the crack tip, and b)* extrinsic *mechanisms, where cyclic loads act to diminish crack-tip shielding and hence elevate the* near-tip *stress-intensity levels.*

and load ratio, and to show evidence of fatigue crack closure; unlike toughness behavior, growth rates were not dependent on through-thickness constraint (Figures 21, 22). Under variable-amplitude cyclic loading conditions, crack-growth rates displayed transient accelerations following low-high block overloads and transient retardations following high-low block overloads or single tensile overloads, again analogous to behavior commonly observed in ductile metals. Cyclic crack-growth rates were observed at stress intensities as low as 50% of K_c, and were typically some 7 orders of magnitude faster than corresponding stress-corrosion crack-growth rates under sustained-loading conditions. Possible mechanisms for cyclic crack advance in ceramic materials were examined (Figure 23).

Spatially-Resolved Raman Spectroscopy of Transformed Zones in MgO-PSZ

R.H. Dauskardt, R.O. Ritchie

Raman vibrational spectroscopy provides an effective phase characterization technique in materials systems containing particle dispersions of the three polymorphs of ZrO_2, each of which yields a unique Raman spectrum. An investigation has been performed in conjunction with D.K.

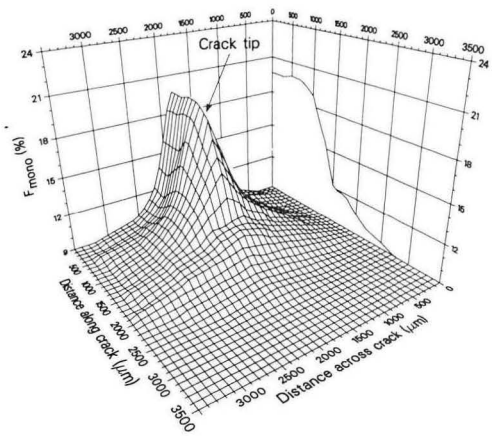


Figure 24
Three-dimensional Raman spectroscopy plot of the morphology of the transformed zone both ahead, and in the wake of the crack tip in peak-toughened (TS) MgO-PSZ ceramic. Plotted along the ordinate is the relative proportion of transformed (monoclinic) phase.

Veirs and G.M. Rosenblatt of the Materials and Chemical Sciences Division to assess a novel, spatially-resolved Raman spectroscopy system in the study of transformed zones surrounding cracks in partially stabilized $MgO\text{-}ZrO_2$ (PSZ). The experimental arrangement makes use of an imaging (2-D) photomultiplier tube to produce a one-dimensional Raman profile of phase compositions along a slit-like laser beam without translation of either the sample or laser beam and without scanning the spectrometer. For the present optical configuration, the spatial resolution was estimated to be equivalent to the detector resolution of 28 μm, and does not appear to be reduced due to secondary scattering events in the PSZ. Results from phase characterization studies of the size, frontal morphology, and extent of transformation of transformation zones surrounding cracks produced under monotonic and cyclic loading conditions were compiled (Figure 24). Particularly large zones were observed in the peak-toughened material, extending 1300 μm ahead of the crack tip with widths of up to 3000 μm. Good agreement was found with similar results determined using optical interference microscopy.

Mechanical Properties of Fiber-Reinforced Brittle Matrix Composite

E. Luh, R.O. Ritchie

The continued need for materials which can perform in high temperature, corrosive environments has coincided with the development of turbine engines. With further progress in the aerospace industry, available materials have been challenged to meet the high demands required for air as well as space vehicles. To meet these demands, research in recent years has turned toward ceramics and ceramic-containing composites in order to fulfill requirements for high strength and toughness at elevated temperatures in corrosive atmospheres. In this study, mechanical properties were examined for a model ceramic-fiber, ceramic-matrix system, namely LAS reinforced with NICALON fibers. Specifically, an experimental study of fracture trends was conducted by systematically changing interfacial properties by heat treatment. To fully consider toughening contributions made by fiber bridging and pull-out, a statistical analysis of pull-out lengths was incorporated into existing formulations. The effects of heat treatment on interfacial properties were also considered photomicrographically to determine physical changes which influence mechanical behavior. The role of subcritical crack growth was examined by cyclic fatigue testing to determine effects in the small-crack regime, such that conclusions could be drawn regarding the role of the fiber-matrix interface in toughness trends and cyclic fatigue behavior.

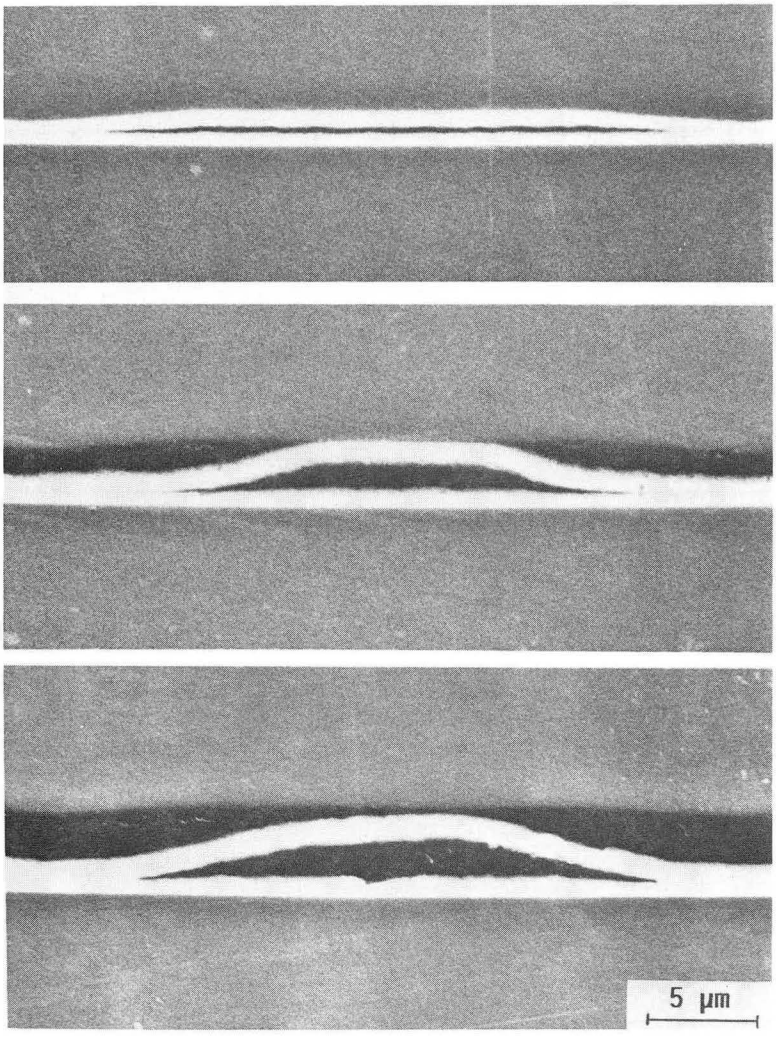
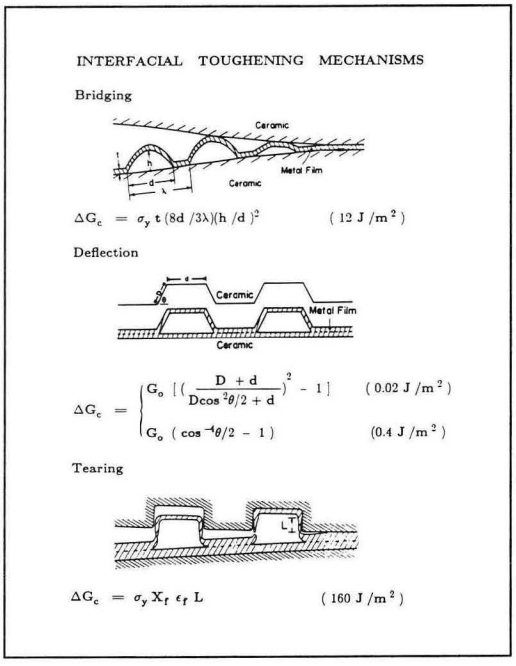


Figure 25 (left)
Micrographs showing the mechanism of crack propagation within the patterned interfacial region of a glass/copper/glass bond, showing a) prior out-of-plane microcracks ahead of the main crack, b) initiation of coplanar microcracks and partial development of the crack-bridging ligaments, and c) plastic stretching of the Cu-film ligaments with simultaneous interfacial bond rupture, before final crack propagation with interfacial failure.

Figure 26 (below)
Models and micro-mechanisms of extrinsic toughening of ceramic/metal interfaces using patterned interfacial regions, showing a) crack-tip shielding via the bridging of metal-film ligaments, b) minimal toughening from crack-tip shielding via crack deflection, and c) tearing of metal-film ligaments.



MECHANICAL PROPERTIES OF CERAMIC/METAL INTERFACES

Methods to toughen ceramic/metal interfaces that employ prescribed arrays of noncoplanar microcrack-like-voids and inclined interface steps have been developed in association with R.M. Cannon of the CAM Electronic Materials Program (see also Electronic Materials Program, Interconnects Project). These features, developed in glass/copper samples made using photolithographic, metal deposition and diffusion bonding processes, promote crack-tip shielding principally from crack bridging by ligaments generated by plastic void growth within the copper (Figure 25). The ensuing plastic stretching, and sometimes tearing of the Cu film ligaments yield the major energy dissipation (Figure 26). Crack deflection can also provide a smaller toughening contribution. Resistance-curve (R-curve) behavior obtains from the bridging, with fracture energies rising to an asymptote that varies from 9 to 160 J/m², compared with inherent

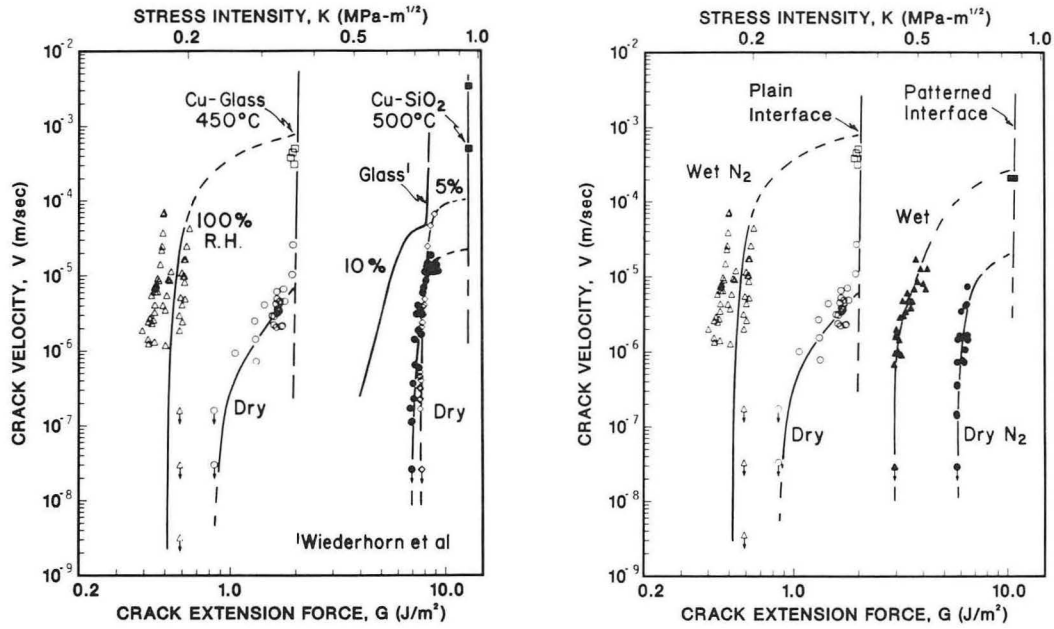


Figure 27
Variation in subcritical crack-growth rates (da/dt) along glass/Cu interfaces as a function of crack extension force in moist and dry gaseous nitrogen: a) compares behavior for plain interfaces bonded at 450 and at 500 C, the latter giving greater inherent fracture resistance; b) compares plain and toughened interfaces, both bonded at 450 C. Note how the presence of arrays of microcrack-voids near the interface results in far lower crack speeds and a 6 to 7-fold increase in both threshold fracture energy and Gc for interfacial fracture.

toughness values of ~2 J/m² for the specific glass/Cu interfaces used. The arrays retard subcritical crack-growth rates, specifically in stress-corrosion crackling and cyclic fatigue; growth rates are higher in moist atmospheres, by orders of magnitude compared to rates for plain interfaces, although the effect in fatigue is not as large (Figure 27).

FRACTURE AND FATIGUE OF TITANIUM ALLOYS

Variable-Amplitude Fatigue-Crack Propagation in Ti Alloys

R.O. Ritchie, C.M. Ward-Close

An experimental and numerical study has been made of the mechanisms of fatigue-crack growth and crack-closure behavior in an α/β titanium alloy Ti-4A1-4Mo-2Sn-0.5Si (IMI 550), following both single and block tensile overloads. Closure *immediately* behind the crack front (near-tip closure), was found to be the main factor controlling load-interaction effects. Single tensile overloads were found to remove *near-tip* closure, and slightly reduce *far-field* closure along the crack length, resulting in an initial acceleration in fatigue-crack growth rates. Subsequent delayed retardation of crack-growth rates was accompanied by an increase in the *near-tip* closure load, due to the enlarged compressive residual stress in the overload plastic zone. High/low block overloads caused greater retardation than single overloads of the same magnitude, and this was attributed to changes in the degree of closure in the wake of the crack. Numerical predictions of such transient behavior, based on a modified Dugdale model, were found to be in close agreement with experimental results, both in terms of observed crack-growth rate and crack opening displacements (Figure 28). Load-interaction effects were found to be most severe when the baseline stress-intensity range (ΔK) was close to the fatigue threshold (ΔK_{TH}), or, when the overload maximum stress intensity (K_{max}) approached the fracture toughness of the material. At low ΔK levels, the magnitude of

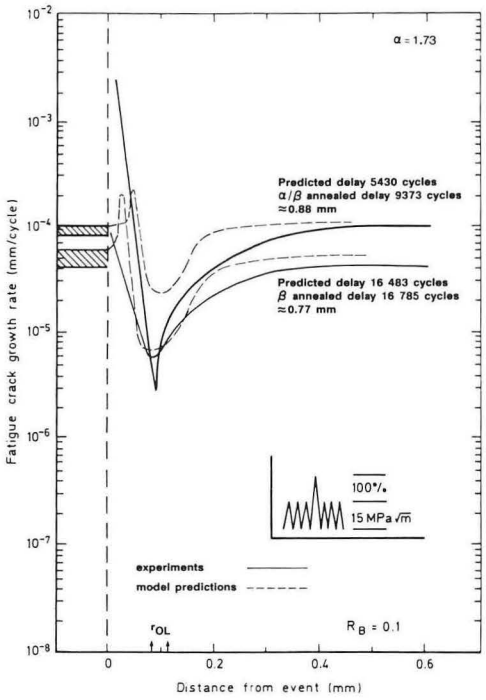


Figure 28
Variation in fatigue crack growth rate in α/β-annealed and β-annealed titanium alloy microstructures following single 100% tensile overloads applied at a baseline ΔK level of 15 MPa/m. Shown are experimental results (solid line) and model predictions (dotted line). Vertical arrows indicate the extent of the overload plastic zone, r_{OL}.

the delay was sensitive to microstructure and found to be enhanced in coarse-grained β-heat-treated microstructures compared to standard fine-grained α/β microstructures. Based on these results, mechanistic sequences have been proposed to explain the transient fatigue-crack growth behavior following single and block tensile overload cycles.

Fatigue-Crack Propagation in Ti-Ni Shape-Memory Material

R.H. Dauskardt, R.O. Ritchie

The fatigue-crack propagation behavior of near-equiatomic Ti-Ni shape-memory alloys has been investigated in collaboration with T. Duerig of Raychem, over a wide spectrum of growth rates from 10^{-11} to 10^{-6} m/cycle. Studies have been performed at room temperature in both nontransforming microstructures (stable austenite and stable martensite) and transforming austenitic microstructures (selected to undergo an *in situ* reversible or nonreversible stress-induced shear transformation to martensite). Crack-growth rates were found to be faster, and fatigue threshold ΔK_{TH} values to be lower, than in other metallic engineering alloys of comparable strength; values of ΔK_{TH} vary from 5.4 to 1.6 MPa√(m) in the stable and unstable (reversible) austenitic microstructures, respectively (Figure 29). Fatigue-crack growth rates were found to be much slower in the nontransforming microstructures; the occurrence of the *in situ* trans-

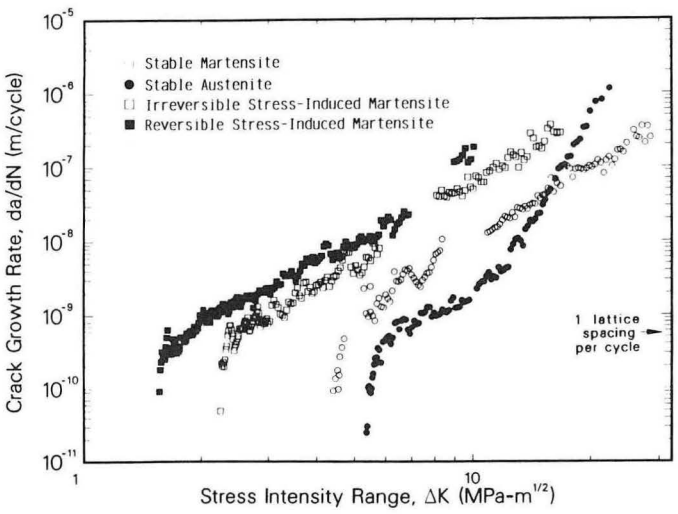


Figure 29
Variation in fatigue-crack growth rates (da/dN) as a function of the stress-intensity range (ΔK) in near-equiatomic Ti-Ni shape-memory alloys at room temperature (R = 0.1). Note the faster growth rates and lower fatigue threshold ΔK_{TH} values in the transforming microstructures, compared to the stable austenitic and stable martensitic microstructures.

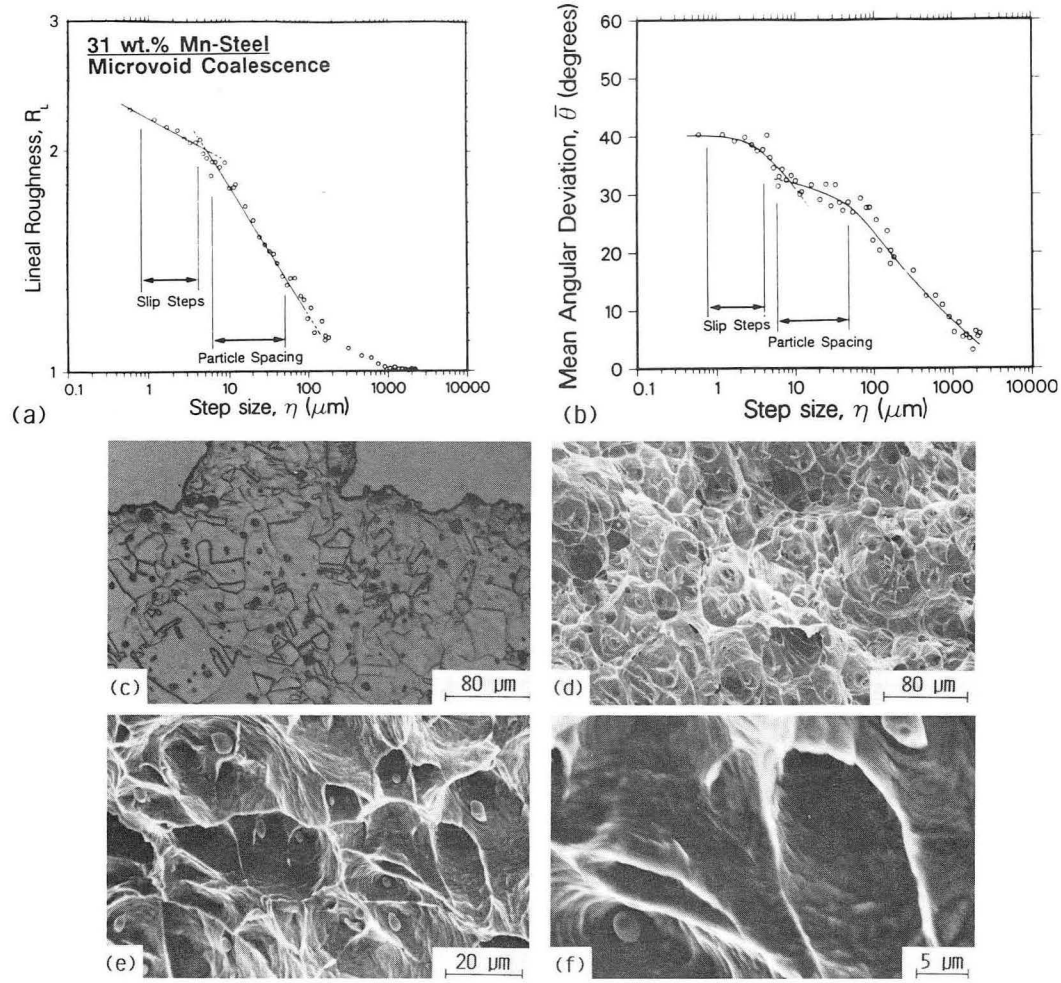


Figure 30 (above)
Fractal characteristics of microvoid coalescence, of Mn-steel at room temperature, showing plots of a) lineal roughness, R_L, and b) mean angular deviation, θ, as a function of measuring step size, η, c) optical micrograph of crack-surface profile, and d-f) scanning electron micrographs of fracture surface at increasing magnifications.

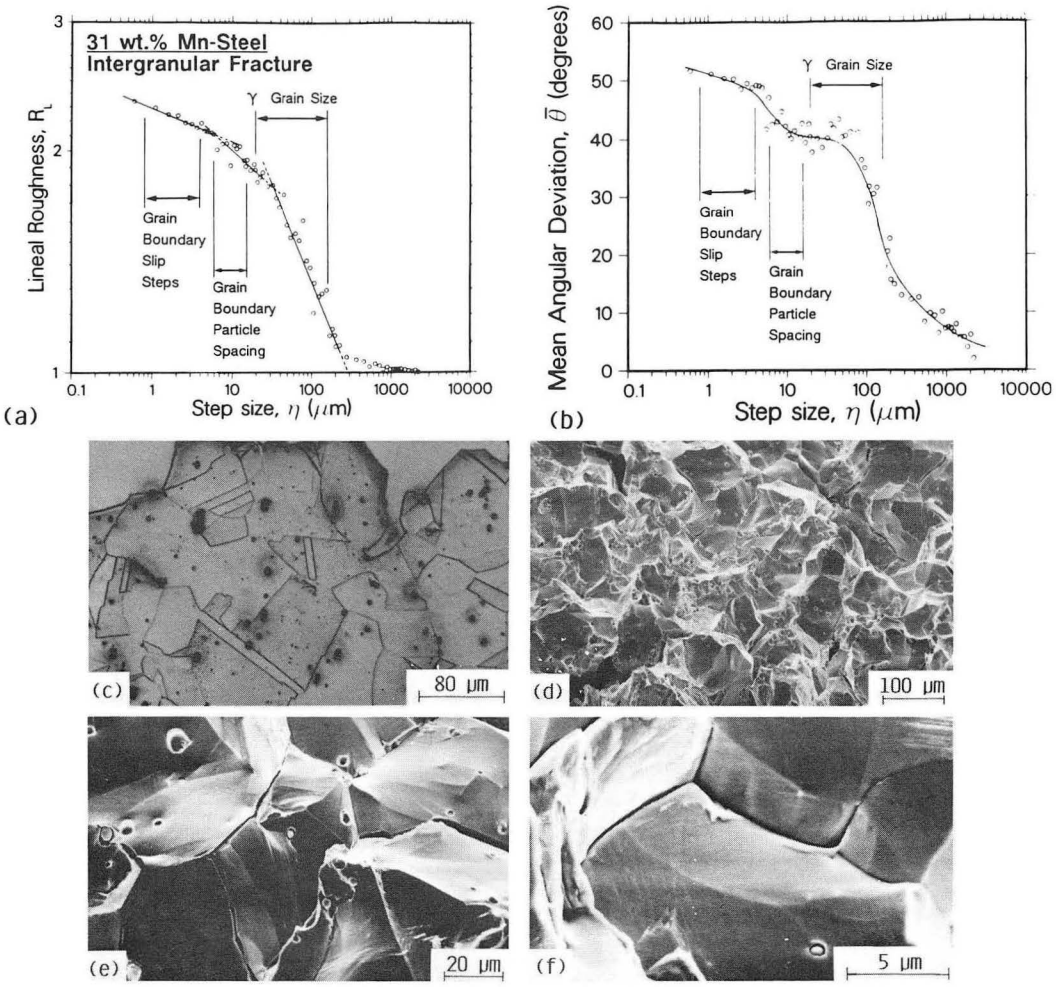
Figure 31 (page 129)
Fractal characteristics of intergranular fracture, of Mn-steel at -196°C, showing plots of a) lineal roughness, R_L, b) mean angular deviation, θ, as a function of measuring step size, η, c) optical micrograph of crack-surface profile, and d-f) scanning electron micrographs of fracture surface at increasing magnifications.

formation, whether reversible or irreversible, led to a significant increase in growth rates and a 50 to 70% decrease in the threshold ΔK_{TH}. Reasons for such behavior were analyzed in terms of the inherent properties of the parent and product phases, the energy of transformation, and dilatant and largely shear components of the phase change, and the role of these factors in suppressing shear localization and inducing crack-tip shielding.

FRACTAL CHARACTERIZATION OF FRACTURE SURFACES

R.H. Dauskardt, F. Haubensak, R.O. Ritchie

To examine the usefulness of the fractal concept in quantitative fractography, a series of classical fracture surfaces, namely transgranular cleavage, intergranular fracture, microvoid coalescence quasicleavage and intergranular microvoid coalescence, were analyzed in terms of fractal geometry through the use of recently developed quantitative fractographic techniques. Specifically, the five brittle and ductile fracture modes were studied, from three well-characterized steels (a mild steel, a low-alloy steel and a 31 wt.% Mn-steel) where the salient microstructural dimen-



sions contributing to the final fracture morphology were measured. Resulting plots of the mean angular deviation, and Richardson (fractal) plots of the lineal roughness, as a function of the measuring step size, were interpreted with the aid of computer-simulated fracture-surface profiles with known characteristics. It was found that the ranges of resolution, over which the fractal dimension was constant, corresponded to the pertinent metallurgical dimensions on the fracture surface and thus could be related to microstructural size-scales (Figures 30 and 31).

CERAMIC PROCESSING

A number of single phase ceramics (MgO, ZnO, alumina, and glass) have served as model materials. Particularly ZnO has been studied most extensively so far, both under conditions of isothermal and of constant heating rate sintering. This work is a collaboration in part, with the Sandia National Laboratory, Albuquerque, where the aim is to develop improved high-field varistors. This work has produced an understanding of how the microstructure of the initial powder compact may be manipulated to eliminate or minimize a limited range of structural imperfections such as those inherently produced when compacting common commercial powders.

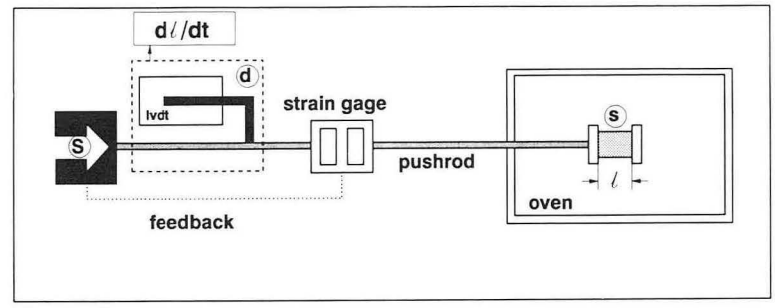


Figure 32
Schematic of the loading dilatometer. The sample (s) is held in a dilatometer (d) at a controlled temperature. The dilatometer monitors the length change, i.e., the densification of the sample, as a function of time and temperature. A small, controlled load is applied by the solenoid (S), so that the total length change of the sample is caused by creep as well as by densification. Results indicate that the creep is simply a constant volume deformation, superimposed on the densification, provided the applied load is small compared to the sintering stress. The creep rate can thus be separated from the simultaneous densification rate in this experiment.

Several model particulate composites have also been examined, particularly ZnO with a SiC dispersion. The generic aspects of the role of a dispersed inert phase on densification and microstructure development has been assessed in this system. This work reveals the importance of achieving the highest degree of uniformity in the initial, compacted structure of particulate composites if high performance materials are to be obtained.

The high temperature structural materials that have been examined include both single phase ceramics as well as particulate composites, and have focused on SiC containing systems. SiC sintered with the aid of aluminum, SiC prepared with incorporation of polycarbosilanes and polycarbosilazanes, and SiC containing a dispersion of TiB_2 are under close investigation. Processing conditions are under development that lead to improved fracture toughness and to increased resistance to high temperature creep and cyclic fatigue.*

(*This work done in collaboration with R. Ritchie of the CAM Mechanical Behavior of Materials project.)

Fundamental Studies in Ceramic Processing

Y. Boiteaux, R. Brook, M.-Y. Chu, L. De Jonghe, M. Ghirlanda, F. Liu, M. Rahaman

An improved understanding of the sintering process can result from the determination of the apparent densification viscosity and the driving

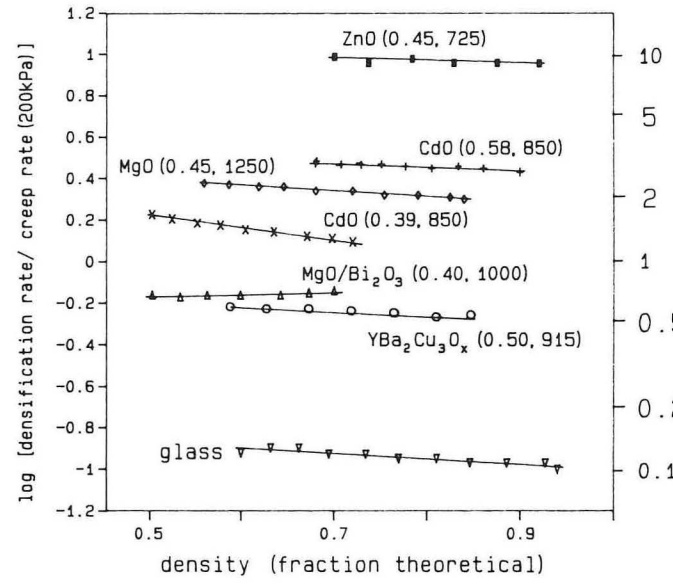


Figure 33
The evolution of the densification rates over the creep rate for a variety of ceramic systems is shown here for isothermal sintering experiments. The remarkable result is that this ratio, which is proportional to the sintering stress, the driving force for the densification, is constant throughout the densification process. The numbers in parenthesis are the starting relative density and the sintering temperature in centigrade.

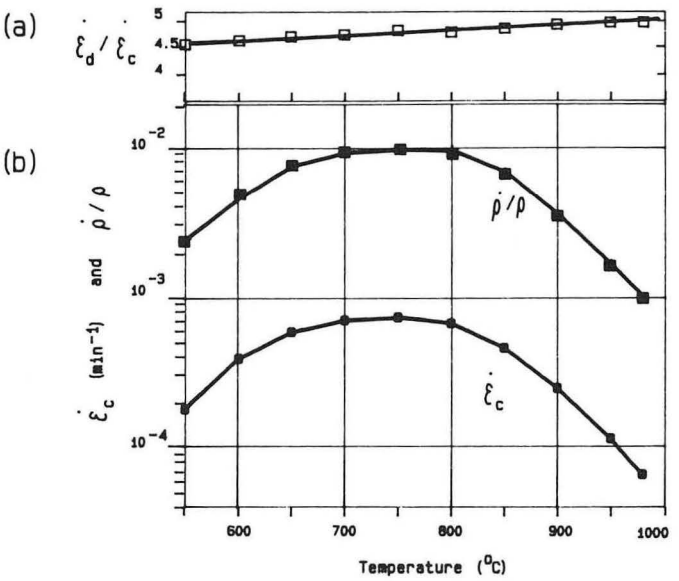


Figure 34
Results are shown here for the non-isothermal densification of ZnO. At the indicated constant heating rate, the ratio of the densification rate over the constant-stress creep rate $\dot{\varepsilon}_d/\dot{\varepsilon}_c$, remains constant. This result, as well as the ones shown in Figure 2, allow for a significant simplification in the analysis of the apparent viscosity of densification and hence of the interaction of microstructure development and densification.

force for densification. To achieve this, the creep of a densifying powder compact under a known constant load was measured simultaneously with its densification. From the ratio of the densification rate over the creep rate, the driving force for densification can be deduced, since the creep viscosity and the densification viscosity were found to be intimately related. A loading dilatometer was used for this purpose (Figure 32). One important finding in these fundamental studies was that the driving force for densification—the densification rate over the creep rate—is mainly determined by the conditions realized in the initial powder compact, and is quite insensitive to further densification. This has been shown to be the case for a wide variety of ceramics, not only in isothermal densification, but also in non-isothermal densification (Figure 33, 34). This remarkable result allows a significantly improved understanding of the sintering process, since it simplifies the interpretation of the kinetics of densification.

Microstructure Development in Ceramics during Fabrication

R. Brook, M.-Y Chu, L. De Jonghe, M. Ghirlanda, F. Liu, M. Rahaman, F. Spaepen

Many of the important mechanical properties of ceramics depend critically on their homogeneity. Uniform grain size at high density for single phase ceramics is especially desirable since it can be expected to improve all forms of mechanical performance. However, the required homogeneity is not readily achieved, especially when low cost, technical powders must be used. Powder processing methods that improve or assure homogeneity of the finished ceramic bodies must be devised .

For single phase ceramic it was found that modifying the heating schedule during densification can lead to significant improvements in the performance of technical powders. The homogeneity of a sintered MgO ceramic was improved significantly by using a 2-step heating schedule (Figure 35). The improvement of the microstrucure during the low-temperature coarsening likely to result from the evolution of the particle and pore structure toward a steady-state one which is more homogeneous

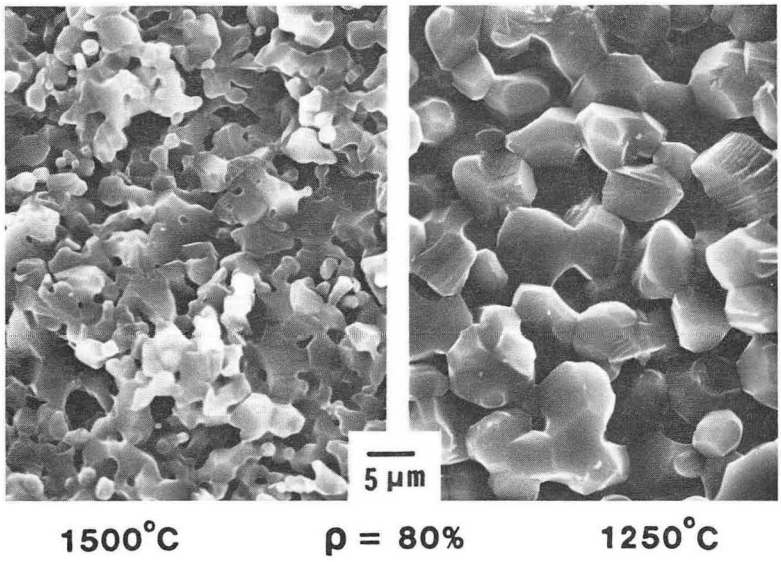


Figure 35
The microstructures are compared of two MgO samples sintered at different time-temperature schedules. The sample on the right was sintered to 80% density by heating directly to 1500°C and holding for one hour, while the more homogeneous microstructure on the right was achieved by a 2-step sintering in which the powder compact is first held for an extended time at 1250°C, and then brought rapidly to 1500°C to sinter to the same density.

than the starting one, under conditions where coarsening is rapid compared to densification. Since all powder compacts, both from monosized or the multisized technical powders, evolve towards a similar normalized steady state microstructure, it becomes possible using the low temperature limited coarsening of the technical powders, to approach the homogenous microstructures that were thought to be obtainable only with monosize powder.

Particulate Ceramic Composites

G. Brown, T. Buchanan, L. DeJonghe, D. Kapolnec,

Homogeneity of the sintered microstructure of particulate composites, e.g. titanium diboride particles in a SiC matrix, have a determining influence on high temperature mechanical properties such as creep and fatigue. In creep of a heterogeneous ceramic, for example, the applied load will progressively be transferred to those regions with a relatively higher

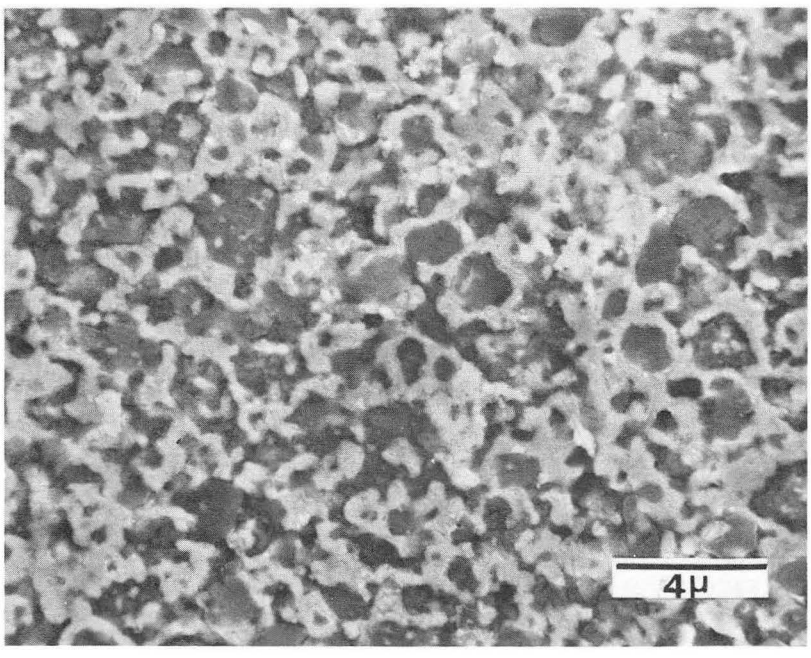


Figure 36
SiC/Cu-matrix composite prepared from silicon carbide powder that was coated with Cu by an electroless plating process. The dark particles are the silicon carbide, while the copper matrix appears light in this optical micrograph of a polished cross section. The SiC particles tend to be isolated from each other by this processing technique.

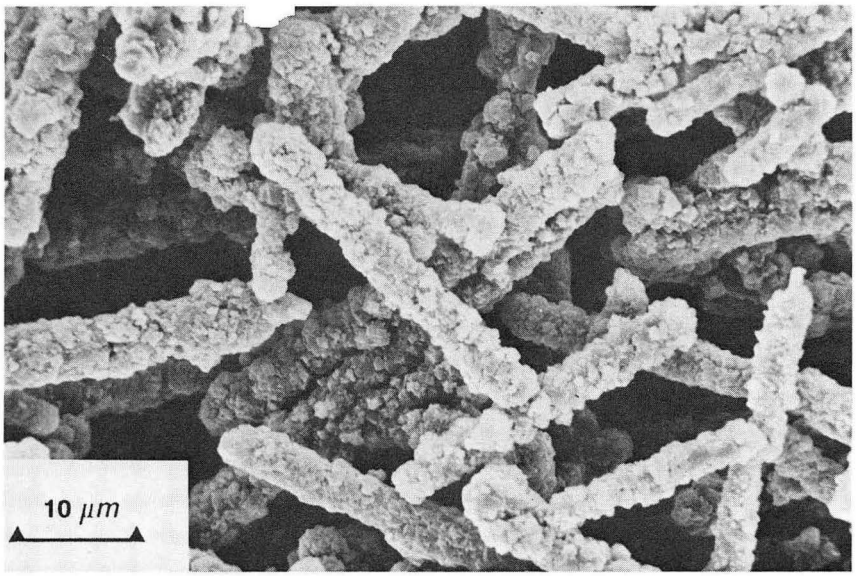


Figure 37
Alumina-coated densification whiskers. These whiskers where coated with aluminum sulfate by heterogeneous precipitation. A heat treatment then converted the aluminum sulfate to aluminum oxide.

viscosity. These are typically large grained regions or clusters of the dispersed phase. Creep-rupture then is initiated from these heterogeneities. It is thus expected that strict control of the spacial homogeneity of particulate compacts will lead to significantly improved high temperature performance. One way of achieving homogeneity in a particulate composite is to start with powders in which the dispersed phase, ideally monomodal, is coated by a layer of the matrix phase. While the preparation of such powders presents a significant technical challenge, initial results on Cu-coated SiC powders have provided a first metal/ceramic composite prepared by this method (Figure 36). The slurry coating methods used in the fabrication of this composite are presently extended to produce ceramic-matrix and even a polymer-matrix composite with second phase loading of over 50 vol% (Figure 37).

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AWARDS

- K.T. Venkateswara Rao won the Outstanding Graduate Student paper contest for the Metals, Minerals and Materials Society of the AIME.

INDUSTRY INTERACTIONS

Gifts

- The gift from ALCOA, their second to the program, is being used to continue studies seeking to understand the basis of exceptional low temperature properties of low density aluminum-lithium alloys.
- Ford, LTV, and Rouge Steel presented a gift as a group for fundamental and application-oriented research on formability of sheet steels.

Advisory Board

Philip E. Bretz (Chairman)	ALCOA
Govind R. Chanani	Northrop Corporation
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Sharon L Langenbeck	Lockheed Corporation
A.L. Wingert	Boeing Commercial Airplane Company

Industrial Collaborations

- In a collaborative project with ALCOA, Low temperature properties of Al-Sc(-Mg) sheet were investigated.
- The formability of electrogalvanized steel was investigated in collaboration between the CAM Structural Metals and Alloys project and the Ford Motor Company, LTV Steel, and Rouge Steel.
- In a collaborative effort with D.B. Marshall of Rockwell International, the subcritical growth of fatigue cracks under (tension-tension) cyclic loading was studied.
- In a collaboration with T. Duerig of Raychem, the fatigue-crack propagation behavior of near-equiatomic Ti-Ni shape-memory alloys was investigated.
- The high-temperature fatigue properties of 8090 Al-Li alloy was investigated with Northrop Corporation.

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Ritchie, R.O., *Fatigue and Fracture of Pyrolytic Carbon-Coated Graphite used in Cardiac Valve Prosthetic Devices*, presentation to the FDA, Washington, DC, August 1988.

Ritchie, R.O., *Fracture and Fatigue Testing of Advanced Materials*, invited presentation to MTS Systems Corporation, Minneapolis, Minnesota, August 1988.

Ritchie, R.O., *Life Prediction of Prosthetic Cardiac Valve Implants*, invited presentation to Shiley, Inc, Vancouver, Canada, August 1988.

Ritchie, R.O., *Mechanisms of Fatigue Crack Propagation in Metals, Ceramics and Composites: Role of Crack-Tip Shielding*, DOE Workshop on Mechanics and Physics of Crack Growth, Keystone, Colorado, August 1988.

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*Joint study with R.M. Cannon of the CAM Electronic Materials Program.

Ceramic Processing Project

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Surface Science and Catalysis

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162 . . . . . Instrumentation for Surface Science

Catalyst Design and Characterization
Surface Structure and Interface Compounds
Instrumentation for Surface Science

Surface Science and Catalysis

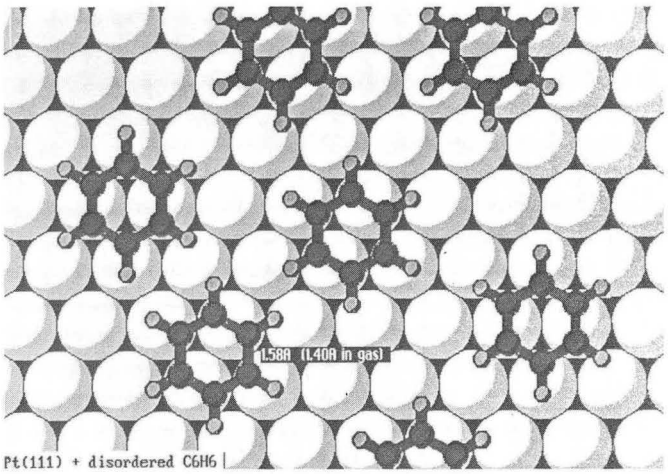
The CAM Surface Science and Catalysis program pursues interdisciplinary, basic research studies of surface and interface materials, phenomena, and processes at the molecular level. The research is focused on the chemical and mechanical properties of surfaces and on the development of new surface instrumentation to permit atomic level characterization of interfaces. Current areas of research include:

- ***CATALYST DESIGN AND CHARACTERIZATION***—the synthesis and characterization of microporous crystalline catalysts such as zeolites; the study of single crystal catalysts as model systems to further the surface science of catalysis; the catalytic hydrogenation of CO and gasification of coal.
- ***SURFACE STRUCTURE AND INTERFACE COMPOUNDS***—the study of the structure of surfaces, the bonding of adsorbed monolayers to them, and the formation and characterization of surface compounds and coatings.
- ***INSTRUMENTATION FOR SURFACE SCIENCE***—the examination of catalyst and other surfaces using scanning tunneling microscopy, non-linear optics, solid state NMR spectroscopy, and low energy electron diffraction for surface crystallography.

The aim of the ***CATALYST DESIGN AND CHARACTERIZATION*** project is to develop a fundamental understanding of the factors governing synthesis and performance of catalysts for a variety of processes. The focus is on the synthesis and characterization of novel microporous materials, including zeolites and transition metal nitrides, carbides, and oxides; the preparation and characterization of single-crystal, model catalysts; and the investigation of the fundamental aspects of the hydrogenation of CO and char gasification. Recent research results include several new findings:

- In a collaboration with the Harshaw/Filtrol Partnership, magic angle NMR was used to follow the elementary processes involved in the synthesis of NaY zeolite. In collaboration with W.R. Grace, NMR was used to characterize the formation of aluminosilicate anions from well-defined silicate and monomeric aluminate anions.
- New catalyst mixtures of alkali and alkaline earth oxides were developed, which permit gasification without deactivation due to ash components in the char.
- Alumina was found to restructure single-crystal iron surfaces to their most active crystallographic face for ammonia synthesis at high pressures.
- Bimetallic Pt-Re surfaces were found to be an order of magnitude more reactive for hydrocarbon conversion than the Re(0001) single-crystal surface at high pressures.

The ***SURFACE STRUCTURE AND INTERFACE COMPOUNDS*** project consists of three closely-linked efforts. The objective of the **Surface Structure and Bonding** group is the development of the molecular science of surface phenomena by means of the understanding of atomic-scale surface structure and chemical bonding of adsorbed monolayers and thin film coatings and their interfaces. Surface crystallography with low-energy electron diffraction (LEED) is used to determine bond distances and bond angles at surfaces.



Vibration analysis by high-resolution electron energy loss spectroscopy is used to study molecular reactions and adsorbed species. Scanning tunneling microscopy (STM) has been used to study the structure of chemisorbed layers of sulfur on Mo and Re single crystals.

The **Coatings** effort produces surface films that impart novel mechanical properties (scratch resistance, hardness) and chemical properties (protection against corrosion, diffusion barriers) to the substrate. Films (TiN, hard amorphous carbon, diamond-like carbon and SiC on metals and semiconductors) are grown using excited state reactants produced by plasmas and sputtering allowing the production of compounds that would otherwise necessitate high temperatures or that could not grow.

The **Surface Compounds** effort involves studies on submonolayers of atomic and molecular adsorbates, as well as metal oxides (TiO_2, Al_2O_3 and FeO), which can modify the chemical and mechanical properties of metal surfaces. These compounds are excellent models for supported metals on oxides in catalysis (in methanation reactions and ammonia synthesis, for example). They also allow the study of interface formation during epitaxial growth, a critical aspect of thin film production both for mechanical protection of surfaces and also as diffusion barriers.

During the past year:

- For the first time, bond lengths and angles were determined for disordered molecules (carbon monoxide and benzene) on single-crystal metal substrates, using diffuse LEED.
- Asymmetric atomic adsorption sites were discovered for sulfur on the Mo(100) surface and the saturation (1x2) structure was imaged in real space at atmospheric pressures.
- Hard carbon films were shown, by STM, to exhibit regions of disordered and diamond-like carbon.
- Thin ordered iron oxide films grown on Pt(111) were observed to restructure into small clusters when several monolayers of sodium were added and the surface was heated to 850 K.

The ***INSTRUMENTATION FOR SURFACE SCIENCE*** project is concerned with the development of new techniques and instruments for the study of surfaces. Its experimental components—scanning tunneling microscopy, and nonlinear optical techniques—are supported by a theory group concerned with surfaces, interfaces and clusters. During the past year:

- The STM was used to study the initial stages of the growth of thin metal films on graphite and to modify surface topography on the atomic scale.
- Second and third harmonic generation were employed to measure nonlinear polarizabilities of molecules, the two-dimensional phase transition of a polymer monolayer, and the bulk-surface diffusion kinetics.
- Infrared-visible sum-frequency generation was developed for surface vibrational spectroscopy of organic molecules adsorbed at air/liquid/solid interfaces.
- *Ab initio* pseudopotential density function calculations and many-body quasiparticle calculations were used to interpret STM images graphite, and to study the new compound BC_3 as well as S chemisorption on Mo surfaces.

CATALYST DESIGN AND CHARACTERIZATION

MICROPOROUS CRYSTALLINE MATERIALS

Aluminosilicates

A.T. Bell, D. M. Ginter, W.M. Hendricks

The understanding of the role of precursors in determining crystal structure of the final product will contribute to the ability to control the synthesis of zeolites with predetermined structures and to synthesize presently unknown but industrially useful zeolites. This question has been approached through the use of such modern techniques as solid state nuclear magnetic resonance (NMR) spectroscopy, electron diffraction, x-ray spectroscopy and electron microscopy, some of which were developed or specifically modified for these applications at CAM.

The characterization of zeolite synthesis gels by standard liquid-line NMR spectroscopy is difficult because the high viscosity of the medium reduces the rate of molecular tumbling, which usually averages out the effects of dipolar and quadrupolar interactions and chemical shift anisotropy. Consequently, liquid-line spectra of aluminosilicate gels are dominated by broad features. In research supported in part by the Harshaw/Filtrol partnership, a technique was developed for obtaining magic-angle spinning NMR (MAS-NMR) spectra of whole gels and wet solids present during the synthesis of NaY zeolite. Resolution was improved by spinning an aluminosilicate gel at 2.6 kHz (Figure 1). The narrow features in the spectrum are due to silicate anions present in the solution phase of the gel; the broad band is due to an amorphous aluminosilicate, which comprises the solid phase of the gel.

A study of the synthesis of NaY zeolite from a silica sol and an alkaline solution of sodium aluminate revealed several features. Initial mixing of the reactants immediately transforms the sol into a gel but does not influence the structure within the sol particles. Dissolution of the gelled sol at room temperature occurs over a 48 hour period. The initial products of sol dissolution are monomeric silicate anions; however, as more silica dissolves, oligomeric silicate species are formed. Reaction of the dissolved silicate anions with aluminate anions produces aluminosilicate species which progressively form an amorphous aluminosilicate gel.

In other research supported in part by W.R. Grace and Company, studies were undertaken to characterize the reactions of well defined silicate anions with aluminate anions. As was previously demonstrated, double-three, double-four, and double-five membered silicate structures can be produced by appropriate choice of organic base (tetra alkyl ammonium hydroxide) and an additive such as methanol or dimethylsulfoxide. Studies are in progress to establish the effects of temperature and

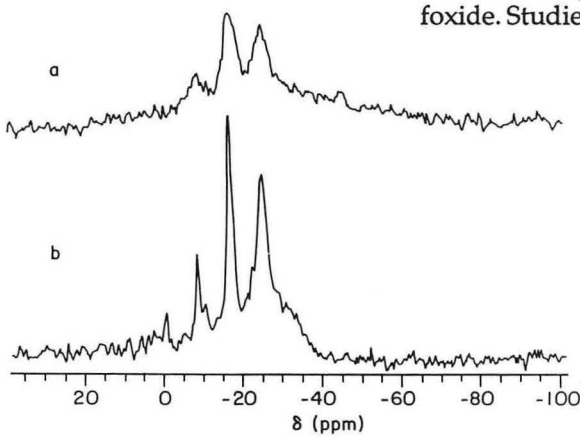


Figure 1
^{29}Si MAS-NMR spectra of a sodium aluminosilicate gel of nominal composition 4.1 Na_2O:1.0 Al_2O_3:13.1 SiO_2:189 H_2O. Spectrum (a) is taken with a static rotor, while spectrum (b) is taken with the rotor spinning at 2.6 kHz. All features are referenced to monomeric $Si(OH)_4$ at 0 ppm (-71.3 ppm relative to TMS).

pH on the relative reactivity of different silicates. Both ^{29}Si and ^{27}Al NMR spectroscopy are being used to characterize the products formed. Preliminary results have confirmed earlier observations that at room temperature, double-four membered rings are significantly less reactive than smaller silicate structures, such as cyclic trimers, dimers, and monomers.

Ferrisilicates

R. Csencsits, R. Gronsky

In a collaborative study with V. Nair of Union Carbide (Tarrytown, NY) and R. Szostak of Georgia Institute of Technology, the microstructure and microchemistry of a ferrisilicate catalyst (FeZSM-5) were monitored as a function of various synthesis conditions. Transmission electron microscopy results indicate that second phase iron-rich particles (< 2.5 nm) are formed after thermal treatment of samples with SiO_2/Fe_2O_3 ratio = 50, and in all FeZSM-5 samples after steam treatment at 550 °C for 2 hours (Figure 2). Hydrothermal treatment of all samples grown from stirred gels produced a homogeneous distribution of iron-rich second phase particles ranging in size from 1.5 to 4 nm for steaming times of 1, 2, or 4 hours at 550 °C. However, when the FeZSM-5 samples were steamed at 700 °C for 4 hours, the second phase particles ranged in size from 5 to 15 nm; particles larger than 10 nm were generally found on the surfaces of the individual FeZSM-5 crystallites within the agglomerate. Prolonged steam treatments resulted in coarsening of the particle size distribution.

Both high resolution phase contrast imaging and microdiffraction indicate that some of the second phase particles are $FeSiO_3$ with iron in the 2+ oxidation state. This contradicts previous Mössbauer data indicating the presence of iron only in the 3+ oxidation state, and suggesting that the particles were therefore α-Fe_2O_3. Further microdiffraction work is needed to verify the statistical sample in this analysis, and to check whether there may be a mixture of oxide phases.

Transition Metal Nitrides and Carbides

A.T. Bell, G.W. Haddix, J.A. Reimer

Transition metal nitrides and carbides, such as Mo_2N, Mo_2C, W_2C, and WC, have been shown to be effective catalysts for a variety of reactions, including CO hydrogenation, olefin hydrogenation, hydrocarbon reforming, ammonia synthesis, and hydrodenitrogenation (HDN). The transition metals are less expensive and more abundant than the noble metals which are currently used for these reactions. Little is known about the reaction chemistry on transition nitrides and carbides, however. The metal nitrides studies examine the surface chemistry of a transition metal

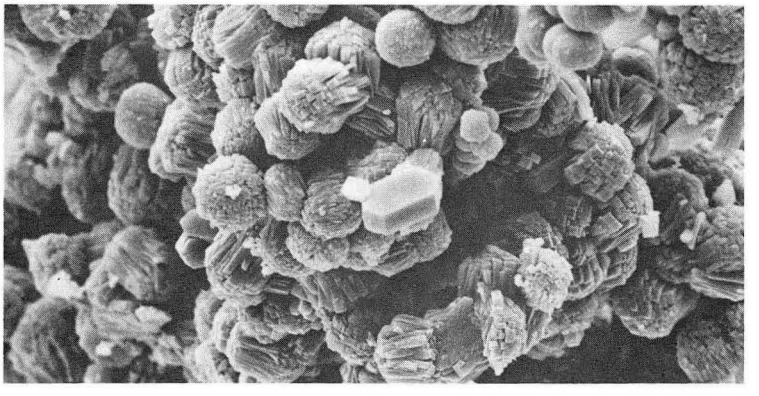


Figure 2
SEM image of iron silicate molecular sieve in the as-synthesized form, grown from an unstirred gel with SiO_2:Fe_2O_3-ratio = 50 showing intergrown crystals and a prominent single crystal of FeZSM-5.

nitride catalyst, gamma-molybdenum nitride (γ-Mo_2N), under conditions representative of hydrodenitrogenation (HDN). The HDN is an important step in the refining of petroleum and is essential for removal of nitrogen in gasoline or fuel oil fractions so that a cleaner-burning fuel is produced.

In previous years we have shown that NMR is an effective technique for identifying surface species on γ-Mo_2N, as well as on other catalysts. In particular, adsorbed ammonia, carbon monoxide, and hydrogen were studied on γ-Mo_2N with NMR. During this past year, this work was extended to include the adsorption and reaction of acetonitrile on this catalyst surface.

After preparing γ-Mo_2N by temperature-programmed reduction of molybdenum oxide, the adsorption and reaction of $CH_3{}^{13}CN$ (acetonitrile) was investigated via *in situ* ^1H and ^{13}C NMR spectroscopy (Figure 3). It was found that acetonitrile adsorbs molecularly at room temperature, with a significant fraction of the adsorbate in a highly mobile state. Upon reduction in flowing H_2 some of the adsorbed CH_3CN converts to adsorbed $CH_3CH_2NH_x$ This hydrogenation product is also mobile at room temperature on the catalyst surface. At the highest reduction temperatures residual proton NMR spectra show that cleavage of the C-N bond has occurred and NH_x fragments are left on the catalyst surface.

These investigations have laid the groundwork for similar studies of adsorbed nitrogen heterocycles, such as pyridine and quinoline, and their HDN products. The selectivity of an HDN catalyst is determined by the ability of the catalyst to promote hydrogenation (i.e., reaction with hydrogen) of only the heterocyclic ring(s) of the nitrogen heterocycles, and not other aromatic rings or olefinic groups. The identification of adsorbed reaction intermediates by NMR may aid in determining the factors which strongly influence the selectivity in HDN catalysis.

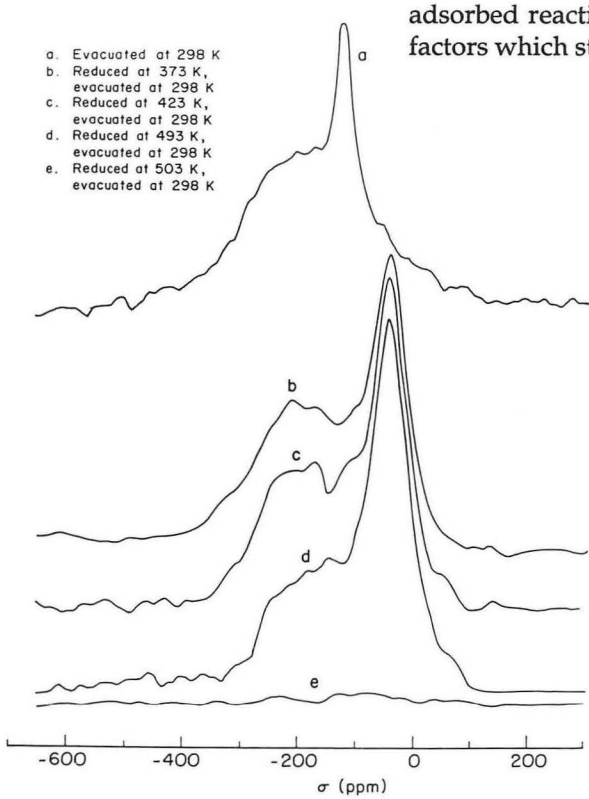


Figure 3
^{13}C NMR spectra obtained after reduction of $CH_3{}^{13}CN$ at increasing temperatures over Mo_2N.

Supported Vanadia

A.T. Bell, T.S. Oyama†, G.A. Somorjai, G.T. Went

Oxide catalysts are used for oxidation reactions that account for more than 25% by volume of the top 20 chemicals produced worldwide. Their use to catalyze NO_x and SO_x oxidations will increase in the U.S. in the next few years as more stringent air pollution laws are enacted. Spectroscopic studies have been aimed at understanding how surface geometry affects activity and selectivity, the structure of the catalyst on the support and how it is affected by dispersion, and the mechanism by which the support affects activity and selectivity.

Raman and NMR spectroscopy are being used to characterize V_2O_5 supported on SiO_2, TiO_2, and Al_2O_3. Both non-invasive techniques provide information about the local environment of oxygen and vanadia. Results obtained by Raman spectroscopy have revealed that at low loadings, V_2O_5 disperses in the form of isolated vanadyl species, whereas at higher loadings, small (<4nm) crystallites of V_2O_5 form. The dispersion of vanadia is considerably better on titania than silica. Preliminary results of ^{17}O NMR spectroscopy suggest that three different oxygen environments can be isolated. Studies are underway to identify the nature of the environments and the manner in which the distribution of environments changes as a function of catalyst preparation conditions.

Metal Oxide Promoters

A.T. Bell, M. Salmeron, G. A. Somorjai, K.J. Williams

Metal oxides have been shown to be effective promoters of metal catalysts used for CO hydrogenation and NO reduction. The effects of titania on rhodium have been investigated using submonolayer quantities of titania deposited onto a rhodium foil. The structure and composition of the titania overlayer have been characterized by ion scattering spectroscopy, Auger electron spectroscopy, and x-ray photoelectron spectroscopy. At submonolayer coverages the titania forms two-dimensional islands surrounded by a high concentration of anionic defects. During the past year, studies were conducted to establish the effects of titania overlayers on the hydrogenation of ethylene, the hydrogenolysis of ethane, and the hydrogenation of acetone. Titania deposition was found to suppress the rates of ethylene hydrogenation and ethane hydrogenolysis in direct proportion to titania coverage and had no effect on the activation energy for either reaction. By contrast, the hydrogenation of acetone to isopropanol was found to pass through a maximum with titania coverage. At a coverage of 0.45, the rate of reaction was six-fold higher than that observed for the clean surface (Figure 4). This behavior is similar to that previously observed for CO hydrogenation.

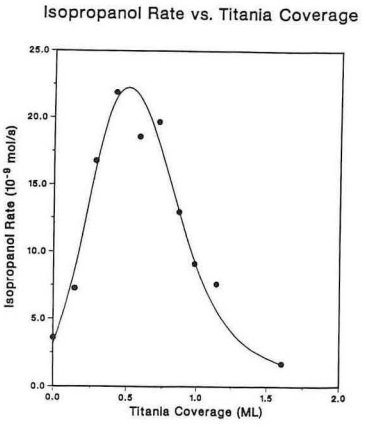


Figure 4
Rate of isopropanol formation from the hydrogenation of acetone on a Rh foil as as function of titania coverage. Reaction conditions are as follows: partial pressure of acetone, 10 torr; partial pressure of hydrogen, 750 torr; temperature, 160°C.

SINGLE CRYSTAL CATALYSTS

Clean, well characterized single crystals (in ultra high vacuum), using a variety of surface science techniques, are enclosed in an isolation cell that can be pressurized up to 100 atm with reactant gases. This cell can serve as a flow or batch microreactor and can be used to determine reaction kinetics. The isolation cell can be evacuated and the single crystal catalyst can be modified by the deposition of promoters (alkali metals, other transition metals, etc.). By changing the structure of the single crystal surface, the structure sensitivity of the catalytic process can also be explored (including the roles of steps and kinks). Ordered oxide or sulfide catalysts are prepared by condensation of metal monolayers from the vapor phase (for example iron onto a platinum crystal surface) and subsequent oxidation or sulfidation. By continuing this process layer by layer, oxide or sulfide thin films are grown and then utilized as model catalysts.

This year, several studies of catalysts and reactions of industrial importance were completed. These include: iron and rhenium promoted by alumina and potassium for studies of ammonia synthesis; molybdenum in its sulfided form for the hydrodesulfurization of thiophene; rhodium for the synthesis of butyronitrile from butanol and ammonia; TiO_2-promoted rhodium for the hydrogenation of carbon monoxide; and Pt-Re alloys for the hydrogenolysis of ethane.

Methods were also developed to grow ordered oxide and sulfide thin films on metal single crystal surfaces (FeO, V_2O_3, and ReS_2). These model systems are being employed to explore the partial oxidation and the isomerization of hydrocarbons.

Alumina and Potassium Promotion of Ammonia Synthesis over Iron Single Crystals

G.A. Somorjai, D.R. Strongin

Combined high pressure and surface science studies show that the (111) and (211) oriented iron crystal surfaces are the most active for ammonia synthesis, while the (100) orientation is much less active and the (110) close packed surface is inactive. The promoter effect of aluminum oxide is due to its interaction with iron oxide during the preparation stage of the catalyst. In the presence of alumina, iron restructures and the most active Fe(111) and Fe(211) crystal faces are stabilized. In the presence of adsorbed potassium, the rate of ammonia synthesis increases markedly on the (111) and (100) crystal faces even though no more than 15% of a monolayer of potassium can be stabilized on the iron surface under the reaction conditions. Adsorbed potassium induces changes in the reaction orders for both ammonia and hydrogen without changing the activation energy for the reaction. The presence of co-adsorbed potassium increases the rate of dinitrogen dissociation mostly by lowering the concentration of adsorbed ammonia, thus making more catalytic sites available for dinitrogen dissociation. Co-adsorbed potassium and alumina form a potassium aluminate compound that a) inhibits the aluminum oxide induced restructuring of iron and b) covers up the active iron sites for ammonia synthesis.

Hydrocarbon Conversion over Pt-Re Bimetallic Crystal Surfaces

G.A. Somorjai, D.J.Godbey

Bimetallic surfaces were prepared by vapor depositing rhenium on platinum crystal surfaces and platinum on rhenium crystal surfaces. The bimetallic surfaces with 20-30% of a monolayer of rhenium chemisorb

20% more H_2 and 40% more CO than platinum alone. The electronic interaction between the two metals modifies the bonding of adsorbates at the mixed Pt-Re metal sites. Platinum also catalyzes the reduction of rhenium oxides to the metallic state. High pressure studies of ethane hydrogenolysis on these bimetallic surfaces show that the bimetallic surface with a Re_2Pt stoichiometry is the most active—about an order of magnitude more active than the rhenium (0001) face alone.

The Synthesis of Butyronitrile from n-Butanol and Ammonia over Rhodium

I. Böszörmenyi, G.A. Somorjai

This is a structure sensitive reaction: the (331) stepped surface is three times more active than the flat (111) crystal face, although it also poisons faster. An overlayer containing C, N, and O covers 95% of the active catalyst surface. Combined high pressure and surface science studies reveal a mechanism by which n-butanol is oxidized first to n-butanal. The aldehyde then reacts with ammonia and the butyronitrile is produced, possibly through an imine intermediate.

Thiophene Hydrodesulfurization over Molybdenum and Rhenium Crystal Surfaces

M.E. Bussell, G.A. Somorjai

Single crystal surface science and high pressure studies show that the conversion of thiophene to butenes is structure insensitive over molybdenum and structure sensitive over rhenium. Rhenium crystal surfaces showed a six-fold variation of activity in the order of (0001) < (1121) < (-1120) < (-1010) (Figure 5). Adsorbed sulfur decreases the rate over both Re and Mo while adsorbed carbon deactivates Re but has no effect on Mo. Radiotracer ^{35}S and ^{14}C studies indicate that the reaction occurs over a carbon adsorbate layer on molybdenum while it occurs on the bare metal surface over rhenium. This difference appears to be responsible for the observed differences in the influence of surface structure on reactivity.

CATALYTIC HYDROGENATION OF CO*

The purpose of this project is to develop an understanding of the fundamental processes involved in the catalytic conversion of carbon monoxide and hydrogen to gaseous and liquid fuels. Attention is focused on defining the factors which limit catalyst activity, selectivity, and resistance to poisoning, and the relationship between catalyst composition/structure and performance. To meet these objectives, a variety of surface diagnostic techniques (LEED, AES, XPS, EELS, NMR, IRS, TPD) are used to characterize supported and unsupported catalysts before, during, and

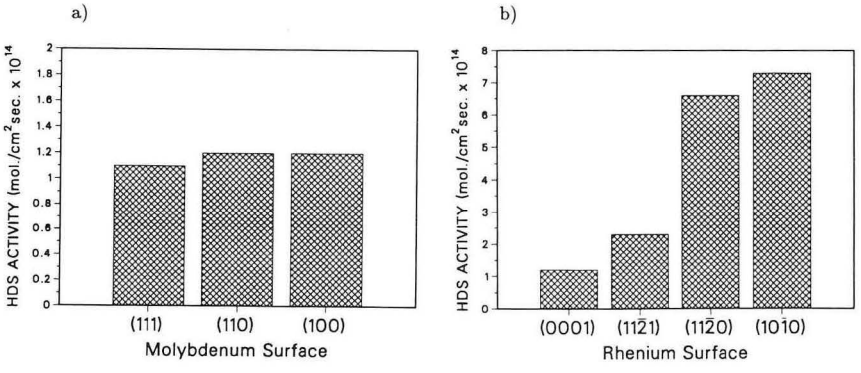


Figure 5
a) Thiophene hydrodesulfurization activities for three low-Miller-index planes of molybdenum at partial pressure of thiophene of 3.0 Torr, and of H_2 of 780 Torr, with temperature of 613K. b) Thiophene HDS activities for four low-Miller-index planes of rhenium (under the same conditions).

after reaction. The information obtained is combined with detailed studies of reaction kinetics to elucidate reaction mechanisms and the influence of modifications in catalyst composition and/or structure on the elementary reactions involved in carbon monoxide hydrogenation.

(*This work was supported by the Division of Chemical Sciences.)

The Thermochemistry of CO on Ruthenium

A.T. Bell, C. Louis, G.H. Yokomizo

Ruthenium is a highly active catalyst for producing hydrocarbons from CO and H_2. Through the use of infrared spectroscopy and isotopic tracers, it has been established that CO chemisorption on supported Ru crystallites is corrosive and leads to the formation of Ru^{2+} cations bound directly to the support. Each of the Ru^{2+} cations is bonded to three CO molecules. Temperature-programmed desorption spectroscopy reveals that the Ru^{2+} cations are released at temperatures below those at which CO desorbs from Ru crystallites. Boudouard carbon is produced solely by disproportionation of CO adsorbed on the crystallites. The dissociation of CO is irreversible at temperatures below 675 K. These studies suggest that the formation of Ru^{2+} cations may contribute to the dispersion, and possible volatization, of metallic Ru, but does not participate in CO hydrogenation.

Monte Carlo Modeling of CO and H_2 Desorption

A.T. Bell, S.J. Lombardo

A Monte Carlo model was developed for describing the temperature-programmed desorption of adsorbates from single crystal surfaces. This model takes into account the effects of surface diffusion and the influence of metal-adsorbate (M-A) and adsorbate-adsorbate (A-A) interactions on the coverage dependence of the activation energy for desorption. The inclusion of M-A and A-A interactions has a pronounced effect on the shape of the predicted TPD spectrum (Figure 6). Where only a single peak is observed in the absence of M-A and A-A interactions, multiple peaks are found when these interactions are included. The inclusion of these interactions is also shown to produce a nonlinear decline in the activation energy for desorption as a function of increasing adsorbate coverage. Simulated TPD spectra for CO desorption from a Pd(100) surface and for H_2 desorption from

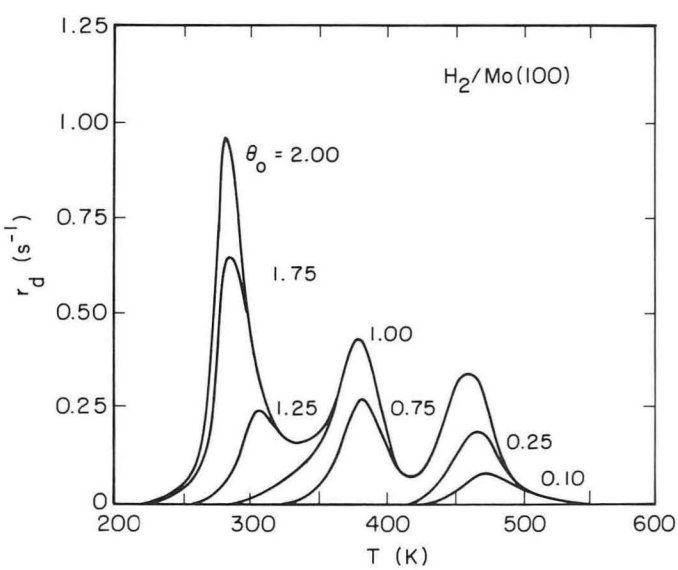


Figure 6
Monte Carlo simulation of the temperature-programmed desorption of H_2 from a Mo(100) surface.

Mo(100) and Ni(111) surfaces are in satisfactory agreement with those observed experimentally. An important feature of the model is that it correctly describes the observed dependence of the activation energy on adsorbate coverage.

THERMOCHEMISTRY OF C_2 HYDROCARBONS

A.T. BELL, E. SHUSTOROVICH‡

In collaboration with E. Shustorovich at Kodak Research Laboratories, a theoretical investigation of the thermochemistry of C_2 hydrocarbon formation and decomposition was carried out using the bond-order-conservation/Morse-potential (BOC-MP) approach. The total energy of C_2H_x species in the adsorbed state were calculated for different coordinations, as were the activation energies for C-H and C-C bond formation and cleavage. The influence of metal composition on the thermal decomposition of C_2H_4 and C_2H_2, the hydrogenation of C_2H_4 and C_2H_2, and the hydrogenolysis of C_2H_6 were examined using the BOC-MP approach.

FUNDAMENTALS OF CATALYTIC GASSIFICATION*

H. HEINEMANN, P. PEREIRA, G.A. SOMORJAI

It is the purpose of this project to achieve gasification of chars with steam at temperatures below 1000 K and to produce essentially only hydrogen and carbon dioxide, and further, to understand the reaction mechanism.

Earlier work has shown that the well known steam gasification of coals and chars in the presence of potassium oxide catalysts proceeds through the formation of a phenoxide with simultaneous release of hydrogen. The phenoxide does not decompose or react with water except at temperatures appreciably above 1000 K. It was shown previously in this laboratory that the addition of transition metal oxides to the potassium oxide leads to a decomposition of the phenoxide at temperatures appreciably below 1000 K. The best catalyst found, a mixture of nickel oxide and potassium oxide, and electron microscopy has shown that this mixture wets the carbon at temperatures of 800-1000 K and gasifies by means of an edge recession mode. During 1988 it was found that in a number of cases ash components in the char interacted with the potassium-transition metal oxide and caused it to lose activity. It was found that mixtures of alkali and alkaline earth oxides and particularly of potassium and calcium oxides have almost the same activity as the potassium nickel oxide but are not subject to deactivation. On the other hand, ash components can have a catalytic effect of their own, furthering gasification. In the absence of a catalyst, some gasification can occur when exposing the char to steam at 800-1000 K. This gasification activity dies fairly rapidly. If the char is demineralized, no gasification occurs at all. The major products of gasification with these catalysts and in the temperature range used are hydrogen and carbon dioxide, while at higher temperatures hydrogen and carbon monoxide prevail.

The catalysts used in this investigation, both calcium-potassium and nickel-potassium types, dissociate water at the temperatures of the investigation. A mechanism has been proposed which involves dissociation of water and attack of oxygen species on the carbon to form oxygenated carbon species. These are then evolved as carbon dioxide with a slow step being the breaking of the carbon-carbon bond in the oxygenated species.

(*This work was supported by the Assistant Secretary for Fossil Energy.)

SURFACE AND INTERFACE COMPOUNDS

SURFACE STRUCTURE AND BONDING

Structure of Disordered Molecular Adsorbates

G.S. Blackman, D.F. Ogletree, G.A. Somorjai, M.A. Van Hove, M.-L. Xu

The use of low-energy electron diffraction (LEED) in determining bond distances and angles of adsorbates on surfaces has been greatly extended in this laboratory in recent years, both experimentally and theoretically. It is now possible to determine the surface structure of disordered monolayers on ordered substrates using a new digital-LEED apparatus and a new diffuse-LEED theory, both developed in this laboratory. For example, the disordered structures of benzene and carbon monoxide adsorbed on the Pt(111) single-crystal surface were determined (Figure 7). This involved the measurement and calculation of diffuse LEED intensities in order to determine the molecular adsorption sites, metal-carbon bond lengths and internal distortions of the molecules.

Ordered Molecular Coadsorption Structures

G.S. Blackman, H. Ohtani, G.A. Somorjai, M.A. Van Hove

The earlier discovery in this laboratory of the important role of coadsorption in aiding the ordering of adsorbed organic molecules was pursued. Thus, it was found that carbon monoxide orders benzene into a periodic arrangement on Pd(111) and the detailed bonding geometry of this structure was determined. It could be compared with three earlier structures determined here for benzene coadsorbed with carbon monoxide on two other metal substrates. It is found that benzene adsorbs much more strongly to platinum than to rhodium, and less strongly to palladium. At the same time, the benzene molecule distorts most on platinum and least on palladium.

Both carbon monoxide and nitric oxide were observed by LEED to significantly stabilize ethylidyne into a periodic arrangement on Rh(111) (Figure 8). The detailed structural results indicate that, as for

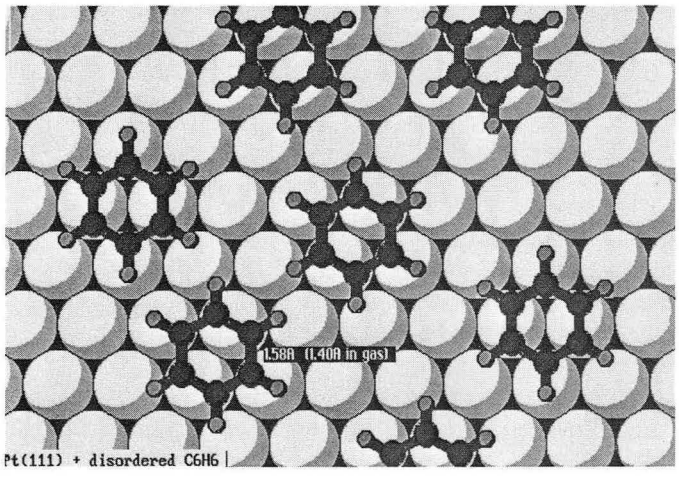


Figure 7
Top view of a disordered benzene overlayer (small connected circles) deposited on Pt(111) (large circles). The average C-C distance is expanded to 1.58 Å from the gas-phase value of 1.40 Å. All benzene molecules are identically bonded to the metal, centered on "bridge sites."

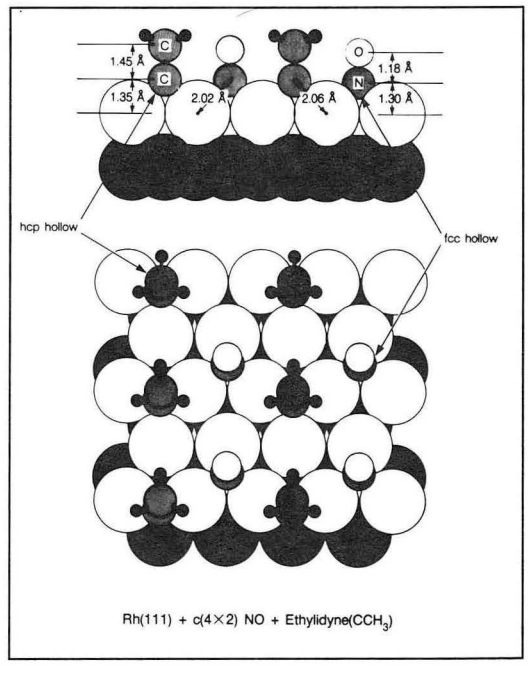


Figure 8
Side view (at top) and top view (at bottom) of ethylidyne mixed with nitric oxide on Rh(11). Bond lengths and layer spacings are indicated.

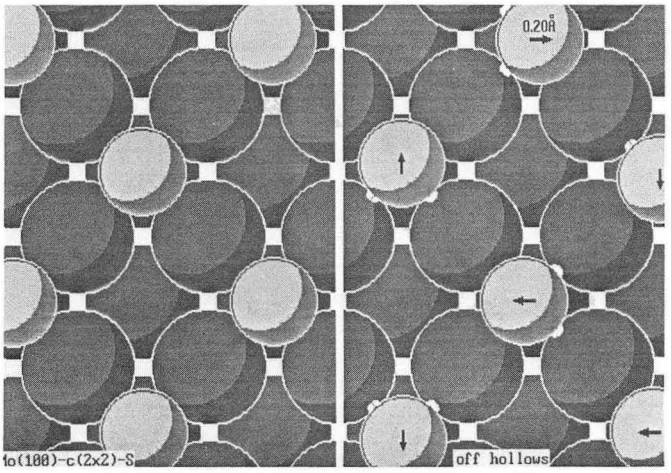


Figure 9
At left: top view of ideal highly-symmetrical adsorption of sulfur (light circles) in hollow sites of Mo(001) (dark circles). At right: actual asymmetrical lateral displacements of sulfur on this surface, in the directions given by arrows.

benzene coadsorbed with CO on Pt, Pd and Rh(111), electric charge is transferred from the hydrocarbon to the metal and then to the CO or NO. The ordering interaction between different molecules can be understood in terms of oppositely oriented surface dipole moments. Similar results were obtained on the (100) face of Rh.

Atomic Adsorption and Clean-Surface Reconstructions

T.E. Felter§, D.G. Kelly, G.D. Kubiak§, R.F. Lin, P.J. Rous, G.A. Somorjai, E. Sowa, R.H. Stulen§, M.A. Van Hove

A structural determination of hydrogen adsorbed on Pd(111) was carried out in collaboration with Sandia National Laboratories at Livermore. It was found that very likely a substantial fraction of the submonolayer of hydrogen is located in octahedral interstitial sites between the first and second metal layers, indicating the onset of the well-known easy hydrogen penetration into the bulk. In that collaboration, the reconstruction of the clean Pt(110) surface was also studied and shown to exhibit facetting to (111) faces, together with relaxations parallel and perpendicular to the surface down to at least the third metal layer. Similar complex relaxations were found in the diamond (111) reconstruction, where a more drastic rebonding occurs to better satisfy the dangling bonds.

The adsorption of sulfur on the relatively loosely-packed (100) surface of a Mo single crystal has been studied. The sulfur atoms choose adsorption sites slightly away from the expected high-symmetry locations (Figure 9). Whether this asymmetry induces lateral relaxations in the underlying metal lattice is being analyzed at present: such distortions would be an example of adsorbate-induced restructuring, a phenomenon whose importance is becoming more and more apparent. This work shows that the clean Mo(100) surface by itself already exhibits such relaxations, indicating intrinsic instability in the surface structure.

Structure Determination with Forward Focused Electrons

M.A. Van Hove, M.L. Xu

A different development in the area of electron diffraction is the use of forward focusing in structural determination. Electrons with energies somewhat higher than in the case of LEED are strongly focused in the forward direction by atoms in their path. This feature allows the directions of interatomic axes to be determined quite easily. It works best with secondary electrons, such as Auger electrons and photoelectrons, and with inelastic electrons. A theory developed in our group was applied to published experimental data for layers of one metal deposited on or

under the surface of another metal, and also for oxygen in Mg(0001). The positions of the buried foreign atoms could be easily determined, yielding substitutional sites for the foreign metal atoms, but interstitial sites for the buried oxygen.

Surface-Cluster Analogy in Bonding

G.A. Somorjai

The various structures for molecules adsorbed on metal surfaces have direct analogues in multinuclear organometallic clusters. This analogy is a powerful tool for relating surface bonding and reaction, which are relevant to heterogeneous catalysis, to the field of homogeneous catalysis.

HREELS Studies of Molecular Surface Bonding

G.S. Blackman, C.T. Kao, C.M. Mate, H. Ohtani, G.A. Somorjai, M.A. Van Hove

The bonding character of organic molecules on metal surfaces has also been studied with high-resolution electron energy loss spectroscopy (HREELS) as the major technique. Thus, acetylene on Rh(111) is found to retain its molecular state at temperatures below 270 K. However, a strong rehybridization is observed, indicative of a strong metal-carbon bond. At higher temperatures, acetylene decomposes to CCH_2 or to CCH and H. When coadsorbed with CO, however, one obtains a mixture of CCH_3 (ethylidyne) and CCH (acetylide), further indicating the role of coadsorbates (Figure 10). Similar studies of ethylene decomposition on Rh(100) yield the same fragments, but their occurence depends more on molecular concentration than on temperature. Ethylene also exhibits a weakening of the C-C bond after adsorption on Rh(111) and Rh(100): the C-C bond order is sharply reduced from 2 to about 1.5 and 1.2, respectively.

Theoretical Modeling of Bonding

C. Minot[++], G.A. Somorjai, M.A. Van Hove

The above results are strongly supported by theoretical analyses performed in collaboration with C. Minot of the University of Paris at Orsay, France. His extended Hückel calculations on the adsorption of benzene on Pd, Rh and Pt(111) as well as on Ru(0001) confirm the strong tendency of unsaturated hydrocarbons to adsorb flat against a metal surface. Thereby the π-orbitals of the multiple C-C bonds participate in the bonding to the metal and a strong rehybridization of the carbons occurs.

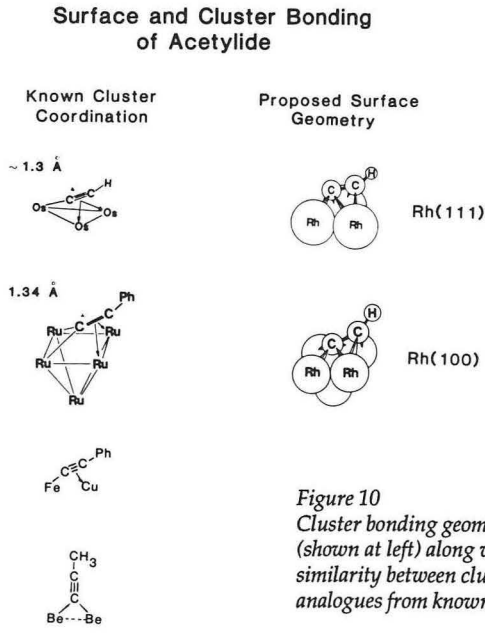
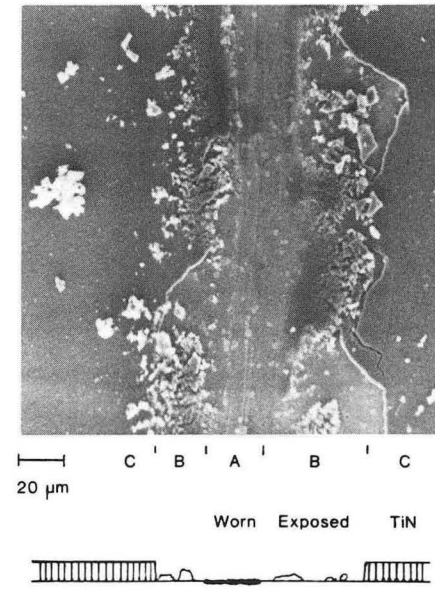


Figure 10
Cluster bonding geometries known for the C_2H (acetylide) ligand in organometallic chemistry (shown at left) along with possible C_2H bonding geometries on Rh(111) and Rh(100). The close similarity between cluster and surface bonding geometries allows the prediction of surface analogues from known cluster structures.

Figure 11
Scanning electron microscopy image of a scratch produced by a diamond indenter on a TiN coating on M2 tool steel. The film failed by de-adhesion in an area around the tip scratch.



Microscopic Theory of Segregation to Grain Boundaries

W. Alba, B. Whaley

Theoretical work on the development of atomistic models of grain boundary segregation involves analyzing the relationship between equilibrium segregation and lateral distribution of segregant along the boundary, investigating two-dimensional segregation and order-disorder phase transitions in the boundary region, and studying the relationship between interfacial and bulk phase transitions, and finally, determining how these depend on structural and chemical factors. Monte Carlo simulations of substitutional segregation to high-angle grain boundaries have been carried out, using grand canonical sampling and simulated annealing techniques. Studies of segregation profiles for a Cu/Bi system yield segregation isotherms, and at low temperature show a boundary induced bulk ordering. These numerical simulations are being complemented by mean field theories which provide independent bounds on bulk ordered structures and information on lateral segregant distributions.

COATINGS, ADHESION AND LUBRICATION

TiN Films

M. Hilton, M. Salmeron, G. Vandentop

TiN films were grown from an RF plasma using the gas phase reactants $TiCl_4$ and either N_2 and H_2 or NH_3 at a total pressure of 1 Torr. When the films were grown at substrate temperatures below 400 °C, sharp interface gradients of Cl were observed by Auger spectroscopy at the interfaces exposed by film de-adhesion. This de-adhesion was observed on the sides of the scratch track produced in UHV by a diamond indenter (Figure 11). These studies revealed that very sharp gradients (on the order of one monolayer), of interface impurities deposited during the initial stages of film growth were responsible for the poor adhesion of the TiN coating. Above 500 °C, very good adhesion was observed with SAT critical load values exceeding 4,000 gr at a film thickness of 6 microns. Auger depth profile studies indicate that in this case the interface is sharp with no accumulation of Cl.

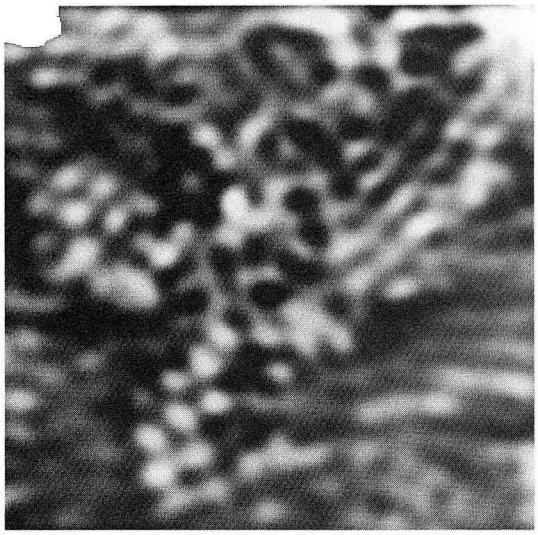


Figure 12
Scanning tunneling microscope image of a 40 x 40 Å area of the surface of a hard carbon coating grown by sputtering. This image was obtained in the local barrier height mode. Small ordered domains are found (brighter spots) that can be interpreted as diamond-like structures in a background of disordered and graphitic-like structures.

Surface Studies of Hard Carbon Coatings

M. Kawasaki, B. Marchon, D.F. Ogletree, M. Salmeron, G. Vandentop

Hard C coatings were formed from plasmas of CH_4 or by sputtering of graphite targets. The films formed have structures that vary from graphitic to amorphous, including partially hydrogenated and diamond types. Our studies using STM of the structure of C films grown by sputtering revealed, for the first time, the presence of small graphitic domains (approximately 15 to 20 Å) as well as regions where irregular configurations of C atoms and diamond structures could be imaged (Figure 12). The "diamond" regions are the bright ordered hexagonal structures. STM is clearly one of the best techniques to investigate the structure of disordered and amorphous materials because it reveals local order on the atomic scale.

Interface Studies of Hard Carbon Coatings

M. Kawasaki, D.F. Ogletree, J. Powers, M. Salmeron, G. Vandentop

The interface structure and bonding between the C coatings and the substrate is important since it determines the adhesion of the film. In the plasma CVD C films grown on Si substrates from CH_4, excellent coatings were obtained that resisted without scratching loads of up to 830 gr, the maximum load before the Si substrate breaks down. On metal substrates however, the adhesion was very poor. Since Auger depth profile studies did not reveal any particular structure or composition change at the C/Si interface, other surface sensitive techniques were used like SIMS depth profiling. The results obtained indicated that an interface compound formed, extending over a depth of 200 Å. This interface compound is SiC that acts as a buffer layer and is responsible for the good adhesion of the C films. These findings suggest that SiC layers, which are excellent for binding the C films, can be used as buffer layers on metal substrates. Recent experiments, in which thin (several hundred Å) SiC films were grown from $(CH_3)_4Si$ plasmas on a gold metal substrate followed by C deposition have confirmed these expectations and good, adhesive C coatings could thus be grown on gold. Experiments are now in progress to investigate the nature of the SiC-metal interfaces responsible for the good adhesion.

Surface Compounds: Restructuring of Oxide Overlayers

M. Salmeron, G. Vurens, K. Williams

In the Surface Compounds project, extensive use is made of surface science techniques to investigate the structure and composition of the surface during overlayer deposition and growth and during subsequent chemisorption and reaction studies. New instrumentation has been developed to study the defect structure of surfaces which is important to catalysis and crystal growth. These techniques include scanning tunneling microscopy (STM) and soon atomic force microscopy (AFM). STM provides a unique opportunity to study mechanical properties of surfaces at the atomic level by using the sharp tip as a tool to contact the surface and to induce other modifications and for subsequent evaluation of the effect on the structure of the surface. With AFM, the forces involved in this mechanical interaction will be measured also.

A unique method, based on the combined use of ion scattering spectroscopy (ISS) and Auger electron spectroscopy (AES), has been utilized for studying the sintering of transition metal oxides as a function of temperature and additive concentration. Iron oxide has been chosen as the model system since it has important catalytic properties and has been shown previously, in our laboratory, to grow ordered for the first monolayer on the Pt(111) surface. Hence, at one monolayer coverage, iron oxide has a dispersion of unity in contrast to three dimensional growth where the dispersion would be lower.

Recent results give insight into the restructuring of the iron oxide. The observation that a coverage of one alkali monolayer does not induce restructuring, but that this occurs when the concentration of alkali is larger, suggests that a liquid-like alkali phase can form, which dissolves or increases the mobility of the iron oxide, thus inducing its restructuring. These surface science results are in excellent agreement with work performed on iron ammonia synthesis catalysts where 1-3 % by weight of sodium fused together with Fe_3O_4-Al_2O_3 produces an active catalyst, upon reduction, with a smaller surface area than iron catalysts where either lithium or potassium were used instead.

Sulfur Monolayers and Defect Structures by Scanning Tunneling Microscopy

B. Marchon, D.F. Ogletree, M. Salmeron

A single monolayer of S is found to passivate the surfaces of such reactive metals as Mo and Re against oxidation in air for hours or even days. The STM was used to image the surfaces of these sulfur-covered metals in air in the topographic and local barrier height modes. On Mo(100) the images re-

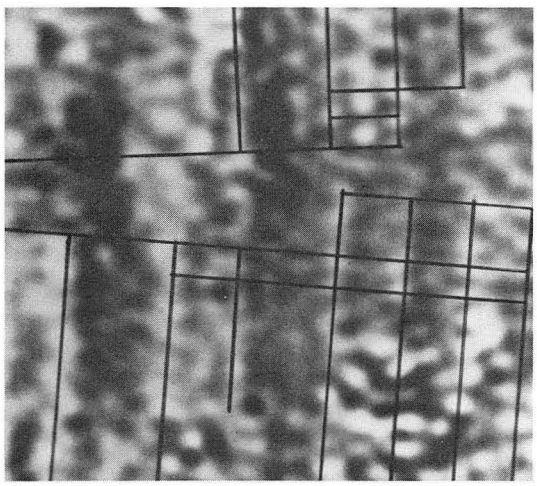


Figure 13
Scanning tunneling microscopy image of a Mo(001) surface with 1 monolayer of sulfur that forms a 1 x 2 periodicity. A defect in the surface structure is shown here as an angular misalignment between the upper and lower parts of this 50 x 50 Å image. The misalignment is interpreted as a small angle grain boundary.

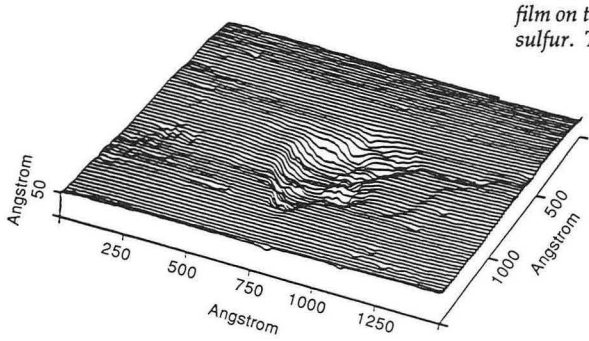


Figure 14
Hole created on the surface of a Re crystal by increasing the tip voltage to -3V in the scanning tunneling microscope while immersed in a diffusion pump oil film on top of a Re (0001) surface passivated by a saturation monolayer of sulfur. The image was acquired after the voltage increase.

vealed the atomic arrangement of sulfur atoms in domains with (1x2) and (2x1) periodicities (Figure 13). Also, a variety of "imperfections" were observed including domain boundaries and antiphase boundaries between two (1x2) (or 2x1) domains, and localized regions showing (1x1) arrangements. Small-angle grain boundaries in the Mo substrate were revealed in the STM images as well. This appears to be the first real-space observation of this type of defect on the surface of a crystal.

Atomic Scale Surface Modification

B. Marchon, D.F. Ogletree, M. Salmeron

The STM can be used as a tool for surface modifications on a nanometer scale. The simplest way to modify a surface is probably by establishing a direct contact with the tip: holes or mounds can be created on the surface, depending on whether or not adhesion occurs during the contact. If the tip does not adhere, only an indentation is formed, whereas in the adhesion case, when retracted, the tip pulls up the top layers of the material, forming a bump on the surface. In addition to this, a new electrochemical method has been used to produce surface modifications on the 100 Å scale. A rhenium (0001) surface was passivated by a saturation monolayer of sulfur and coated with a film of oil. By applying a potential of +3V to the crystal, one can locally dissolve away part of the surface, creating a 50 Å deep hole (Figure 14). Reversing the bias from +3 to -3V leads to migration of material from the tip onto the surface. Similar features were produced after gently touching the surface with the tip.

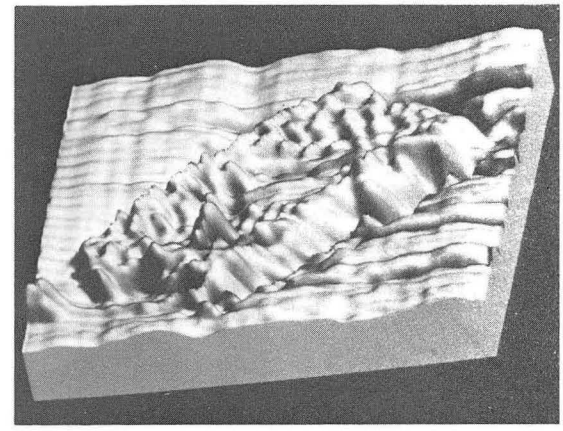
INSTRUMENTATION FOR SURFACE SCIENCE

SCANNING TUNNELING MICROSCOPY

J. Clarke, M. Gustafsson, M. Johnson, R.E. Thomson, S. Whitfield

The scanning tunneling microscope (STM) can image local surface structure and ordering on a previously unobtainable scale. A number of these instruments have been designed and built by members of the Surface Science and Catalysis program. During the past year, we have used an STM in an ultrahigh vacuum (UHV) system to study the growth of thin films of metal deposited *in situ* on graphite, and the migration of metallic clusters to grain boundaries. We have used a second, variable-temperature STM to investigate the structure of charge density waves

Figure 15
220 Å x 220 Å image obtained in the constant current mode of the STM showing a Cu crystal deposited on a cleaved graphite substrate in a UHV chamber at room temperature. The crystal is approximately 160 Å long, 70 Å wide, and 25 Å high, and was presumably formed by the surface diffusion of Cu atoms. The image was made by illuminating the three-dimensional image in the computer with a light source and projecting the resulting picture onto a two-dimensional surface.



(CDW) in 1T-TaS_2 and to address the question of whether or not they form domains in the incommensurate phases.

In the work on thin metal films, highly oriented pyrolitic graphite was cleaved in UHV. Submonolayer thicknesses of Al, Cu, Ag, or Au were evaporated on to the freshly cleaved surface, and the sample was transferred to the STM which was operated at a pressure of about 10-10 torr. A rich variety of structures was observed, ranging from clusters of two or three atoms to two-dimensional lattices to three-dimensional islands. A projected view of a Cu island approximately 160 Å long, 70 Å wide, and 25 Å high obtained in the topographical (constant current) mode of the STM (Figure 15).

Rare step edges on the graphite surface after Cu was deposited were seen and several Cu clusters, which either migrated to the step and were captured or nucleated and grew there were observed (Figure 16). The clusters straddle the step, approximately 10 Å high. The boundary in the STM was followed for about 5000 Å, during which it changed direction by 120° three times, and attached clusters were found over the entire length. The cluster diameter ranged from 20 Å to 80 Å, with a mean of 44 Å.

An important issue in the formation of CDW that are incommensurate with the crystal lattice is whether they are uniformly incommensurate throughout the surface or whether they form domains in which they are

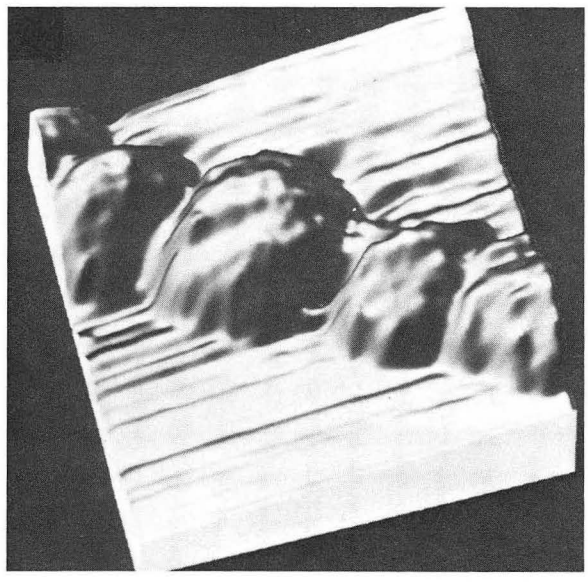


Figure 16
Projected, illuminated view of a 208 x 208 image of Cu clusters at a 10 Å high step edge of a cleaved graphite surface. Similar images were obtained along a 5000 Å length of the step. The image is projected and illuminated.

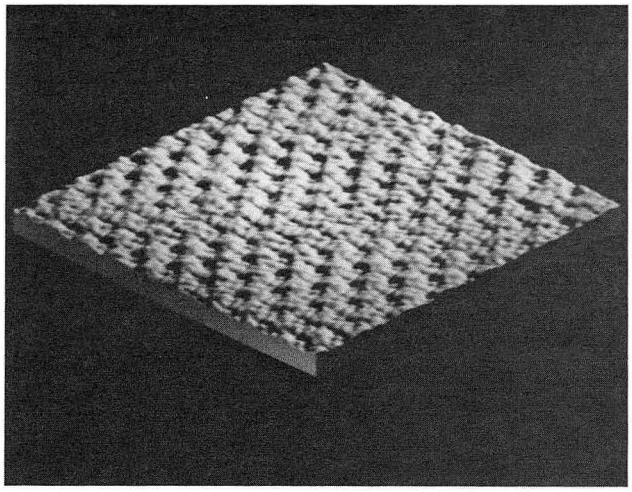


Figure 17
Three-dimensional projected view. The existence of the CDW domains is easily seen if one views the image at a glancing angle.

commensurate, and discommensurate at the grain boundaries. The experiment was designed to tackle this issue. The STM was immersed in liquid N_2 for measurements at 77 K, in n-pentane for measurements between 150 K and 295 K, and in pump oil for measurements above room temperature. The freshly cleaved samples were mounted on the STM immediately before it was immersed in the appropriate liquid, and images were obtained in the constant height mode.

Pictures were obtained in which both the CDW and the lattice in all 4 phases in which the CDW exists, were simultaneously imaged. In the commensurate phase, the direction of the CDW was rotated at an angle of 13° with the direction of the lattice, in agreement with the generally accepted value. In the noncommensurate (NC) phase, however, O was always less than 13.9° in many of the images that we analyzed. This result implies that the CDW is uniformly commensurate throughout the crystal, and does not form domains. On the other hand, in a study of the T-phase, long narrow sections were found where the CDW amplitude was large, separated by walls where it was suppressed. The phase slips at the domain boundaries are immediately apparent (Figure 17).

The work on CDW was carried out in collaboration with U. Walter and A. Zettl of the Physics Department and P. Rauch and F.J. DiSalvo at Cornell.

Nonlinear Optical Techniques

W. Daum, J. Huang, M.W. Kim, Y. R. Shen, V. Vogel, X.-D. Xiao

Optical second harmonic generation (SHG) and sum-frequency generation (SFG), which were developed at CAM for surface and interface studies, have been used to study organic and polymeric molecules adsorbed at various interfaces. Both static and dynamic properties of molecular monolayers have been measured.

The successful development of infrared-visible SFG as a surface probe allows the vibrational spectrum of a monolayer of pentadecanoic acid (PDA) on a water surface in the CH stretch region to be obtained. From the polarization dependence of the spectrum, the molecular orientations of PDA at different surface densities were deduced (Figure 18). It was found that the molecules in the liquid-condensed phase had their alkane chains extended and oriented nearly normal to the surface, but the molecules in the liquid-expanded phase are highly disordered chains.

The SFG technique was also shown to be applicable to liquid/solid interfaces. The spectra in the CH stretch region of a monolayer of octadecyltrichlorosilane (OTS) adsorbed at various interfaces bound by a fused silica substrate and different liquids were measured and compared. In every case, it was found that the OTS molecules were oriented with the alkane chains normal to the surface. The spectra appeared to be insensi-

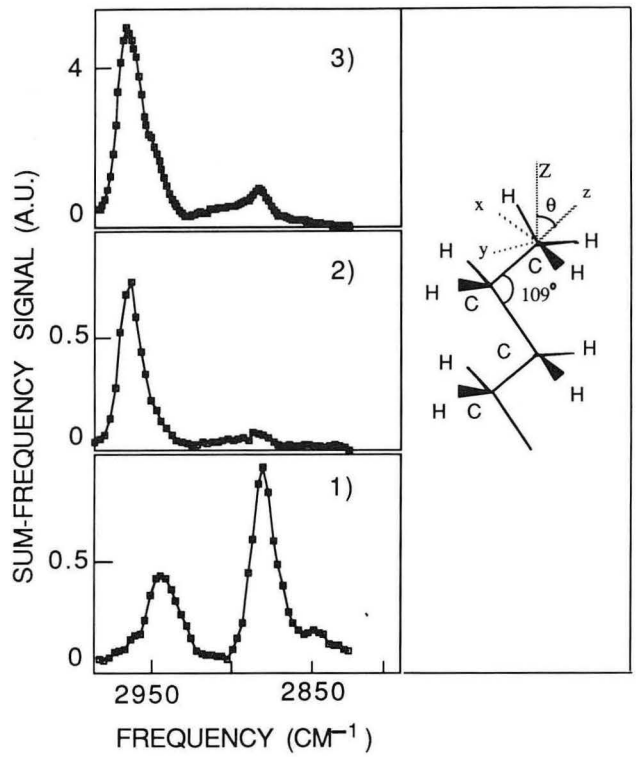


Figure 18
SFG spectra of PDA at different surface coverages normalized per molecules. (1a)-(1c) were taken with the s-visible, p-IR polarization combination. (2a)-(2c) were taken with p visible, s IR.

tive to the bulk CH vibrations illustrating the highly surface-specific nature of the technique. The adsorption of OTS on silica from a solution was also monitored *in-situ* and in real time.

The SFG technique can also be used to obtain surface vibrational spectra of molecules adsorbed on metals and semiconductors. The spectra of CH stretches of OTS on silicon and aluminum and ethylidyne on Rh(111) were measured (Figure 19). The results suggest that nondestructive in-situ monitoring of surface reactions by SFG is possible.

Nonlinear polarizabilities of molecules were determined using SHG from monolayers of molecules spread on water or glass. Organics with inherently high optical nonlinearities have the potential of becoming the basic nonlinear optical materials in future optoelectronic applications. Among the many candidates, molecules with the stilbazolium chromophores have the largest second-order polarizabilities. In collaboration with G. Marowsky et al. at Max Planck Institute in Gottingen, a large nonlinear polarizability for hemicyanine dye molecules was found. It was shown that this results from a strong charge transfer in the molecules and that protonation of the molecules reduces the charge transfer and the nonlinear polarizability.

In collaboration with P.N. Prasad at the State University of New York at Buffalo, monolayers of several diacetylene monomers and polymers spread at the air-water interface were studied, using SHG and third harmonic generation (THG). Owing to the centrosymmetry of the diacetylene core, SHG from these molecules arises mainly from their side groups, and is relatively weak and insensitive to polymerization or phase change of the adsorbed monolayer. The very large third-order nonlinearity of polydiacetylene, however, allows the detection of THG from a monolayer above the background bulk signal. The two-dimensional

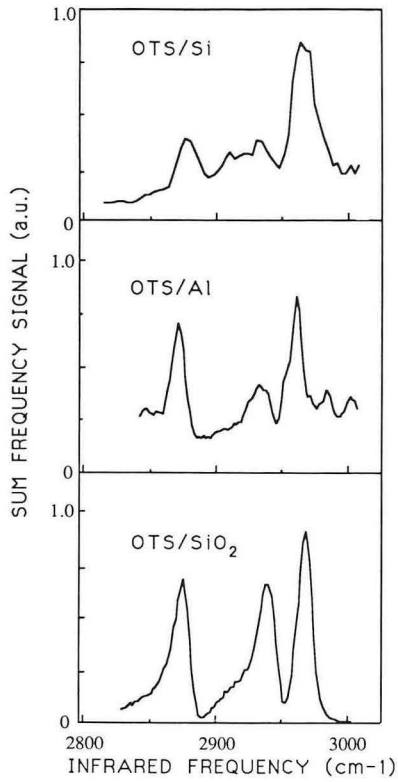


Figure 19
Sum-frequency spectra of OTS on silicon. OTS on freshly evaporated aluminum and OTS on glass, as described in the text.

phase transition from the yellow to the red form was observed using THG.

In collaboration with M.W. Kim at Exxon, the kinetics of surfactant adsorption from the bulk to the water-air interface was studied by SHG. An initial fast adsorption regime due to bulk-surface diffusion and a subsequent slower adsorption regime due to the decrease of the sticking probability were observed (Figure 20). The same technique could be used to study impurity diffusion from the bulk to the surface of a solid.

Theory

S. Louie, D. Tomanek, X.-W. Wang

First-principle calculations were carried out for the compound BC_3, a material with graphite-like structure recently synthesized by N. Bartlett at LBL. This material is a new member of the important class of B-C-N materials which possesses many interesting and potentially useful properties (light weight, electric conductivity, hardness, etc.). In addition to determining equilibrium bond distances from total energy minimization, the calculation has given detailed information on the electron energy band structure, density of states, and charge distribution. The calculated bond distances explain the observed density of BC_3. We show that, unlike graphite, the physical origin of the conductivity of this material arises from interlayer interaction of states of mostly s-character. It is further predicted that the density of states near the Fermi energy and the scanning tunneling microscopy characteristics of the BC_3 surface are significantly different from that of graphite.

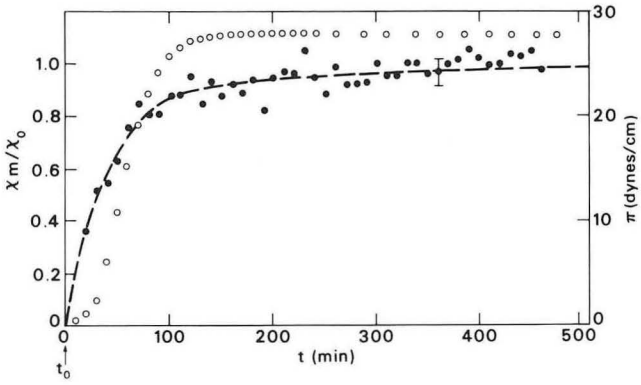


Figure 20
Observed surface pressure (open circle) and nonlinear susceptibility X for an air interface as a function of time after surface was SDNS saturated solution cleared. The dashed line is a Langmuir-type fit for the change in surface coverage.

A study of the energetics of Ag in various two-dimensional structures was performed. This work was motivated by STM results in the Clarke group that show a rectangular lattice for some Ag islands on graphite. *Ab initio* total energy results showed that an isolated monolayer of Ag strongly favors a two-dimensional close-packed structure. In particular, the rectangular lattice was found to be higher in energy by nearly 0.25 eV/atom. This study thus indicates that the rectangular structures observed for monolayer Ag islands on graphite are not intrinsic to 2-D Ag layers layers and that the observed structures are likely consequences of interaction of the Ag adlayer with the graphite substrate and/or with the island boundary.

A program was initiated to investigate the interaction of sulfur with molybdenum surfaces. Total energy and electronic structure calculations are carried out to determine the structure and properties of the various phases of S atoms on the Mo(001) surface. For the case of half monolayer coverage, theoretical determined surface geometry for the C(2x2) S/Mo(001) surface is in excellent agreement with experimental results from LEED, ion scattering, and photoelectron diffraction measurements.

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† Former CAM Industrial Fellow, Catalytica Associates, 1987.
‡ Collaborator from Kodak Research Laboratories.
§ Collaborators from Sandia National Laboratory.
†† Collaborator from University of Paris.

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Gabor Somorjai

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John Clarke—Instrumentation for Surface Science
Heinz Heinemann—Coal Gasification
Miquel Salmeron—Surface and Interface Compounds

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D. Frank Ogletree

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S. Travis Palomares
Sue Whitfield

Administrative Support

Gloria Osterloh
Brigid Tung

AWARDS

- Alexis T. Bell was B.F. Dodge Lecturer, Department of Chemical Engineering at Yale University.
- Alexis T. Bell was elected Fellow by the American Association for the Advancement of Science.
- Jung Huang was awarded an IBM Postdoctoral Fellowship.
- Jeffrey Reimer was awarded the Camille and Henry Dreyfus Foundation Teacher-Scholar Grant.
- Michel A. Van Hove was elected to the New York Academy of Sciences.

INDUSTRY INTERACTIONS

Technology Transfer

- The Instrumentation for Surface Science group worked with McAllister Company of Berkeley, CA, on the design of a scanning tunneling microscope which is now commercially available.
- A. Bell of the Catalyst Design and Characterizations project developed a novel zirconia spinner that can be used to study the synthesis of zeolites in highly alkaline gels by magic-angle-spinning nuclear magnectic resonance (MAS-NMR) spectroscopy. The technique has been adopted by W.R. Grace & Co., the Harshaw-Filtrol Partership, and Mobil Oil Corporation for studies of the chemical transformation occurring during the synthesis of zeolites.

Gifts and Contracts

- The Chevron Research Company and IBM Corporation helped to support the Surface Science and Catalysis Seminars.
- The 3M Corporation renewed its support of work focusing on nonlinear optical sutdies of surfaces and adsorbates.
- The Harshaw/Filtrol Partnership renewed its support of research on nuclear magnetic resonance spectroscopy studies of NaY zeolite
- W.R. Grace and Company renewed its support of research involving the study of the silicate and aluminosilicate specis involved in zeolite synthesis.

Advisory Board

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Industrial Collaborations

- V. Nair of Union Carbide, Tarrytown, NY collaborated with the Surface and Interface compounds group in a study of the various synthesis conditions of a ferrisilicate catalyst (FeZSM-5).
- Hiroko Ohtani of IBM, San Jose and program leader Gabor Somorjai used the STM to obtain the first photographic images of benzene rings.
- E. Shustorovich of Kodak Research Laboratories collaborated in a theoretical investigation of the thermochemistry of C_2 hydrocarbon formation and decompositon.

Industrial Fellows

- Glen Woolery of Mobil Research and Development Corporation worked with the Catalyst Design and Characterization project on the evaluation of the possibility of characterizing the carbon deposits formed on zeolites as a result of the cracking of petroleum products.
- Mahn-Won Kim of Exxon Research and Engineering spent three months with the Instrumentation for Surface Science project working on the application of second harmonic generation to the study of surfaces and monolayers.

SURFACE SCIENCE AND CATALYSIS SCIENCE SEMINARS

(Supported in part by gifts Chevron Research Corporation and IBM.)

M. Mundschau—Technical University, Clausthal, West Germany, "Low Energy Electron Microscopy."

R. Tromp—IBM, Yorktown Heights, "Scanning Tunneling Microscopy of Semiconductor Surfaces."

J.M. White—University of Texas, Austin, "Preparation and Decomposition of Methyl Groups on Pt and Ni."

P. Fleishauer—Aerospace Corporation, El Segundo, CA, "Electronic Structure and Lubrication Properties of MoS2: A Qualitative Molecular Orbital Approach."

D. Avnir—Dept of Organic Chemistry, Hebrew University, Jerusalem, "Structure Sensitivity Sealing Laws in Heterogeneous Catalysis. Fractal and Non-Fractal Interpretations of the Reaction Dimension."

H. Gerischer—Max-Planck-Institut, Berlin, and University of California Berkeley, "Decomposition and Photodecomposition of Semiconductors."

C.T. Campbell—Indiana University, Bloomington, IN, "Testing Ensemble Sizes in Chemisorption and Catalysis."

D.G. Castner—University of Washington, Seattle, WA, "XPS and Static SIMS Characterization of Polyurethanes for Biomedical Applications."

J. Smith—Arizona State University, Tempe, AZ, "Atomic Resolution Studies of Surface Structure and Reactions."

N. Winograd—Pennsylvania State University, University Park, PA, "Surface Structure Studies Using Ion Beams and Lasers."

K.D. Schmitt—Mobil Research and Development, Princeton, New Jersey, "Solid-State NMR of Catalysts. Avoiding the Pitfalls."

J. Horsley—Catalytica, Mountain View, CA, "Structure and Bonding of Adsorbed Species from MEXAFS and Multiple Scattering Calculations."

N. Sheppard—University of East Anglia, Norwich, England, "Vibrational Spectroscopy of Hydrocarbons on Single-Crystal and Finely-Divided Metal Surfaces."

J. Labinger—California Institute of Technology, Pasadena, CA, "Mechanistic Studies on the Oxidative Coupling of Methane."

R. Pearson—Kaiser Chemical, Pleasanton, CA, (retired) "NMR Studies in Catalysis and Surface Science—A Practical Approach."

J.D. Dunitz—Federal Institute of Technology, Zurich, Switzerland, "Molecular Motions in Crystals. What Can We Learn from Diffraction Studies?"

R.F. Willis, Penn State and University of Cambridge, MA, "Metastable Magnetic Epitaxial Layers."

J.B. Pendry—Imperial College, London, England, "Structure of Disordered O/Ni(100) from Diffuse LEED."

R.S. Williams—University of California at Los Angeles, "Surface Structure of Gold-Reconstructed Si(111) Surfaces From Ion Scattering Spectroscopy."

S.A. Chambers—Boeing, Seattle, WA, "Auger and Photoelectron Diffraction in Ultrathin Epitaxial Films."

S. Zones—Chevron, Richmond, CA, "Use of Organo Cations in Zeolite Synthesis."

P.I. Cohen—University of Minnesota, MN, "Diffraction Studies of Epitaxy."

K. Pratt—CSIRO, Melbourne, Australia, "Morphology and Activity of Molybdenum Sulfide on Various Supports."

M. Kiskinova—Bulgarian Academy of Sciences, and University of Pittsburgh, PA, "Comparison Between CO, NO and O_2 Interactions with Alkali-Modified Transition Metal Surfaces - Evidence for Surface Compound Formation."

D.L. Cocke—Texas A&M, College Station, TX, "Oxides and Carbides of Metals and Alloys."

D. Trimm—The University of New South Wales, Australia, "Copper Based Catalysts, Structure and Performance."

R. Varma—Argonne National Laboratory, IL, "Microwave-Enhanced Chemical Reactions."

Dr. Richard Joyner—The University of Liverpool, Liverpool, England, "Poisoning and Promotion in Heterogeneous Catalysis."

Dr. J. Oudar—Universite Pierre et Marie Curie, Paris, "Diolefin Hydrogenation on Platinum and Palladium."

Dr. W. Hölderich—BASF, Ludwigshafen, West Germany, "Zeolites: Catalysts for Organic Synthesis."

Dr. P. Taylor—University of Pittsburgh, PA, "Reactive Hydrocarbon Chemistry on Si(100)."

J.H. Fendler—Syracuse University, NY, "Semiconductors and Magnetic Particles in Bilayer Lipid Membranes."

J.P. Biberian—University of Marseille, Marseille, France, "Lead and Bismuth Growth of Microfacets on (100) Copper Surfaces."

A.T. Bell—University of California, Berkeley, "Applications of the Bond Order Conservation—Morse Potential Method for Predicting the Energetics of Surface Processes."

A. L. Cabrera—Air Products & Chemicals, Inc. Allentown, PA, "Surface Modification of Iron and Ferrous Alloys with SiH4."

H. Knözinger—University of Munich, West Germany, "Solid-Solid Wetting and Catalyst Preparation."

P. Davidson—ICI-Bellingham Catalysis Centre, Bellingham, England, "Base Metal Catalysis and Reactor Design for Synthesis Gas Processing and Manufacture."

P.A. Thiel—Iowa State University, Ames, IA, "Growth Modes and Structures of Thin Metal Films: Some New Twists."

K. Hermann—Hahn-Meitner-Institut, Berlin, Germany, "Recent Results of Computer Based Models for 3:00 PM Adsorbate and Surface Systems."

R. Srinivasan—IBM, Yorktown Heights, NJ, "Interaction of Ultraviolet Laser Pulses with Polymers and Biological Tissue."

D.G.H. Ballard—ICI, Great Britain, "The Influence of Biology on the Development of Macromolecular Science."

Prof. J. Reimer, University of California Berkeley, "NMR Studies of Model Hydrodenitrogenation Catalysis."

L.H. Dubois—AT&T Bell Laboratories, Murray Hill, NJ, "Synthesis Structure and Reactivity of Model Organic Surfaces."

Dr. B.E. Nleuwenhuys—Leiden University, Holland, "A Comparative Study of the Behavior of Single Crystal Surfaces and Supported Catalysts Towards Reduction and CO Oxidation over Pt-Rh Alloys."

H.L. Davis—Oak Ridge National Laboratory, TN, "Atomic Structure of Metallic Surfaces by a LEED Analysis: From Cu(100) to NiAl(111)."

J.H. Lu—Tsinghua University, Beijing, China, "Improvements in LEED Intensity Measurements by Camera/Computer Method."

Dr. Jory Yarmoff—National Institute of Science and Technology, Washington, DC, "Synchrotron Radiation Study of the Fluorine-Silicon Interaction."

E.L. Garfunkel—Rutgers University, New Brunswick, NJ, "Low Temperature Adsorption: Precursor States and Metal Overlayers."

S.H. Overbury—Oak Ridge National Laboratory, TN, "The Use of Low-Energy Alkali Ion Scattering to Study Surface Structure: Adsorbate Layers on W(001)."

Prof. M. Graetzel—University of Lousanne, Switzerland, "Fixation of Carbon Dioxide by Catalytic and Photocatalytic Methanation at Room Temperature and Ambient Pressure."

S.Y. Tong—National Science Foundation and University of Wisconsin, "Bonding and Reconstruction on Semiconductor Surfaces."

L.D. Roelofs—Sandia, Livermore, CA, and Haverford College, PA, "The Energetics and Kinetics of a Missing-Row Phase: Au(110)."

C. Sandroff—Bellcore, New Jersey, "Better Semiconductors Through Chemistry: The Electronic Passivation of GaAs Surfaces via Sulfide Reactions."

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IndustryParticipation

Advisory Boards
Workshops
Industrial Fellowships
Research Contracts and Gifts
Publications
Visits
Research Collaborations

Advisory Boards
Workshops
Industrial Fellowships
Research Contracts and Gifts
Publications
Visits
Research Collaborations

Industry Participation

CAM's mission statement calls for basic research in materials science. The research programs described in the preceding sections of this report are devoted to increasing our understanding of the fundamental properties of materials and materials systems. The mission statement also states that this research should support U. S. industry and that there be direct and continuing collaboration between CAM and U. S. industrial research laboratories. The selection of CAM research topics and the design of its programs are governed by the basic materials research needs of industry and a major thrust of the programs involves information flow to and from industry. This includes discussions, research collaborations, gifts, contracts, industrial fellowships, visits, publication of results in the scientific journals, and publications from the Center, such as Research Notes, and this Annual Report.

The CAM Industry Participation Office, in the office of the CAM Director, is charged with the development and management of these interactions with industry. Activities supported by that office include:

- program advisory board meetings
- industry participation workshops
- research collaborations
- CAM industrial fellowships
- research contracts, gifts and fellowships
- publications
- visits of industry scientists and research managers

ADVISORY BOARDS

Each CAM program, and some projects, are supported by an advisory board made up of industrial research managers serving two or three year renewable terms. The boards meet formally once each year to review the focus and goals of the program and the research progress made since the last meeting. A report is prepared on these aspects of the program with specific suggestions and criticisms, primarily focused on the question of which research directions are appropriate to CAM and of greatest potential benefit to U. S. industry. Members of the advisory board also consult with the program and project leaders informally throughout the year. Listings of the advisory board members follow each chapter of this report.

WORKSHOPS

Each CAM program holds, at two to three year intervals, a formal workshop for industry. These are open to all interested representatives of U. S. industry. The workshops, which usually run for two days, involve presentations by the CAM investigators of the research of their programs, and their planned directions for the following few years. Industrial scientists attending the workshop are invited to discuss the research and to express their views on appropriate directions of the research programs—directions that will produce beneficial results for their own companies and for U. S. industry in general. The workshops also include visits to the CAM laboratories and informal discussions with its scientists and students.

INDUSTRIAL FELLOWS

The Industrial Fellows Program at CAM is one of our most effective means of technology transfer to industry. Under the program, industrial scientists come to CAM to spend from three months to a year as integral members of one of the research programs. The fellowships can also be arranged for one week each month for a year, or, with local companies, for one or two days each week during the year. Industrial Fellows not only pursue research projects while in residence, adding their own background and experience to that of the programs staff, but also serve as excellent technology transfer agents when they return to their company's laboratories. Some of the Fellows devote their time at CAM to the development

and design of collaborative research programs between their laboratories and the CAM Program. Six Industrial Fellows worked at CAM during 1988. Eight are scheduled for appointment in 1989 and eight more are now being planned for 1990.

INDUSTRIAL FELLOWS •1988

D. Bliss, Engineering Manager	M/A-Com
M.-W Kim, Sr. Staff Physicist	Exxon
W. Link, Research Scientist	Raychem
C. G. Shirley, Manager, Reliability	Intel Corporation
G. Woolery, Sr. Research Chemist	Mobil Resarch and Development
A. E. Zachariades, Research Scientist	IBM

The value of this program has been recognized by the Department of Energy. Arrangements have been made for DOE support of the laboratory, living, and travel expenses of many of the Industrial Fellows while at work at CAM through the Industry-Laboratory Technology Exchange Program of the DOE Office of Energy Research.

GIFTS

Unrestricted gifts to CAM during 1988 totaled $181,000, raising the 5 year total to $337,000. This type of funding is the most valuable to the CAM programs because it gives them the required flexibility to deal with important and unexpected research needs as they arise.

GIFTS OF MATERIALS AND EQUIPMENT

Programs at the Center benefit greatly from donations of used or new processing or analytical equipment, or materials that are unavailable commercially. This year, the Microwave Technology Division at Hewlett Packard gave the Electronic Materials Program a computer-controlled crystal growth furnace. The equipment is valued at an estimated replacement cost of one million dollars, bringing the value of donated materials and equipment at CAM to more than two million dollars.

RESEARCH CONTRACTS

1988 research contracts totaled $304,000, bringing that 5 year total to $509,000. The contracts allow for focused work on specific projects of direct interest to the company involved, and enable the sponsors to maintain close contact with the investigators and students. A number of CAM students are also supported on industrial and other types of fellowships administered through their departments at the University of California at Berkeley.

Figure 1
Electronic Materials Investigator Edith Bourret with two crystal-growing furnaces and associated equipment donated by Hewlett-Packard.

PUBLICATIONS

All CAM work is published in the open literature. This year CAM researchers published 235 articles in books, journals and conference proceedings, 29 doctoral or masters theses, 163 invited papers, 119 contributed papers. An additional 164 journal articles are now in press. The Center also produces a number of its own publications throughout the year. These include this Annual Report, and the triannual Research Notes describing recent research highlights. Research Notes also includes the list of recent journal articles. These CAM publications are sent, along with announcements of workshops and other meetings, to those on our mailing list. The attached form should be used for adding names to that list.

INDUSTRIAL VISITORS

Representatives from U.S. industrial companies are encouraged to visit the Center; visits range from one day to a week or more. First visits usually involve discussions with CAM management, industry participation officials, and selected program leaders. Subsequent visits are focused on more detailed scientific discussions with program staff and often lead to continuing relationships including periodic exchanges of ideas and results, or active, formal collaborations.

RESEARCH COLLABORATIONS

CAM programs have established research collaborations with scientists in many U.S. industrial laboratories. These are described in detail in the preceeding sections of this report and involve companies in areas from petrochemical to automobile manufacturing to biotechnology. In some cases, the collaboration involves exchange of proprietary information or materials. Results of this work are published in the open literature by University of California and Lawrence Berkeley Laboratory policy, but only after protection of the proprietary information is assured.

STUDENTS AND POSTDOCTORAL FELLOWS

During the past five years, 71 students received their masters or doctoral degrees (39 in 1988) and 14 completed postdoctoral fellowships (6 in 1988). Of this group, 46 have moved on to industrial research positions, and 11 more have taken University teaching positions. Others continued their studies after leaving CAM.

1988 Degree Recipients

Name	Degree	Current Employer	CAM Program
G. S. Blackman	Ph.D	IBM, San Jose	Surface Science and Catalysis
D. Bliss	Masters	Continuing studies for Ph.D	Electronic Materials
M. Bussell	Ph.D	Ecole Nationale Superieurer*	Surface Science and Catalysis
R. Csencsits	Ph.D	Digital Equipment Corporation	Surface Science and Catalysis
D. Dietderich	Ph.D	National Research Institute	Structural Materials
T. S. Edgecumb	Masters	Continuing studies for Ph.D	Structural Materials
B. Freeman	Masters	ESPCI, France	Polymers and Composites
E. Ganz	Harvard	Surface Science and Catalysis	
G. Haddix	Ph.D	Shell Development	Surface Science and Catalysis
M. Hilton	Ph.D	The Aerospace Corporation, SURF	Surface Science and Catalysis
J. H. Hunt	Ph.D	Rockwell International	Surface Science and Catalysis
J. Hurd	Masters	IBM	Electronic Materials
Y. Im	Ph.D	Digital Equipment Corporation	Structural Materials
C. Jaggers	Ph.D	Union Carbide	Surface Science and Catalysis
C. J. Jou	Ph.D	Ecole Polytechnique, France	Electronic Materials
D. Kalika	Ph.D	IBM	Polymers and Composites
C. -T. Kao	Ph.D	AT&T Bell Laboratories *	Surface Science and Catalysis
B. -T. Lee	Ph.D	Lawrence Berkeley Laboratory	Electronic Materials
K. Lewis	Ph.D	University of Washington*	Surface Science and Catalysis
M. Lin	Ph.D	Institute of Nuclear Energy Research	Structural Materials
E. Y. Luh	Ph.D	W. R. Grace and Company	Structural Materials
A. McCormick	Ph.D	University of Minnesota	Surface Science and Catalysis
W. McIntyre	Masters	Continuing studies for Ph.D	Polymers and Composites
B. A. Malcolm	Ph.D	Cor Theraputics, Incorporated	Polymers and Composites
J. Mason	Masters	Continuing studies for Ph.D	Structural Materials
K. Moran	Ph.D	Environmental Science Association	Surface Science and Catalysis
D. D. Nolte	Ph.D	AT&T Bell Laboratories	Electronic Materials
T. Oh	Ph.D	IBM, Thomas Watson Center *	Structural Materials
H. Ohtani	Ph.D	IBM, Japan	Surface Science and Catalysis
L. Quan	Ph.D	Integrated Device Technology	Structural Materials
A. Rey	Ph.D	McGill University	Polymers and Composites
R. R. Sawtell	Ph.D	Alcoa	Structural Materials
P. Skerker	Ph.D	Repligen Research Corporation	Polymers and Composites
R. Spontak	Ph.D	University of Cambridge *	Polymers and Composites
D. R. Strongin	Ph.D	IBM Almaden	Surface Science and Catalysis
R. Van De Griend	Ph.D	Lookheed	Polymers and Composites
M. J. Werner	Ph.D	Electronic Engineering Department, University of California, Berkeley	Electronic Materials
K.T. Venkateswara Rao	Ph.D	Department of Materials Science and Mineral Engineering, University of California, Berkeley*	Structural Materials
F. Wellstood	Ph.D	IBM	Surface Science and Catalysis
G. Yokomizo	Ph.D	Mobil Oil Corporation	Surface Science and Catalysis

* Indicates students appointed to postdoctoral positions.

LAWRENCE BERKELEY LABORATORY FIGURE IDENTIFICATION NUMBERS

ELECTRONIC MATERIALS
figure
1. XBB 883-2259
2. XBB 886-5753
3. XBL 895-6218
4. XBL 884-9630
5. XBL 8811-9797
6. XBL 8801-6107
7. XBL 885-1824
8. XBL 895-1870
9. XBL 8810-3551
10. XBL 8812-4162
11. XBL 888-2747
12. XBL 881-8006
13. XBL 8510-4315A
14. XBB 870-10294
15. XBL 883-8385
16. XBB 870-9368
17. XBB 888-7334
18. XBB 898-6451, XBL 898-6450
19. XBL 898-2960
20. XBB 884-4124
21. XBL 897-2851
22. XBL 895-1871
23. XBB 889-9035
24. XBB 984-2940
25. XBB 887-7165
26. XBL 895-1866
27. XBL 897-2849
28. XBL 897-2848
29. XBB 896-5108
30. XBL 896-2350
31. XBB 879 7150
32. XBB 887-7084
33. XBB 887-7083
34. XBB 885-5419
35. XBB 881-644
36. XBL 894-1377, XBL 894-1376
37. XBB 894-2588
38. XBB 894-2588
39. XBB 894-2589
40. XBL 896-2449

HIGH-T_c SUPERCONDUCTIVITY
figure
1. XBL 894-1495
2. XBL 891-360
3. XBL 892-603
4. XBL 897-2850
5. XBL 889-3440
6. XBL 888-7517
7. XBL 879-3890
8. XBB 888-7559
9. XBL 894-1669
10. XBL 894-1668
11. XBB 895-4987
12. XBL 8711-4633
13. XBL 8712-5391
14. XBB 880-11525
15. XBL 887-8915

POLYMERS AND COMPOSITES
figure
1. XBL 894-1578
2. XBL 894-1579
3. XBL 894-1580
4. XBL 894-1581
5. XBL 894-1582
6. XBL 894-1583
7. XBL 894-1585
8. XBL 894-1584
9. XBL 897-2870
10. XBL 897-2869
11. XBL 897-2868
13. XBL 897-2871
14. XBB 892-1106

STRUCTURAL MATERIALS
figure
1. XBB 883-2252
2. XBL 897-2697
3. XBL 897-2680
4. XBL 882-593
5. XBB 892-1302
6. XBB 892-1300
7. XBB 880-11499
8. XBL 897-2687
9. XBL 897-2677
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13. XBL 861-7432
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23. XBL 8811-3880
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36. XBB 892-929
37. XBB 894-3077

SURFACE SCIENCE AND CATALYSIS
figure
1. XBL 895-1818
2. XBB 870-10114
3. XBL 895-1868
4. XBL 895-1819
5. XBL 878-3473
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8. XBL 877-7005
9. XBB 880-11274
10. XBL 8610-4101
11. XBB 863-1997
12. XBB 884-4055
13. XBB 886-6283A
14. XBB 895-1875
15. XBB 883-2219
16. XBB 886-5521A
17. XBB 888-7485A
18. XBL 877-3071
19. XBL 889-3390
20. XBL 883-7321

INDUSTRY PARTICIPATION
figure
1. XBC 889-9455

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