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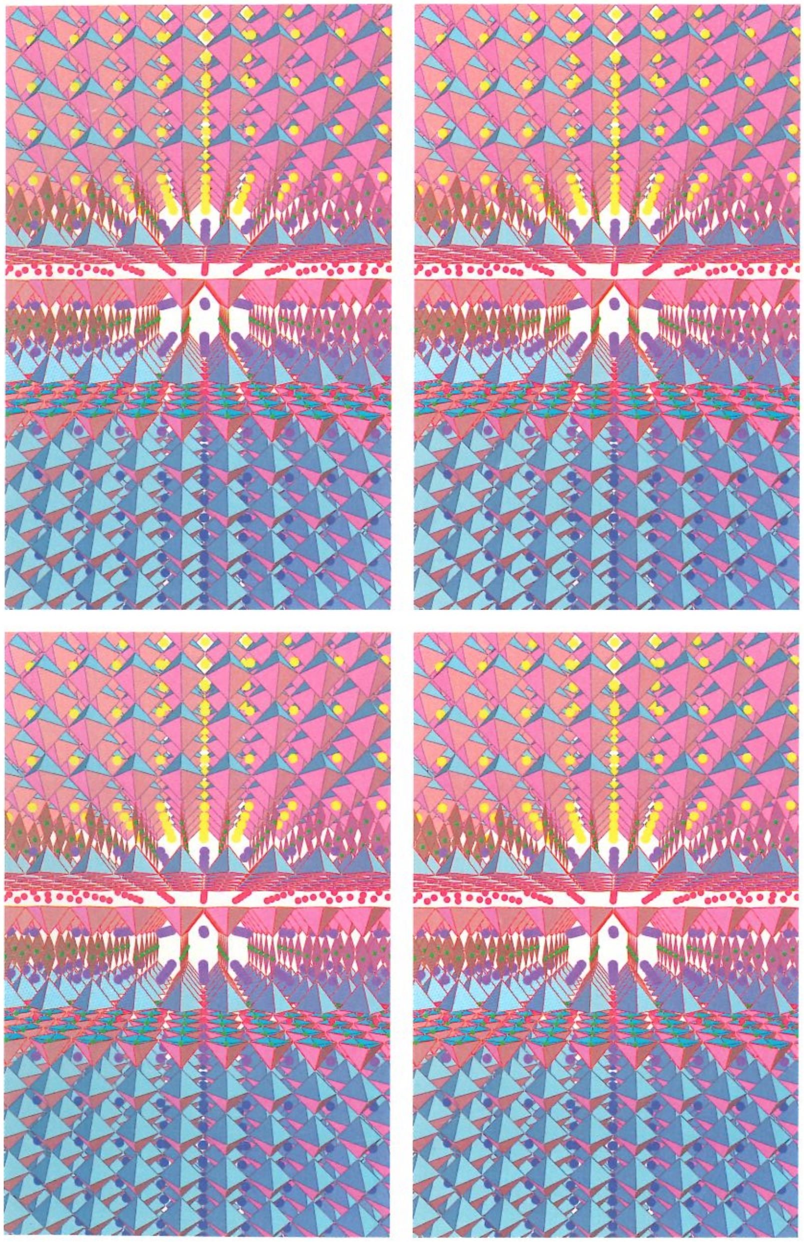
Materials Science and Engineering



PENNSTATE

cover:

s-sectional view of the crystal structure (coordination polyhe-
f a metal-ferroelectric-superconductor field-effect-transistor
ET) heterostructure. The MFSFET consists of a ferroelectric
nsulator ($PbTiO_3$, top), an ultrathin superconducting channel
$u_3O_{7-\delta}$, middle), and a substrate ($SrTiO_3$, bottom). The
concentration of the oxide superconductor-channel layer
hus, its resistance are modulated by the polarization of the
lectric gate insulator. This polarization direction may be
d by briefly applying a voltage between the gate electrode
e channel. The atomic structure of the interfaces between the

Penn State is a major, comprehensive research university. It counts among its faculty many leading scientists and scholars, and ranks among the top universities in terms of the amount of research support obtained from government and industry.

Graduate study in materials science and engineering is centered at the Penn State University Park Campus. The University Park Campus, the original and largest campus, has almost 32,000 undergraduates, more than 6,000 graduate students, and more than 2,300 faculty, and offers more than 240 degree programs, plus numerous additional options. It is located in the Allegheny Mountains, adjacent to the town of State College in the geographic center of Pennsylvania.

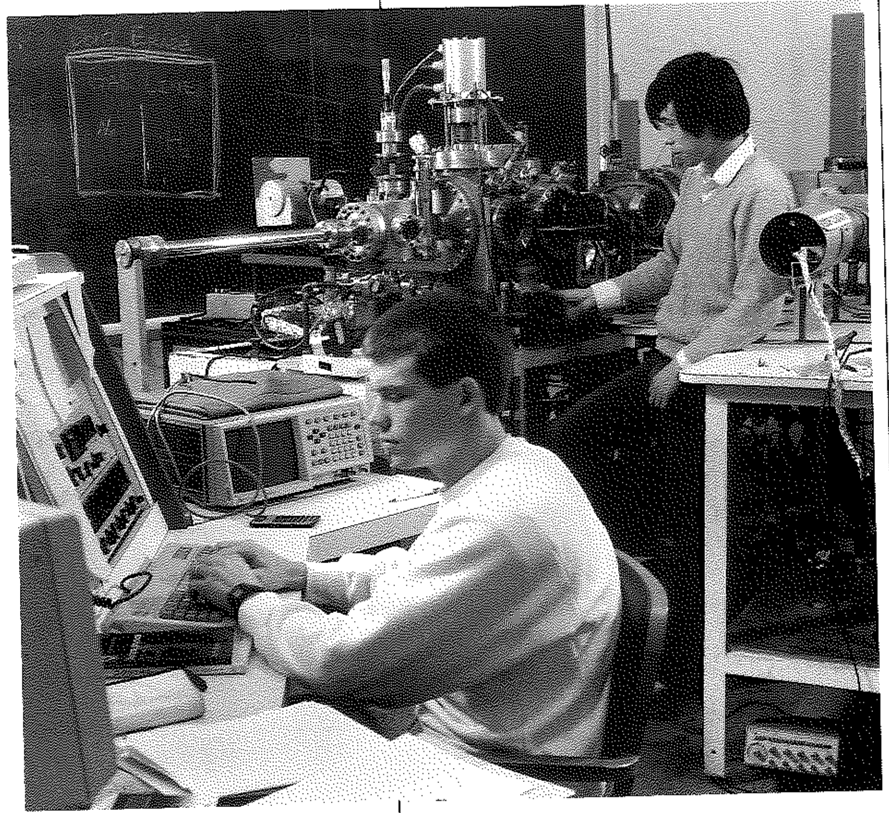
Materials Science and Engineering is one of six departments in the College of Earth and Mineral Sciences. The college has a strong focus on research and graduate education, with programs in materials and mineral engineering and earth sciences.

Faculty in the Department of Materials Science and Engineering also participate in the interdisciplinary Intercollege Graduate Degree in Materials. Many also participate in research projects in the various cross-disciplinary centers such as the Center for Advanced Materials, the Particulate Materials Center, the Energy and Fuels Research Center, the Intercollege Materials Research Laboratory, and the Electronic Materials and Processing Laboratory. Several materials science faculty members have been appointed to the Materials Research Institute Advisory Board, the umbrella coordinating group in materials research at Penn State.

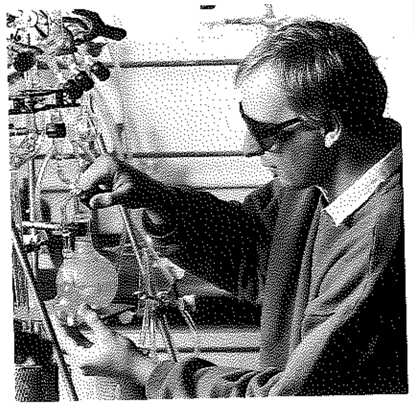
Penn State offers all the facilities of a major university and a full calendar of University lectures and other academic events. The performing arts series brings leading performers from around the world and exciting professional musical, theatrical, and dance productions to campus. A number of other organizations sponsor a wide range of cultural events. The newly renovated Palmer Museum of Art, an important center for the visual arts, hosts a range of exhibitions. The University has truly outstanding recreational facilities and is the site of regularly scheduled sporting events.

The University Libraries has holdings of about 3.3 million volumes with online catalog access. The central library, Pattee Library, is supplemented by specialized libraries, including the College of Earth and Mineral Sciences Library housed in Deike Building.

ırtment of Materials Science and Engineering

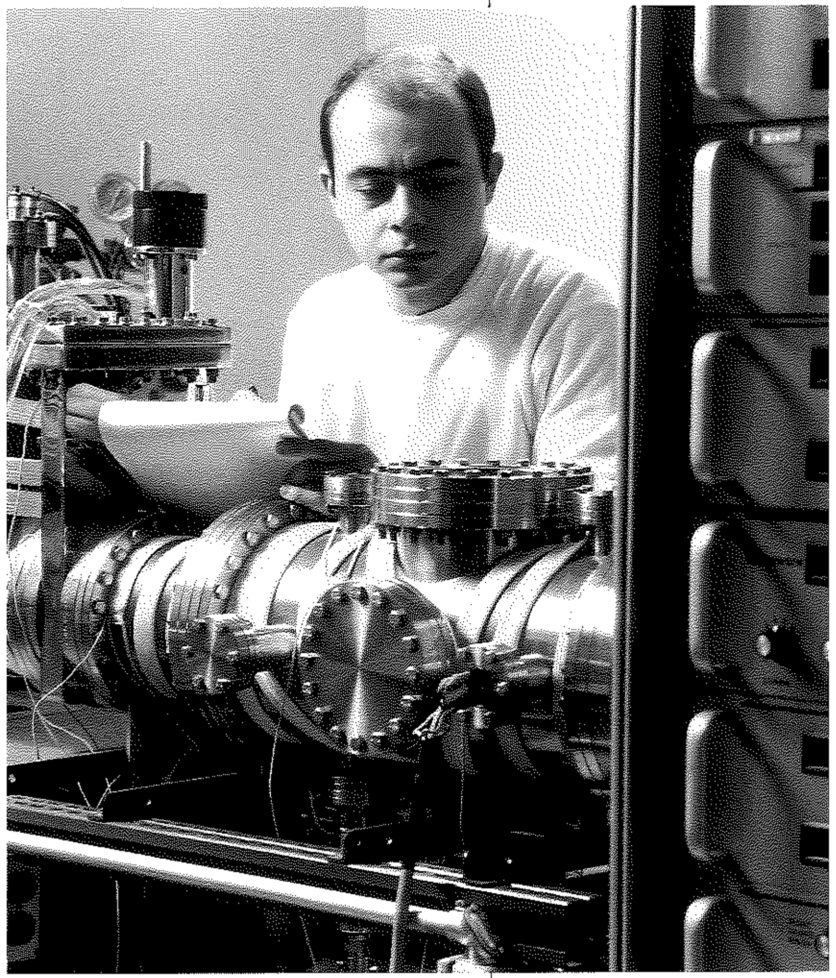


Graduate students operating the Atomic Probe Field Ion Microscope.



Wet chemistry in a polymer science laboratory.

A fuel science student analyzing synthetic liquid fuel using a gas chromatograph/mass spectrometer.



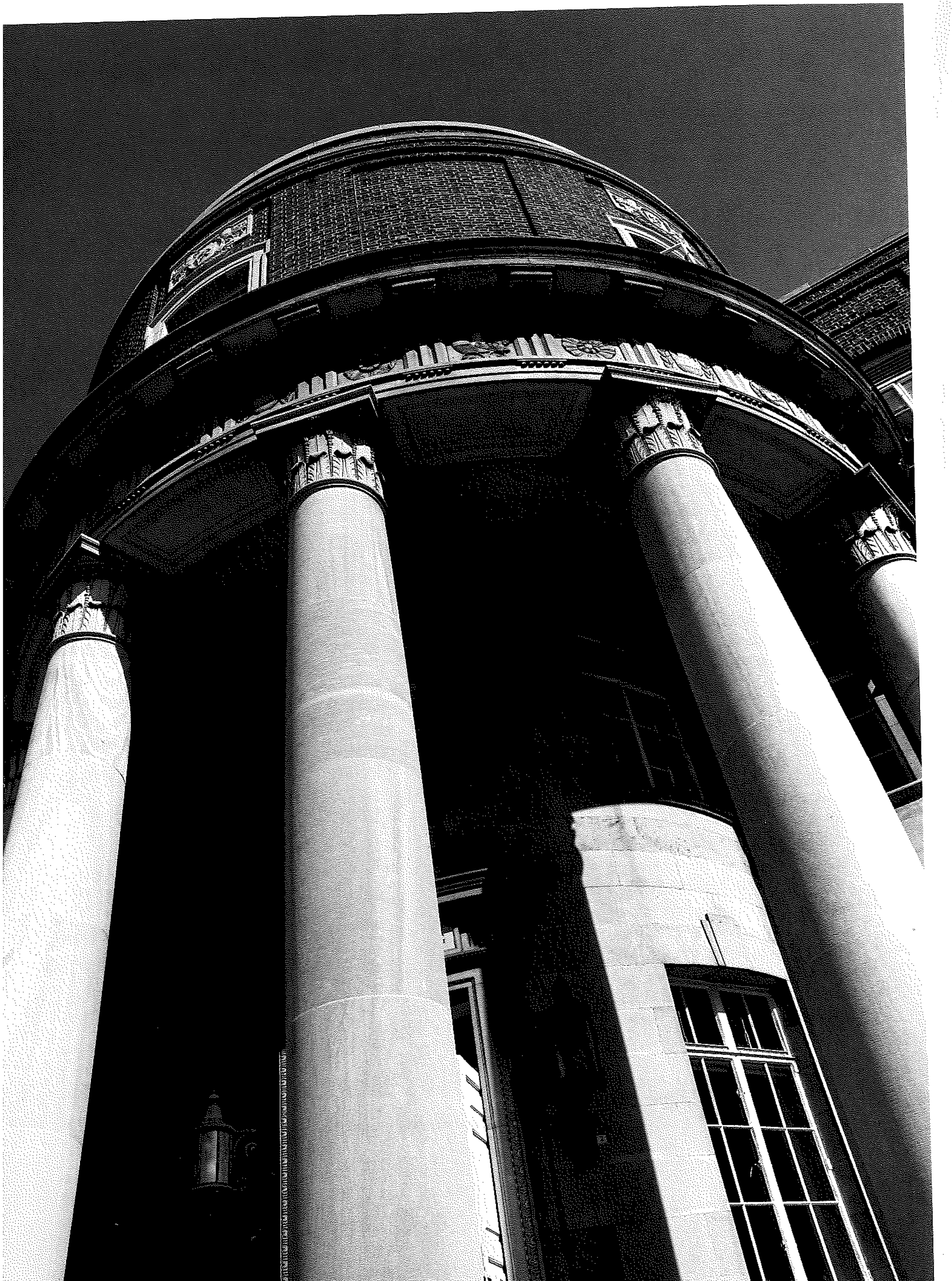
Molecular beam processing chamber used for processing and surface analysis.

The Department of Materials Science and Engineering at Penn State, as now organized, was formed in 1967. Its evolution, however, was unlike most such departments across the country that were initiated and dominated by one of the classic materials science disciplines. At Penn State, the Department of Materials Science and Engineering has its roots firmly planted in the College of Earth and Mineral Sciences, a college with an established tradition in mineralogy and earth sciences. Strong academic programs were established in metallurgy in 1907–1908 and in ceramic technology in 1923. Fuel science, another subject with a rich history at Penn State, was first offered as a major in 1934. These three disciplines were the nucleus of the newly formed department in 1967. The addition of the Polymer Science program in 1972, and the interaction with the multidisciplinary Intercollege Graduate Program in Materials, completes what is today one of the finest and best-balanced departments of materials science and engineering in the country.

The department offers graduate degrees (M.S. and Ph.D.) in Materials Science and Engineering with specialties in Ceramic Science, Fuel Science, Metals Science and Engineering, and Polymer Science. An interdisciplinary graduate program, the Intercollege Graduate Program in Materials, is administered through the Graduate School.

The department is large and diverse, affording students the opportunity to interact with faculty and with post-doctoral and graduate students from a wide spectrum of disciplines. There are 40 full-time faculty members, some 200 graduate students, and about 175 undergraduates currently in the department. Materials Science courses that cut across disciplines are offered, in addition to those offered in the specialties. Students are encouraged to broaden their horizons by taking these and other University-wide courses.

Faculty members in the Department of Materials Science and Engineering have many responsibilities, including teaching and advising students, undertaking research and disseminating results, maintaining academic standards, and performing other services for the University. The faculty have consistently been rated well above average as teachers by students and alumni. Eight of the current faculty have won collegewide teaching awards. Research productivity of the faculty as a whole is outstanding, as measured by the national and international recognition of their peers, the number and quality of papers published, and the amount of research dollars generated (in excess of $13 million in outside funding in 1992–93).



General Admission Requirements for the Graduate Program

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All graduate programs in the department have many more applicants each year than can be accommodated. Usually, 40 to 100 people apply for each opening. No general criteria will guarantee admission. Only the best-qualified applicants are admitted for each option depending on the number of openings available and the compatibility of students' interests with current research projects.

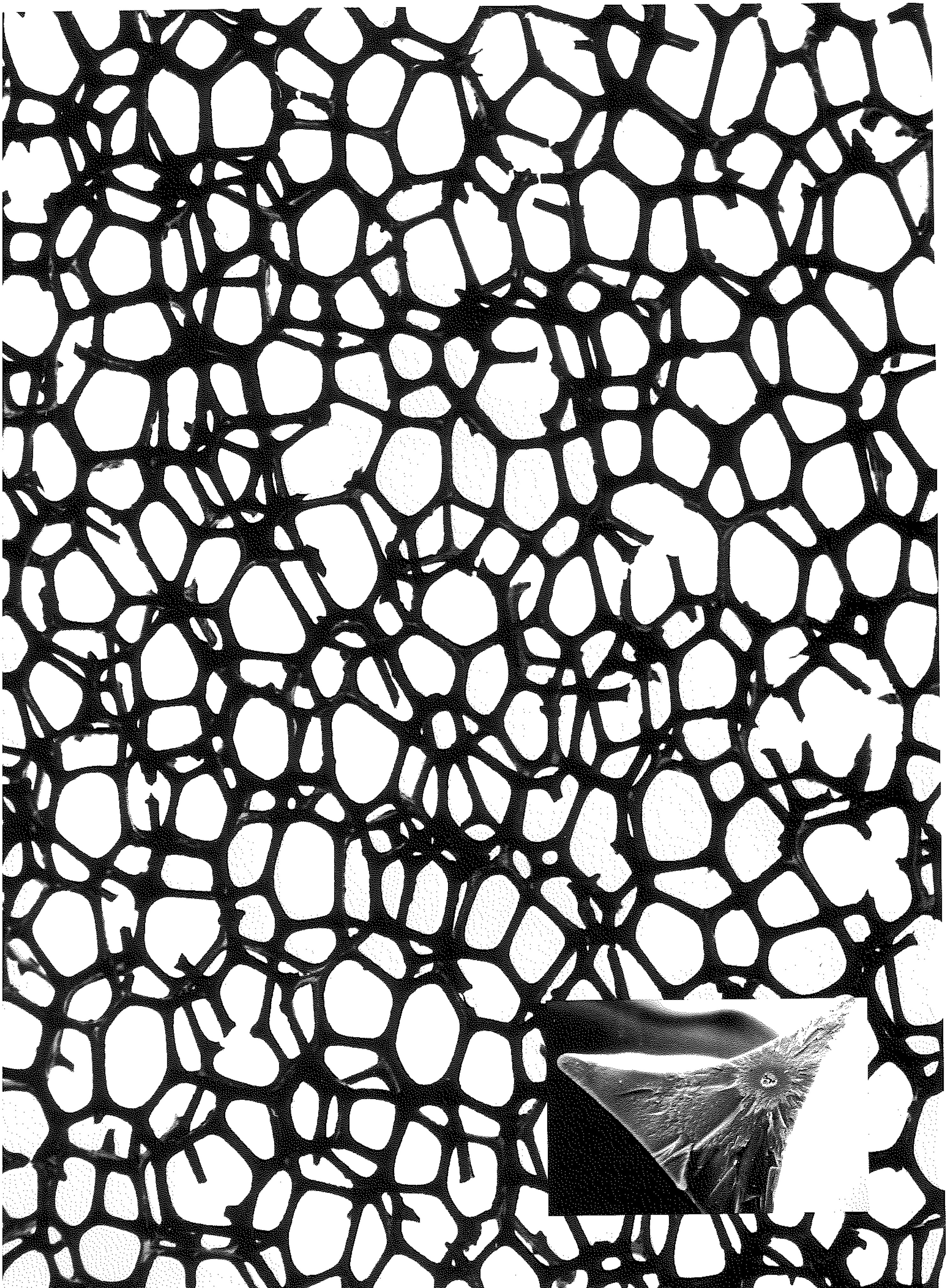
Applicants must have received, from an accredited institution, a baccalaureate degree earned under residence and credit conditions substantially equivalent to those required by Penn State. No fixed minimum grade-point average (GPA) is required for admission, but a junior-senior grade-point average of at least 2.50 on the scale of A (4.00) to D (1.00) is recommended by the Graduate School. Most incoming students have a GPA of at least 3.00.

Scores on the Graduate Record Examination (GRE)—verbal, quantitative, and analytical—are no longer required by the Graduate School for completion of the admission process. However, all students, especially those from foreign countries, are strongly advised to submit GRE scores with their applications. In many cases, the GRE is the only common factor that can be used to compare applications of similar merit.

The general graduate admission requirements are stated in the General Information section of the *Graduate Degree Programs Bulletin.* Application forms for admission are sent out by the department and should be returned to the Graduate School. Application forms for research assistantships should be forwarded to the graduate program coordinator in the Department of Materials Science and Engineering, whose address appears above. Applicants also should arrange for two or three letters of recommendation to be sent to the same address. Copies of academic transcripts need be sent only to the Graduate School.

Most students admitted to our graduate program are offered financial assistance in the form of research or teaching assistantships. For the 1993-94 academic year, these paid between $12,680 and $13,600 for two semesters plus the summer session, with all tuition paid.

Students who wish to apply for graduate studies in the Department of Materials Science and Engineering should contact the graduate student coordinator at the address above.



Microstructure of an open cell, vitreous carbon. Inset shows the fracture surface of one of the struts that make up the microstruc-

Ceramic Science (CERSC)

DR. DAVID J. GREEN, IN CHARGE OF GRADUATE OPTION

The Ceramic Science specialty covers a wide field with special emphases in ceramic processing, physical ceramics, chemical ceramics, and glass science. Special facilities exist for research in areas of electroceramics, phase equilibria, mechanical properties, thermal properties, surface characterization and properties, high-temperature reaction kinetics, coatings and thin films, solid-state synthesis, dielectric and ferroelectric studies, corrosion studies, and composite materials.

FACULTY

Paul W. Brown, Professor of Materials Science and Engineering, B.S., M.S., Ph.D. (Wisconsin)

Altaf H. Carim, Assistant Professor of Ceramic Science and Engineering, B.S. (MIT), M.S., Ph.D. (Stanford)

Robert F. Cook, Adjunct Associate Professor of Ceramic Science and Engineering, B.S. (Monash), Ph.D. (New South Wales)

David J. Green, Professor of Ceramic Science and Engineering; Chair, Ceramic Science and Engineering option, B.Sc. (Liverpool), M.Sc., Ph.D. (McMaster)

John R. Hellmann, Assistant Professor of Ceramic Science and Engineering; Associate Director, Center for Advanced Materials, B.S., Ph.D. (Penn State)

Gary L. Messing, Professor of Ceramic Science and Engineering; Director, Particulate Materials Center, B.S. (Alfred), M.S., Ph.D. (Florida)

Robert E. Newnham, Alcoa Professor of Solid State Science, B.S. (Hartwick), M.S. (Colorado), Ph.D. (Penn State), Ph.D. (Cambridge)

Carlo G. Pantano, Professor of Materials Science and Engineering; Director, Materials Characterization Laboratory, B.S. (NJIT), M.E., Ph.D. (Florida)

Dann E. Passoja, Adjunct Professor of Ceramic Science and Engineering, B.S. (Purdue), Ph.D. (Rensselaer)

Guy E. Rindone, Professor Emeritus of Ceramic Science and Engineering, Ph.D. (Penn State)

Karl E. Spear, Professor of Ceramic Science, B.S. (Baker), Ph.D. (Kansas)

Vladimir S. Stubican, Professor Emeritus of Materials Science and Engineering, D.Sc., Ph.D. (Zagreb)

Richard E. Tressler, Professor of Materials Science and Engineering; Head, Department of Materials Science and Engineering, B.S. (Penn State), M.S. (MIT), Ph.D. (Penn State)

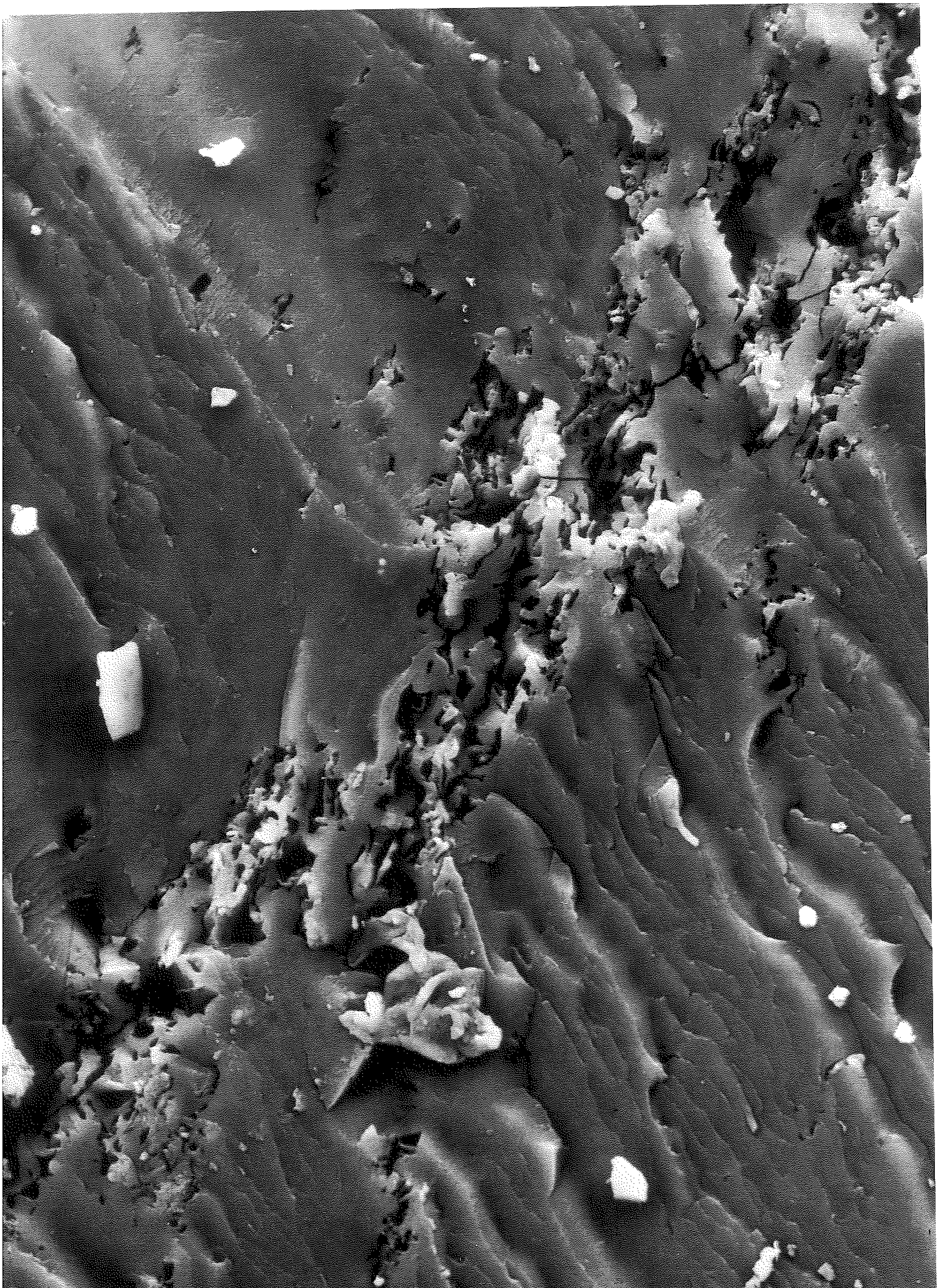
William O. Williamson, Professor Emeritus of Ceramic Science and Engineering, D.Sc. (London)

Long-Qing Chen, Assistant Professor of Ceramic Science and Enginering, B.S. (Zhejiang Univ.), M.S. (SUNY), Ph.D. (MIT)

Darrell G. Schlom, Assistant Professor of Materials Science and Engineering, B.S. (Calif. Inst. Tech.), M.S., Ph.D. (Stanford)

Susan Trolier-McKinstry, Assistant Professor of Materials Science and Engineering, B.S., M.S., Ph.D. (Penn State)

Walter A. Yarbrough, Assistant Professor of Ceramic Science and Engineering, B.S. (Univ. NC), Ph.D. (Penn State)



Scanning electron micrograph of a coalified wood of Miocene age, demonstrating the propensity of cellular material to coalesce and

Fuel Science (F SC)

DR. HAROLD H. SCHOBERT, IN CHARGE OF GRADUATE OPTION

The Fuel Science specialty at Penn State provides advanced knowledge and research opportunities in the characteristics and use of fuels, including their conversion to other fuels and to other materials. Special facilities exist for research in areas of combustion of fuels, coal ash behavior, coal pyrolysis, catalysis, fluidized-bed combustion, shock-tube studies, coal and carbon characterization, carbonization, coal gasification and liquefaction, activated carbon preparation and properties, and fundamental flame studies.

FACULTY

Semih Eser, Assistant Professor of Fuel Science, M.S. (Middle East Tech. Univ., Ankara), Ph.D. (Penn State)

Michael Y. Frenklach, Professor of Fuel Science, M.Sc. (Moscow), Ph.D. (Hebrew)

Patrick G. Hatcher, Associate Professor of Fuel Science, B.S. (NC State), M.S. (Miami), Ph.D. (Maryland)

Howard B. Palmer, Professor Emeritus of Energy Science, B.S. (Carnegie Tech), Ph.D. (Wisconsin)

Ljubisa R. Radovic, Associate Professor of Fuel Science, B.S. (Belgrade), Ph.D. (Penn State)

Alan W. Scaroni, Professor of Fuel Science; Director, Energy and Fuels Research Center, B.E. (New South Wales), M.S., Ph.D. (Penn State)

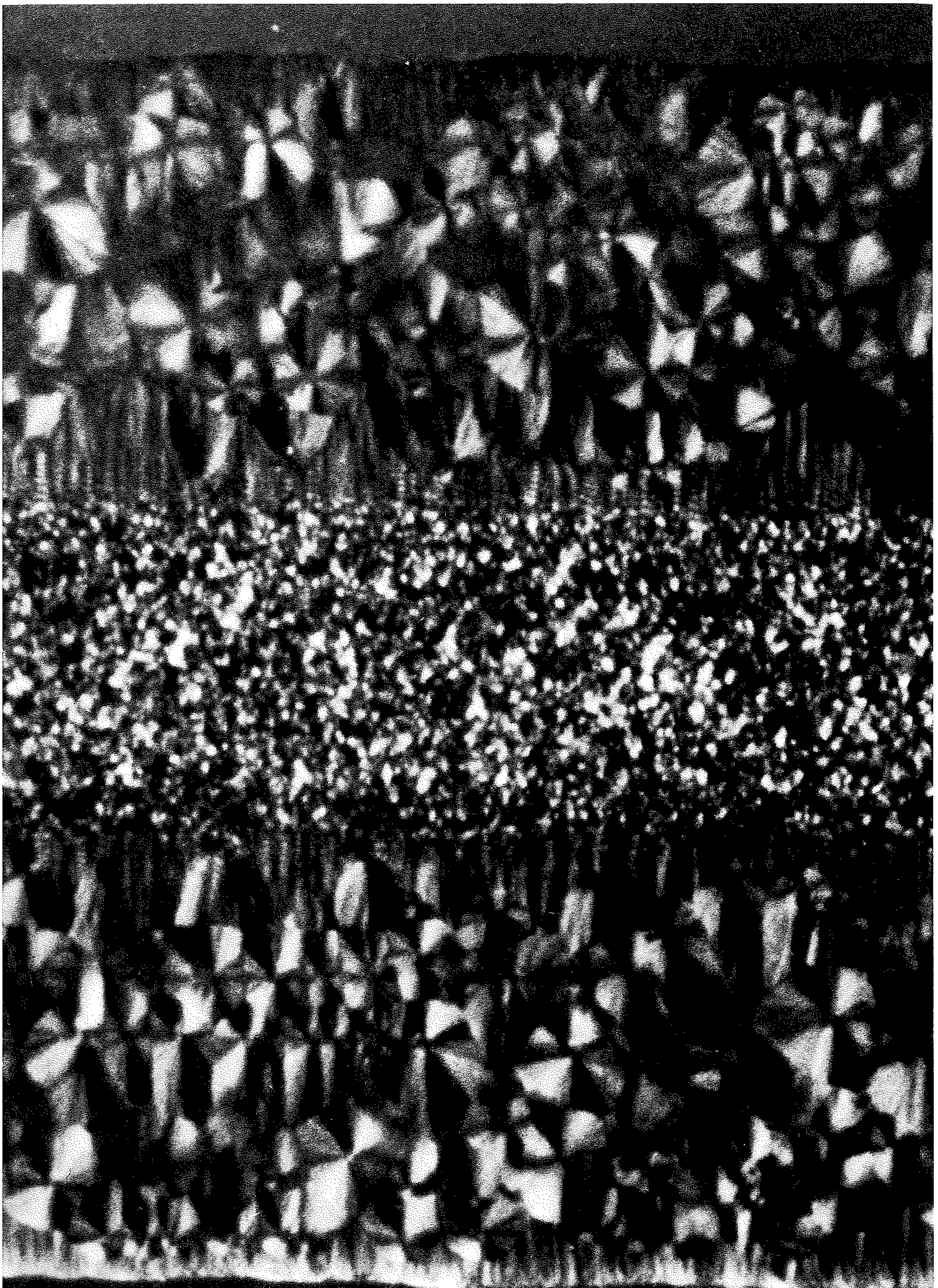
Harold H. Schobert, Associate Professor of Fuel Science; Chair, Fuel Science option, B.S. (Bucknell), Ph.D. (Iowa State)

Peter A. Thrower, Professor of Materials Science, B.A., M.A., Ph.D. (Cambridge)

Francis J. Vastola, Professor Emeritus of Fuel Science, Ph.D. (Penn State)

Philip L. Walker, Jr., Evan Pugh Professor Emeritus of Materials Science, Ph.D. (Penn State)

Peter M. Walsh, Associate Professor of Fuel Science, B.S. (Robert College, Istanbul), M.A. (Wesleyan), Ph.D. (Cornell)



Polymer Science (PLMSC)

DR. PAUL C. PAINTER, IN CHARGE OF GRADUATE OPTION

Polymer science at Penn State is a multidisciplinary subject concerned with the study of macromolecules. Such molecules are pervasive in today's technological society and find numerous applications in such diverse fields as plastics, elastomers, adhesives, surface coatings, textiles, packaging, and composites. Students work with faculty on a wide range of research projects, some of which are outlined in these pages. In addition, special facilities exist for research in the areas of polymer synthesis, polymer blends, surface science, mechanical properties, modeling and theoretical studies, diffraction and scattering, multicomponent systems, polymer characterization, high-temperature-stable polymers, conducting polymers, microscopy, vibrational spectroscopy, and thermal analysis.

FACULTY

David L. Allara, Professor of Materials Science and Chemistry, B.S. (California), Ph.D. (UCLA)

Tze-Chiang Chung, Professor of Polymer Science, B.S. (Chung-Yuan, Taiwan), Ph.D. (Pennsylvania)

Michael M. Coleman, Professor of Polymer Science, B.S. (Borough Polytechnic, London), M.S., Ph.D. (Case Western)

Bernard Gordon III, Associate Professor of Polymer Science, B.S. (Cal Poly), Ph.D. (Arizona)

Ian R. Harrison, Professor of Polymer Science, B.Sc. (Leeds), M.S., Ph.D. (Case Western)

Donald E. Kline, Professor Emeritus of Materials Science, B.S., Ph.D. (Penn State)

Sanat Kumar, Associate Professor of Polymer Science, B.S. (Indian Inst Tech), M.S., Sc.D. (MIT)

Paul C. Painter, Professor of Polymer Science, Chair, Polymer Science option, B.S., M.S. (London), Ph.D. (Case Western)

James P. Runt, Professor of Polymer Science; B.S., Ph.D. (Penn State)

Polyethylene (PE) laminate with linear low-density and high-den-

avid L. Allara *Chemistry at Interfaces*

unique molecular and atomic features of
nterfaces between materials often control
gnificantly influence the useful functions of
synthetic and naturally occurring struc-
;. Examples include the rate and specificity
ectrochemical processes, the adhesive
ıgth and conductivity of thin metal-film
ings on polymer or ceramic substrates in an
ronic circuit component, the biological
patibility of a synthetic biomedical im-
t, the efficiency of a semiconductor transis-
vith a chemically modified interface, and
corrosion of a structural metal part induced
s working environment.

he major objective of Professor Allara's
arch program is the development of a fun-
ental understanding of the chemical struc-
s and processes that occur at these
rfaces. Particular emphasis is placed on in-
ıces where one of the adjoining phases is
nic.

An interface is a complex boundary region
can be viewed as a slice of material, often
ıin as one or two molecules. Extreme de-
ıds are placed on the chemical and struc-
l probes needed to study these regions.
ra researches both the development of sensi-
molecular-structure probes, and the devel-
ıent of informative model chemical
ctures.

One type of model consists of a supported
of monolayer dimensions such that all the
ecular groups examined will be part of the
rface. For example, to learn about the inter-
between a polymer and a metal oxide,
ra has studied the properties of an absorbed
ymer monolayer on a smooth, planar metal
strate covered by a thin oxide film. Another
del system of great utility is an organized
nolayer assembly of multifunctional
anosulfur compounds on a gold surface.
achment to the gold occurs via a bivalent
ur atom. Other groups such as amino, hy-
xyl carboxylate and derived esters, methyl,
fluoroalkyl arrange themselves in the inte-
or at the ambient interface as dictated by
rmodynamics and molecular structure.
ese model structures have provided details
ut the molecular basis of the wetting of liq-
s by an organic surface, the transport of elec-
ns and ions through layers of alkyl groups,
l adhesive chemical-bonding interactions in
ymer coatings. Other research groups re-
tly have extended this work to the prepara-
n of biologically active surfaces, and Allara's
up is now examining these structures for use
pecific chemical sensors. One of the fasci-
ing aspects of these systems is the alteration
chemical-reaction mechanisms of organic
ups because of the "two-dimensional" na-
e of the assembly. New activity in the re-
rch program will develop additional model

structures on technologically important substrates such as glass, carbon, and various semiconductors.

Characterization of the above and related structures has been performed primarily by infrared vibrational spectroscopy, optical wavelength ellipsometry, X-ray photoelectron spectroscopy, and electrochemistry. In the case of vibrational spectroscopy, it has been necessary to develop new types of experimental and theoretical approaches in order to provide quantitative characterization of structural features such as surface orientation, group conformations, and intermolecular interactions. Both Fourier-transform and laser techniques have been applied experimentally, while a combination of molecular vibration analysis and classical electromagnetic theory have proved useful for theoretical interpretations. In addition, other promising techniques are continually being evaluated. Of recent interest are scanning tunneling microscopy, quartz crystal microgravimetry, surface plasmon resonance spectroscopy, secondary ion mass spectrometry, forward recoil spectroscopy, and valence band spectroscopy.

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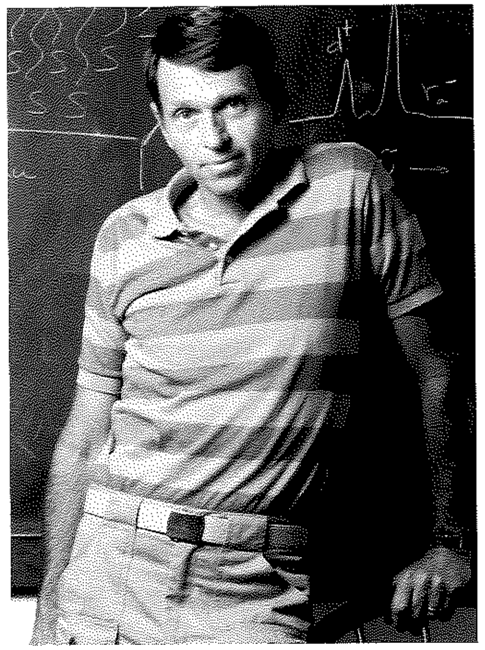

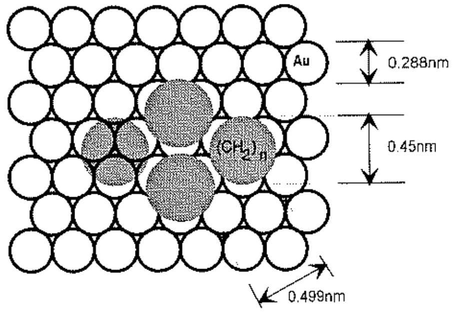

ALKYL CHAINS SPACED AS NEXT-NEAREST NEIGHBORS ON A Au(111) SURFACE.

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Keywords
surface chemistry, chemical kinetics, vibrational spectroscopy, condensed matter interfaces including polymers, surface analysis, materials chemistry

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André L. Boehman *Heat and Mass Transfer in Combustion and Pollution Control Systems*

Professor Boehman's research interests involve the study of combustion and pollution control systems for applications ranging from automobile catalytic converters to catalytic combustors for power plants. These research efforts have included the development of experimental facilities designed specifically for the study of pollution control catalysts and numerical models for the dynamic behavior and stress formation within catalytic combustors for natural gas-fired co-generation plants.

Many combustion and pollution control research problems involve the interaction of convective heat and mass transfer and heterogeneous chemistry. Such systems are of tremendous practical importance, and understanding their behavior and finding ways to enhance their performance are essential areas of research.

Within the Fuel Science program, Professor Boehman is constructing laboratory facilities for studying pollution control devices and advanced catalysts for use in diverse applications including diesel oxidation and lean-NO_x catalysts, and NO_x abatement systems for industrial coal boilers.

Other ongoing research includes the development of a numerical model for the transient behavior of natural gas-fired catalytic combustors. The current form of this computer code is 2-D and includes surface chemistry for an advanced palladium oxide catalyst formulation and thermal stress formation in the ceramic combustor substrate. Further development of this code will include addition of gas phase reactions and 3-D stress formation within the substrate. The goal is to provide design and operational guidelines for use of catalytic combustors in power generation facilities.

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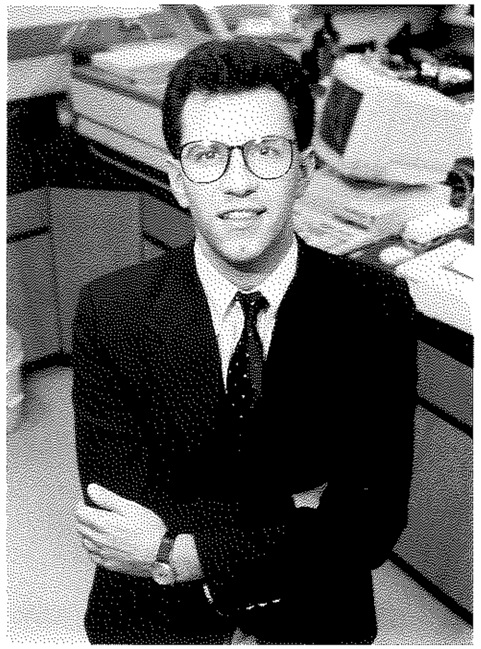

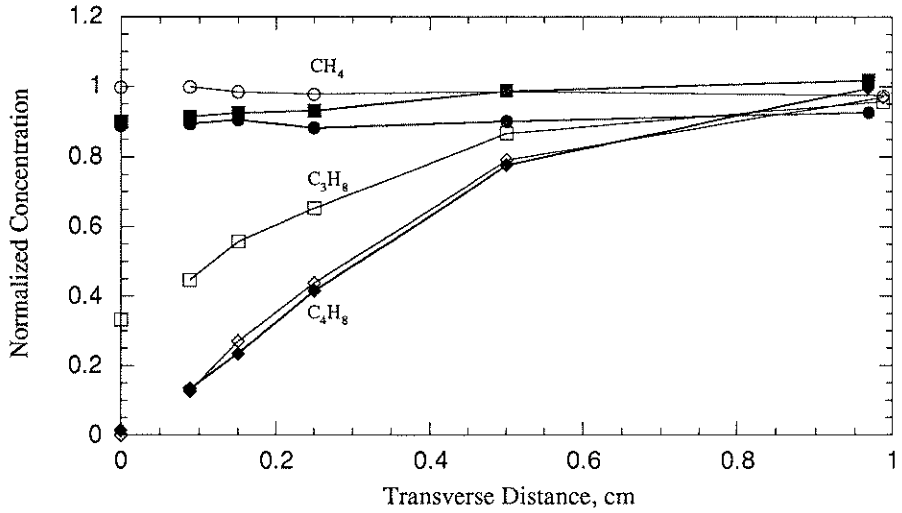

Concentration profiles from a catalytic flow reactor during multicomponent oxidation with (filled symbols) and without (open symbols) the presence of 500 ppm nitric oxide, over a palladium on alumina catalyst at 320°C.

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Keywords
pollution control, heterogeneous catalysis, combustion systems

William R. Bitler *Solid State Reaction Kinetics*

Dr. Bitler is currently conducting research in the area of steel processing. Steel used in commercial products such as automobiles is galvanized to reduce corrosion. The two principal techniques for galvanization are zinc electroplating and hot dipping. In order to minimize the cost of this process while retaining a durable coating, it is necessary to control the reaction products between the Zn-steel interface. An electron microscopy study of the reaction between zinc and steel and the products it forms during commercial galvanized steel processing has been performed, and a new sample preparation technique was developed for the industry.

The δ phase was found to have quasi-crystal features. Intermediate phases also play an important role in the mechanical integrity of galvanized steels. Bitler's work has been funded by Inland Steel and the American Electroplating Society.

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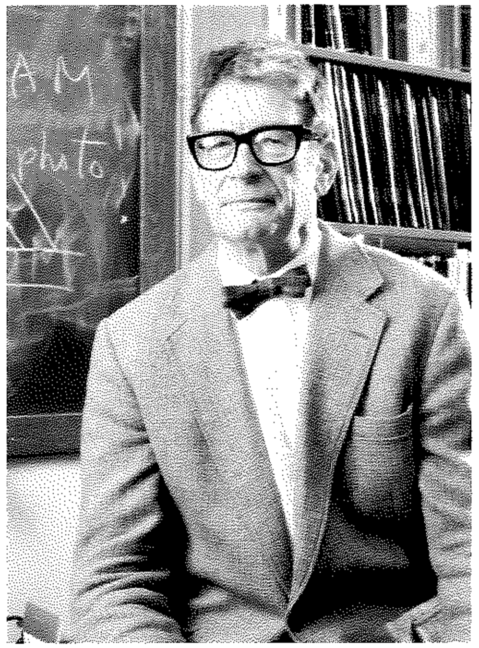
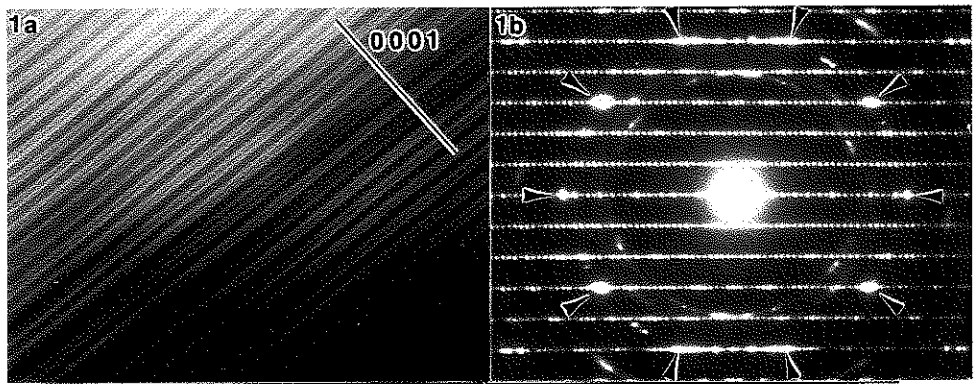
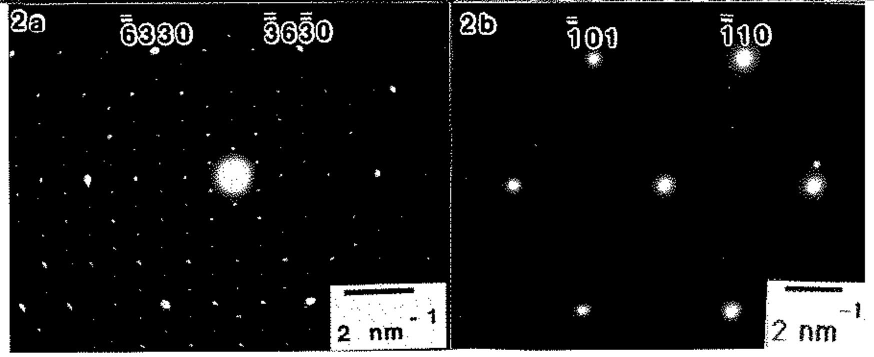


Figure 1. (a) Lattice image of the δ phase, and (b) δ [$2\bar{1}\bar{1}0$] Selected Area Diffraction Pattern (SADP) from the image in Figure 1a.
Figure 2. δ [0001] SADP and αFE [111] SADP.





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Keywords

solid-state diffusion, solid-solid reaction kinetics, soft and hard magnetic materials, steel processing, galvanization, electroplating

aul W. Brown *Chemical Formation of Ceramics and Composites*

ıntrast to the conventional sintering pro-
;or inorganic ceramics at temperatures in
:s of 1,000°C, advanced ceramics and novel
ɔosites can be formed at low temperature
ıtmospheric pressure through controlled
ıical reaction. This method of property
.opment has broad applicability to the for-
ɔn of both monolithic materials and ce-
:-matrix composites. Unlike sol–gel
ions, chemical reactions produce near net
: results so that subsequent high-tempera-
ɔrocessing is not required. Fabrication at
ıape, as well as low temperature and pres-
involves minimal geometric constraints.
, composites can be made using combina-
of materials that would be precluded if
:ssing were to occur at high temperature
ɪressure. For example, ceramic–matrix
ɪosites combining nontraditional constitu-
such as metals or polymers, can now be
esized. In addition, precursor phases of
nuous fibers can be introduced to produce
toughness composites, even in composites
ıre not fully dense.

ı a generic example of a benefit of chemi-
rmation, sequential chemical reactions can
:d to first form a fibrous phase that is sub-
ntly infilled by a matrix phase as the result
:cond set of reactions. If the nonmatrix
is organic, it can be functionalized to
r specific desirable properties to these
osites. Applications for chemically pro-
l ceramics and composites range in scope
the structural to electronic fields. For
ural application, high toughness can be
ved; for electronic applications, useful
rties such as chirality can be conferred on
ganic constituent to produce piezoelectric,
lectric, or chromophoric composites.

:. Brown's group has demonstrated the
.cal formation of a variety of ceramics and
osites including the formation of hy-
apatite (HAp) and HAp-collagen compos-
f the cristobalite polymorph of aluminum
hate, and of alkali zirconium phosphates.
has been synthesized within a few hours at
ılogical temperatures and under condi-
:ompatible with those in vivo.

ase pure, porous monoliths of the high-
rature cristobalite polymorph of $AlPO_4$
ıeen synthesized at 130°C, approximately
: below the temperature at which
ıalite is in the thermodynamically stable
Phase pure monolithic alkali zirconium
hate has been prepared at 500°C; mono-
f the precursor phases have been prepared
as 60°C. This later class of ceramics is
ıely multifunctional and is of interest as a
tate electrolyte, low thermal expansion
al, and low thermal conductive material.

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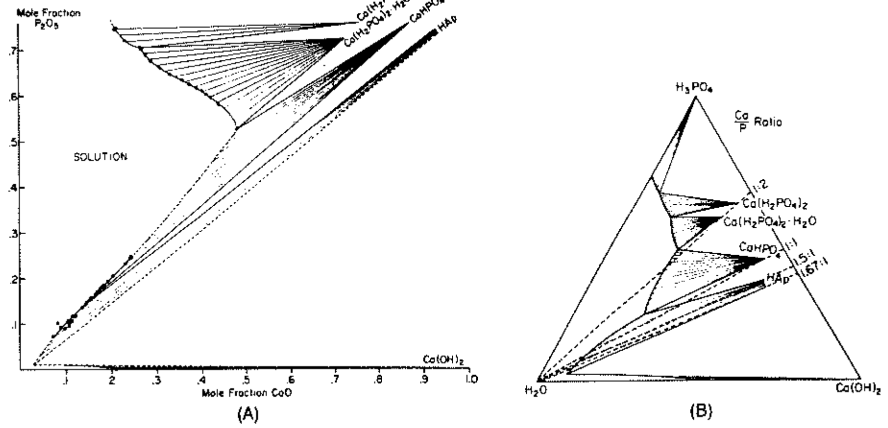
Figure 1. The ternary diagram: $CaO\text{-}P_2O_5\text{-}H_2O$ at 25°C showing the stability regions of biologically important compositions.



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Keywords

chemical formation of ceramics and composites, bioceramics, biocomposites, multicomponent phase equilibria, low-temperature synthesis

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Altaf H. Carim *Microstructure at Solid-State Interfaces*

Professor Carim's research interests are centered around the microstructure and microchemistry of solid-state interfaces. The primary research tool in this work is the transmission electron microscope (TEM). Current studies include an exploration of the dilute ceramic compounds formed as interfacial phases during brazing of ceramics, and an atomic-level investigation of interface structure and defects in oxide superconductor thin films. Some aspects of the latter project are briefly described here.

There are now many ways to produce high-quality films of the $YBa_2Cu_3O_{7-x}$ material that was recently found to be a superconductor at temperatures up to about 92K. For all of these deposition techniques, however, it is the final microstructure that controls the crystallographic properties. Orientation of the films is critically important, as is the number and nature of crystallographic defects such as stacking faults, grain boundaries, phase boundaries, and dislocations. High-resolution transmission electron microscopy (HREM) allows us to image individual atomic columns in a sufficiently thin sample. Specific defects and atomic arrangements at interfaces can thus be directly observed on the sub-nanometer scale.

An example of a structure in which stacking faults and dislocations are associated with a particular type of grain boundary is shown in Figure 1. Although high-resolution micrographs appear to represent the atomic columns that are viewed end-on as simple black or white dots, the actual correlation of the images to the atomic positions is often more complex. Fortunately, simulated HREM images can be generated based on the atomic structure of the sample and a knowledge of the microscope parameters and operating conditions. By comparing the experimentally obtained images with such simulations, one can determine the terminating planes at interfaces or find the correct displacement associated with defects.

Identification of interfacial phases and defects is important for understanding current flow and for optimizing processing of superconductor thin films. These microstructural issues, however, are vital for a much wider range of materials as well. For example, the adhesion and mechanical strength of ceramic–metal joints are critically dependent on the microstructure at the interface. The fracture toughness and high-temperature stability of structural composites are also governed by matrix-inclusion boundaries. Investigations of interfacial structure can help to elucidate the fundamental origins of many materials properties and may suggest how to tailor the processing of real materials in order to improve their performance.

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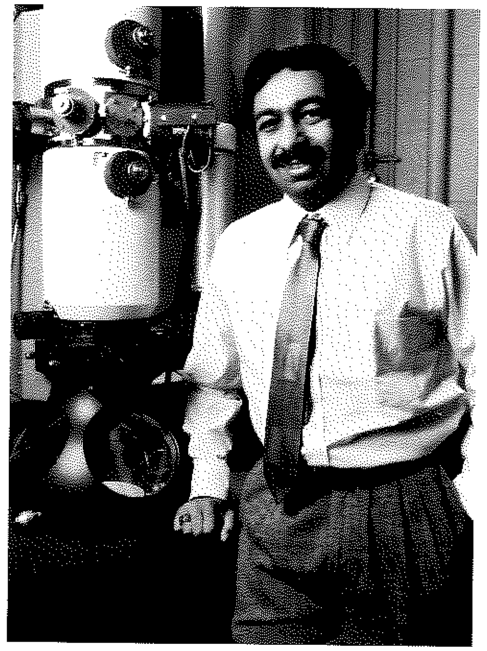

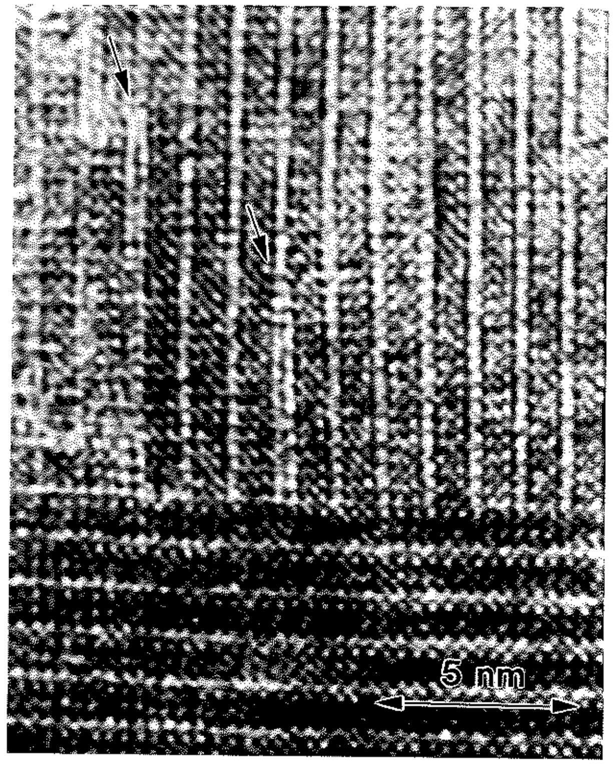

Figure 1. High-resolution TEM micrograph of a grain boundary in $YBa_2Cu_3O_{7-x}$ with a rotation of 90° from one side to the other. The brightest rows of dots represent the Cu-O basal planes of the unit cell and are spaced by 1.17 nm. The geometrical mismatch at the interface results in defects, including additional atomic layers (stacking faults) in the upper grain (arrowed). The faults terminate within 10 nm of the boundary at dislocations, which are aligned parallel to the viewing direction.

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Keywords

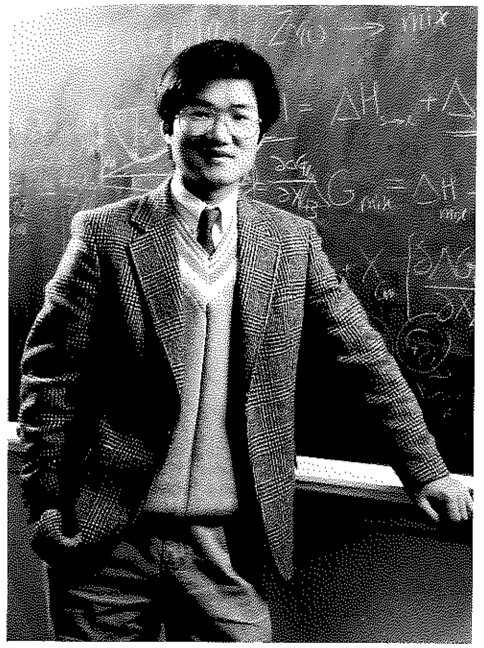
transmission electron microscopy, interfaces, ceramic joining, superconductors, ferroelectrics, thin films, crystal defects

ong-Qing Chen *Structural Phase Transformations*

f Dr. Chen's research projects involves a
atic investigation of microstructural evo-
during solid-to-solid phase transforma-
Results are obtained through computer
ation techniques combined with modern
ic theories.

very common type of phase transforma-
solids is the decomposition reaction of a
geneous single-phase into a two-phase
re, which is called a *precipitation reaction.*
ntionally, there are two kinds of mecha-
that are employed to interpret the kinet-
decomposition, namely classical
tion and growth, and spinodal phase de-
sition. The spinodal mechanism is ap-
nly to isostructural decomposition,
as the decomposition of a homogeneous
phase to a mixture of two phases with
nt crystalline symmetries has always been
ed to occur through classical nucleation
owth. However, recent computer simula-
f a disordered phase decomposition into
phase mixture of ordered and disordered
concludes otherwise. The computer
tion shows that the conventional decom-
n mechanism through nucleation and
h of an equilibrium ordered phase occurs
y a very narrow region of the two-phase
the phase diagram. For the most part,
position always starts from a congruent
ng, which produces a transient
ichiometric-ordered single-phase state
he same composition as the parent disor-
phase and the same symmetry as the
ct intermetallic phase. Decomposition of
nsient ordered phase occurs predomi-
at the antiphase domain boundaries,
results in a two-phase morphology with
of disordered films separating antiphase
ns of the ordered phase. Currently Chen
ing into the case of how microstructure
ps during a decomposition of a cubic
into a two-phase mixture of cubic and
nal phases (i.e., the crystal systems of the
oduct phases are different). A typical ex-
is the precipitation of the tetragonal
from the partially stabilized ZrO_2 alloys.

en is also interested in the influence of
ange interactions on the morphologies
ped during a solid-to-solid phase trans-
ion. The types of long-range interactions
consideration are the long-range elastic
dipole interactions, electric dipole-dipole
tions, magnetic dipole-dipole interac-
and the long-range Coulombic interac-
They are the underlying interactions
sible for various interesting phenomena
rostructural evolutions in solids including
coarsening (a small particle grows at the
e of a large one and the particle splits
aller particles), and strong spatial corre-
in alloys and ceramic systems, domain
res in ferroelectrics and ferromagnetics,
in relaxors. A typical example from a computer simulation is shown in Figure 1, where twin structures are formed as a result of long-range elastic interactions in an ordering transition of a model binary system. Chen is also conducting computer simulations on the dynamics of microstructural evolution under external fields such as applied stress, magnetic fields, and electric fields.



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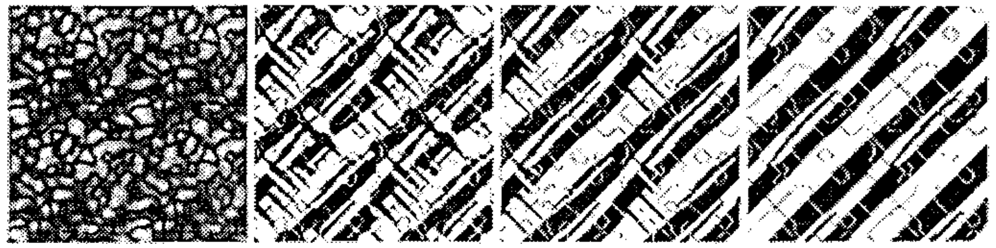

Figure 1. Kinetics of tweed and twin formation.

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materials theory and modeling, phase transformation, grain boundaries

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T.C.(Mike) Chung *New Polymer Chemistry and Materials*

Professor Chung is interested in the development of new polymer chemistry that can lead to new materials. One of his current research projects is the functionalization of polyolefins via borane monomers and transition metal catalysts. It is known that the incorporation of functional groups to polyolefin is a useful method for modifying the chemical and physical properties of polymers, (e.g., adhesiveness, compatibility, and dyeability). However, functional groups containing polymers normally are very difficult to prepare using transition metal catalysts such as Ziegler-Natta and Metathesis because of catalyst poisoning and other side reactions.

Chung's study investigates a new approach to preparing functional groups by using the intermediacy of borane monomers and polymers. Borane moieties have been found to be stable to a wide range of transition metal catalysts during polymerizations. In turn, the borane polymers are easily converted to a variety of other functionalities under mild reactional conditions. A broad range of polyolefins, such as PE and PP, with various functional groups (e.g., OH, NH_2, and halides), have been prepared.

The borane-containing polymers have also been used for the preparation of block and graft copolymers. The borane groups can be easily converted to free radical initiators for the graft-from (free radical) polymerizations. Under some reaction conditions, the oxidation of borane groups is selective and graft efficiency is close to quantitative. This chemistry covers a broad range of copolymer compositions, including both hydrophobic and hydrophilic polymeric segments. Several interesting graft polymers consisted of polypropylene, poly (1-octene), and polyisobutylene as the backbones, and several free radical polymers, such as PMMA, PVA, PAN, have been obtained as the side chains.

Several applications of the resulting new polymers have also been investigated in our laboratory, such as the immobilized catalyst using functionalized polyolefin as the supported materials. The catalyst can be recovered and reused for many reaction cycles. The functionalized and grafted polyolefin copolymers are very effective interfacial materials to improve the compatibility in polyolefin coating, blends, and composites. By using our copolymers, several new high-impact plastics and composites have been prepared. We are also extending the borane-containing copolymers to prepare boron-containing carbon fiber which could have oxidative stability at high temperature.

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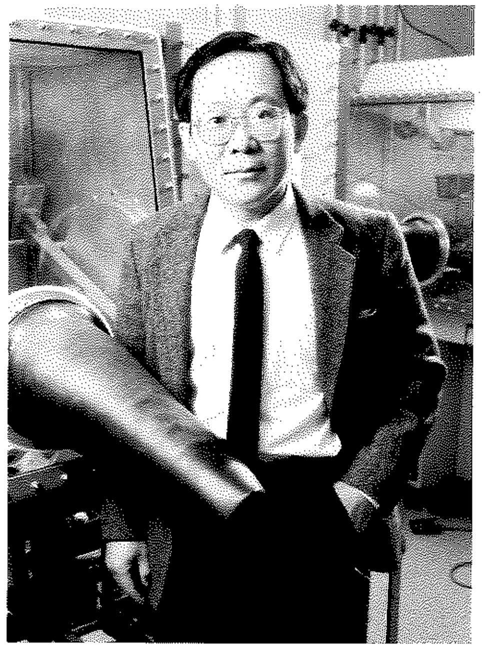
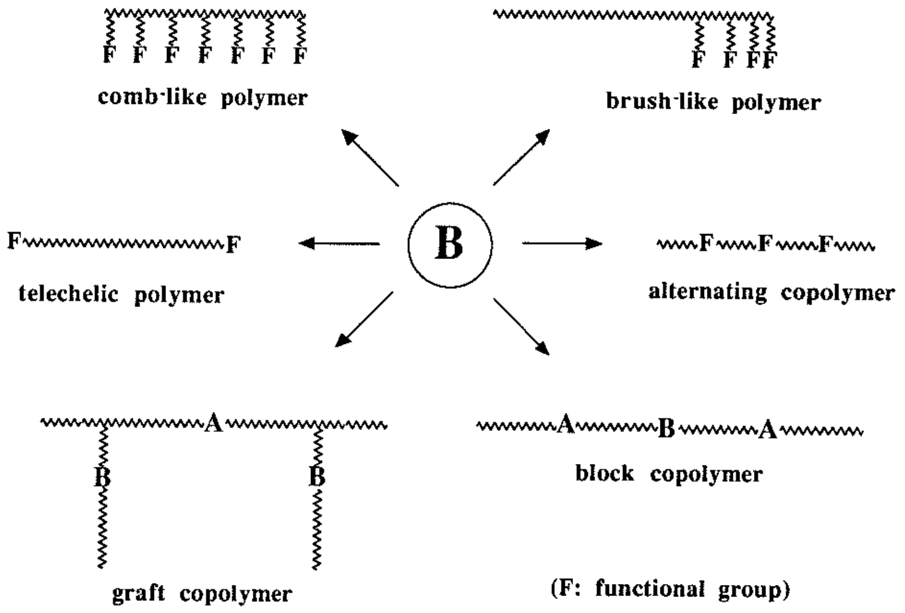


Figure 1. Versatility of borane-containing polymers in functionalization of polymers.



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Keywords
functional polyolefin, borane polymer, block/graft copolymer, immobilized catalyst

ichael M. Coleman

Multicomponent Polymer Systems

:ssor Coleman is interested in the applica-
of vibrational (infrared and Raman) spec-
opy to the study of multicomponent
ner systems. In favorable cases, the frac-
of groups that are directly involved in spe-
intermolecular interactions (usually
ogen bonds) can be measured. From these
the equilibrium constants can be obtained
lescribe the self-association in pure com-
nt (co)polymers and the interassociation
een two polymers of a binary blend. With
nformation it is not a long step to a de-
tion of the thermodynamics of polymer
ls that involve strong specific interactions.
xpression for the free energy of mixing of
systems has been developed using an asso-
n model, and Coleman's group has been
ssful in predicting phase diagrams, misci-
windows, and maps for a wide variety of
ner blends. Extension to more complex
ns such as ternary blends and copolymers
ining multiple specific interaction sites
rrently being studied.

nother research area of interest to
nan involves the search for additives that
l the formation of carbonaceous solids in
els at temperatures exceeding 400°C. De-
ls upon the thermal stability of jet fuels
nticipated to become much more stringent
: next century, when advanced aircraft are
ted to fly at speeds exceeding Mach 4.

addition to the complex chemistry of
ing and reforming reactions that occur
jet fuels are subjected to thermal stresses
nperatures above 400°C, carbonaceous
at these temperatures are being studied
vibrational and NMR spectroscopies.
; these results as a guide, a number of ad-
s have been identified, most notably ben-
cohol and 1,4-benzenedimethanol, that
l the formation for carbonaceous solids in
-1 fuels at 425°C.

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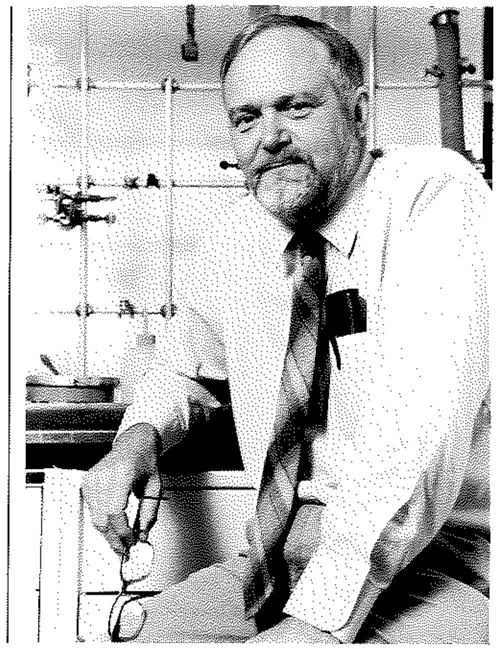
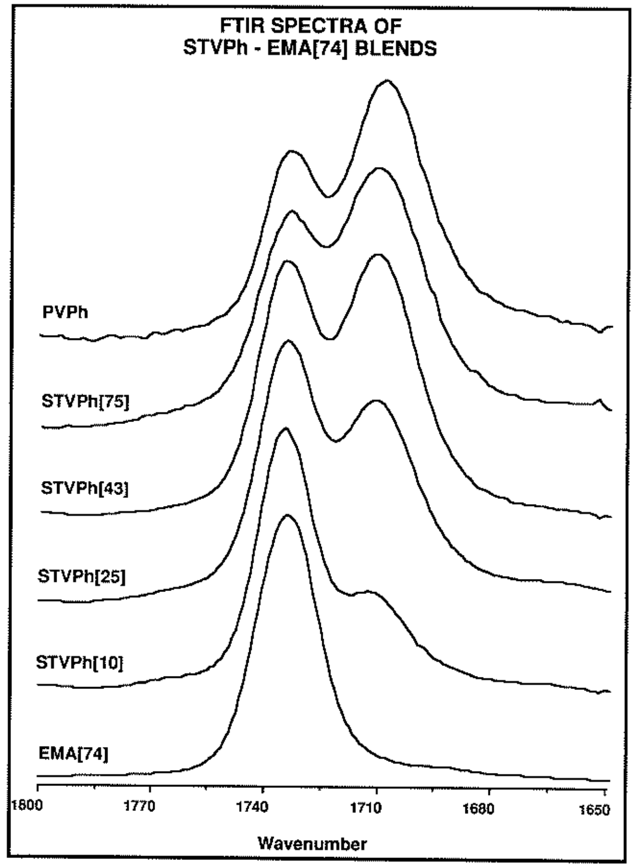


Figure 1. FTIR Spectra of STVPh-EMA[74] Blends



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Keywords
polymer blends, phase behavior, polymer vibrational spectroscopy, hydrogen bonding in polymeric materials, jet fuels stabilization

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Ralph H. Colby

Polymer Dynamics, Rheology of Polymer Melts, Blends, Solutions, Gels, and other Complex Fluids

Using rheological techniques to experimentally probe the dynamics of polymer liquids is the thrust of Dr. Colby's research program. Simple notions of scaling are used to construct models for polymer dynamics, allowing for interpretation of the rheology data. Current interests include polyelectrolytes, ionomers, liquid crystalline polymers, block copolymers, miscible polymer blends, branched polymers, networks of both charged and uncharged polymers, surfactants, and colloidal suspensions.

In many cases, polymer dynamics are controlled exclusively by the motion of individual chains. In these cases, on time scales longer than the time it takes for molecules to diffuse a distance equal to their size, the material flows like a simple liquid. However, when there is large-scale structure present in the fluid (such as in liquid crystalline polymers or surfactant solutions) viscoelastic response is evident on time scales much longer than the molecular diffusion time.

An example of this is shown in Figure 1, which plots oscillatory shear data for a liquid crystalline polymer. In this experiment, the frequency ω of mechanical oscillation is varied, so as to probe the response of the polymer on different time scales. The arrow indicates the frequency corresponding to the reciprocal of the molecular diffusion time. In its nematic phase (solid curves) the viscoelastic response is liquid-like at frequencies smaller than the frequency for molecular diffusion (reflected in the fact that the loss modulus G" is dominating the response at low frequencies).

In contrast, the smectic phase (open symbols) is still highly viscoelastic on time scales much longer than the molecular frequency for molecular diffusion (because the storage modulus G' is comparable to G" at low frequencies). The smectic structure apparently gives rise to viscoelastic response of this polymer on long time scales. We are currently designing experiments to explore the relation between structure and properties of similar systems in a systematic fashion.

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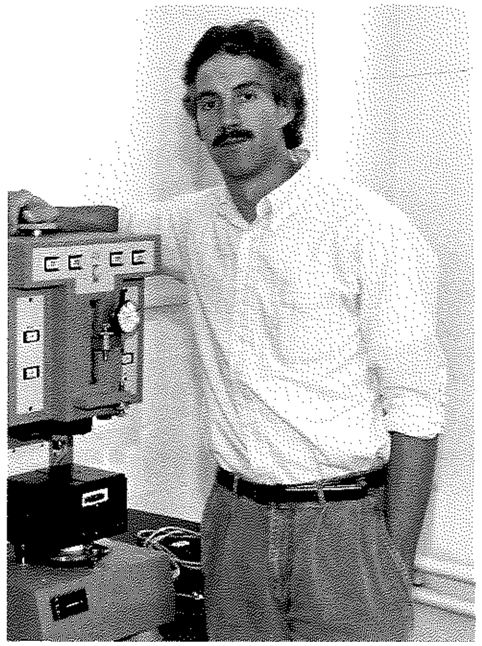
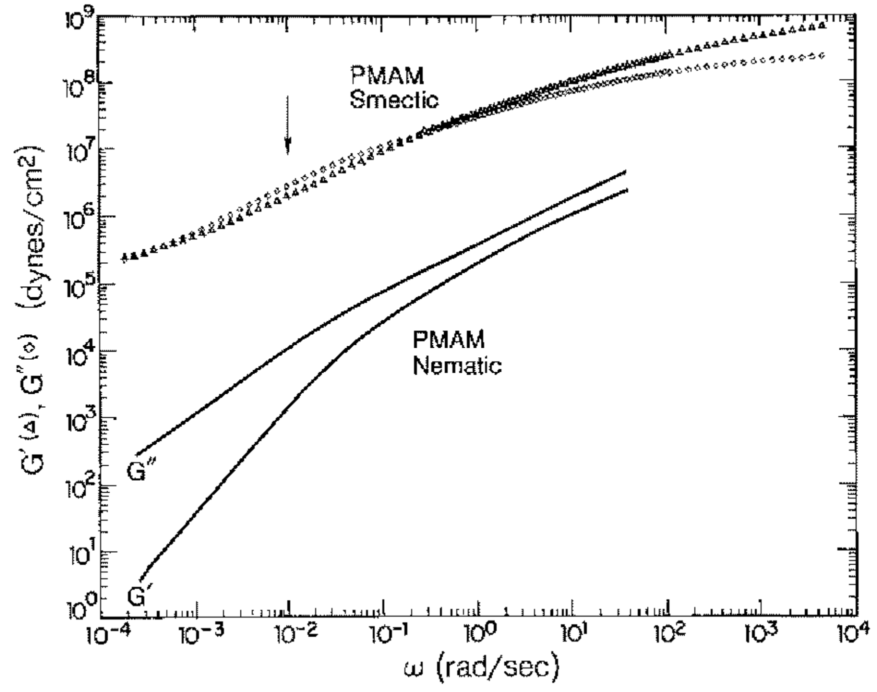


Figure 1. Viscoelastic response of a liquid crystalline polymer in its smectic phase at 84°C (open symbols) and in its nematic phase shifted to 84°C (solid curves). The arrow indicates the reciprocal of the time it takes for the polymer to diffuse a distance equal to its coil size.



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Keywords
polymer physics, rheology, viscoelasticity, structured fluids, complex fluids, scaling models

Lee J. Cuddy

Effects of Compositional and Processing Variables on the Structure and Properties of Wrought and Powder-Processed Alloys and Metal–Matrix Composites

The optimization of processing parameters to properly control gas–metal reactions at metallic surfaces, internal reactions at interfaces in metals and composites, and the redistribution of elements in alloys is essential to the improvement of existing structural materials as well as to the development of materials needed to meet demands for high-temperature strength and corrosion resistance.

Such studies require a high degree of parameter control to clearly separate the effects of the several-process variables and to establish the controlling mechanisms. Because this degree of constraint is rarely realized in commercial operations, laboratory procedures must be developed that can readily be translated into industrial applications—a step that is frequently overlooked at the interface between science and technology. The scope of such studies is quite broad, ranging from the effects of the heating environment upon the formation of surface compounds that influence difussional processes, appearances, and properties, to the effects of micro levels of impurities on the transformation products developed in alloy steels.

One such example is an examination of the interaction of species that form during gas–metal reactions. Figure 1 illustrates the decrease in weight gain of 309 stainless steel as the oxidizing potential of the nitrogen-base annealing atmosphere increases. This apparent contradiction arises because the primary cause of weight gain in this instance is not oxide formation, but is due to the formation of internal nitrides. Nitride formation is suppressed with the increased formation of an oxide film which inhibits diffusion of nitrogen across the gas–metal interface.

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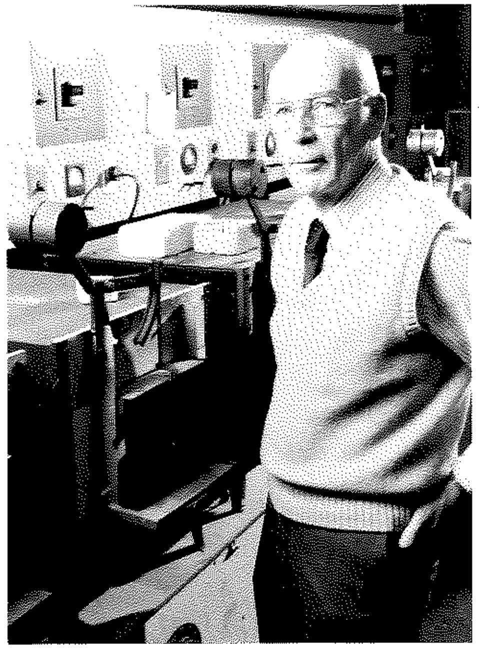
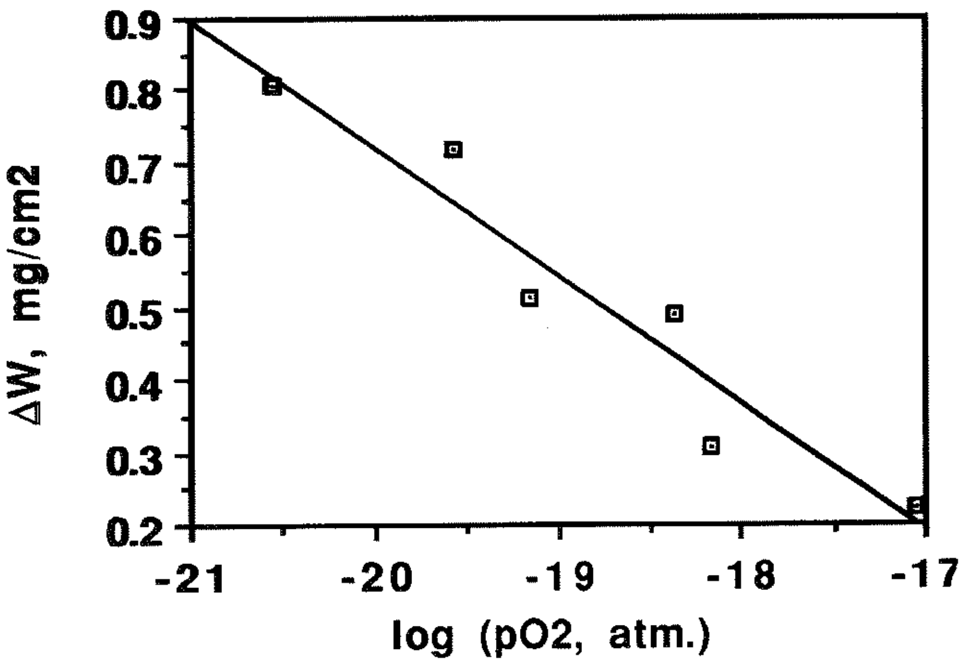


Figure 1. 309-Weight Change vs. pO_2



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Keywords

gas–metal reactions, processing parameters, interfaces, element redistribution in alloys

rasankar DebRoy *Materials Processing and Rate Phenomena*

ncipal investigator of several sponsored h programs, Professor Tarasankar y's current research covers a broad of contemporary problems in materials sing, all related to rate phenomena at mperatures. His research involves use rray of sophisticated modern experi- l tools and physical and mathematical tion techniques. These sponsored re- programs include understanding the f oxidation of aluminum alloys for the sis of oxide matrix composites, and tion of transport phenomena prin- and surface chemistry to better under- he chemical vapor deposition of nd. He has developed a new process for temperature deposition of diamond- rbon (DLC) films on a variety of poly- nd other materials, and is now scaling process to achieve uniform deposition C films on large surfaces.

nother major sponsored program, y is examining the alloying element zation, liquid metal expulsion, and the ning of impurities between the laser- liquid pool and its environment. He studying the interfacial phenomena laser–materials interaction, particu- uring laser welding. The work has ma- plications for weld metal composition l and the evaluation of the environ- impact of a particular welding system. , DebRoy is studying the role of oxy- the development of weld pool geom- d structure.

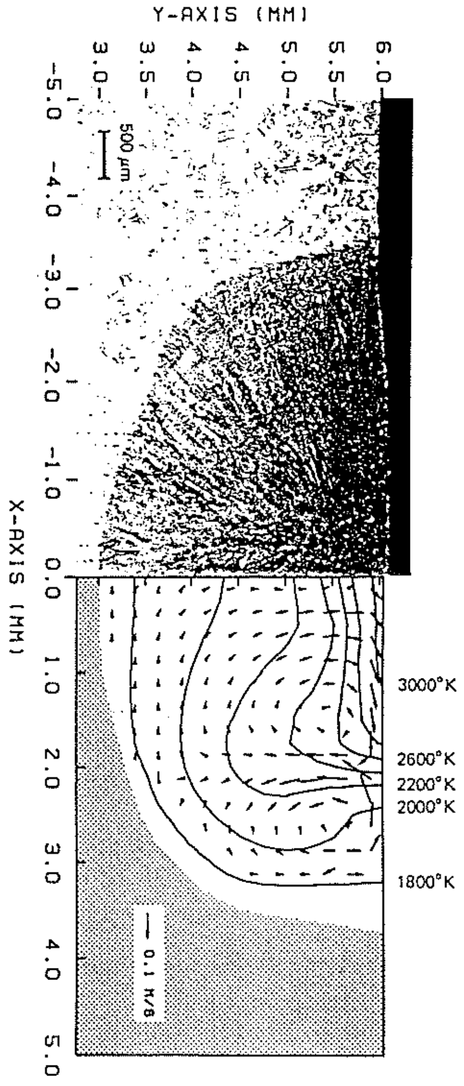

Figure 1. Comparison of the calculated and experimentally observed weld fusion zone. The figure shows that numerical simulation of heat transfer and fluid flow is useful for the prediction of weld pool geometry. From Zacharia, David, Vitek, and DebRoy, *Welding J. Res. Suppl.*, December 1989, pp 510s–519s.

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Keywords

plasma processing, welding, laser processing, thin films, numerical calculation of heat transfer and fluid flow, rate phenomena

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Semih Eser *Carbonization, Mesophase Development, Carbon Deposition, Coal Swelling under Pressure*

Semih Eser is carrying out research on carbonization of petroleum feedstocks, microscopic characterization of solid carbons, solid carbon deposition on metal and carbon surfaces, thermal degradation of hydrocarbons under supercritical conditions, and coal swelling under high pressure in reactive environments.

Delayed coking of the petroleum-heavy feedstocks (e.g., the bottom of the barrel of crude oil or heavy ends from catalytic and thermal cracking of petroleum fractions) produces light distillates (e.g., gasoline and kerosene) and petroleum coke. Depending on the microstructure and composition, petroleum coke can be used for (1) manufacturing graphite electrodes to produce steel in electric-arc furnaces, (2) making anodes used in aluminum production or in other electrolytic processes, (3) burning to raise industrial steam without producing ash.

The most significant process that takes place during carbonization in a delayed coker is *carbonaceous mesophase* development. The structure and properties of the solid carbons produced by thermal treatment of hydrocarbons (e.g., graphite electrodes and carbon fibers) are governed principally by the characteristics of the carbonaceous mesophase formed during low-temperature carbonization. Carbonaceous mesophase has properties similar to those of nematic liquid crystals, and it is easily characterized by polarized-light microscopy. Figure 1 shows a polarized-light micrograph of carbonaceous mesophase from a decant-oil sample, indicating the nucleation of anisotropic mesophase spheres that coalesce to form anisotropic solid carbon structures. A high degree of anisotropy or a well-developed mesophase in the form of elongated microstructures is required to manufacture high-performance graphite electrodes or carbon fibers.

A major challenge in the coking industry has been the establishment of basic relationships between the chemical constitution of the coker feeds and the microstructure of the resulting cokes. The complexity of the feed streams has forced the researchers to use averaged data from spectroscopic techniques such as n.m.r. and FTIR. Our research is focused on identifying the molecular species present in coker feeds, particularly in decant oils, which are used for producing highly graphitizable premium petroleum cokes called *needle cokes.* Chromatographic separation techniques such as column chromatography, thin-layer chromatography, and high-performance liquid chromatography in conjunction with GC/MS and heated probe/MS have been useful for determining the molecular composition of decant oils. This information, in turn, allows us to seek correlations between the molecular make-up of the feeds and the quality of the resulting cokes.

A rationalization of such correlations is possible through understanding the relationships between the molecular parameters of the aromatic hydrocarbons and the mesophase devel-

anthracene and phenanthrene have shown that the kinetics and chemistry involved in the formation of large molecules can be closely related to the mesophase development during carbonization. The substantial differences in the reaction mechanisms, kinetics, and mesophase development during carbonization of these two isomers have been related to the differences in their electronic structures.

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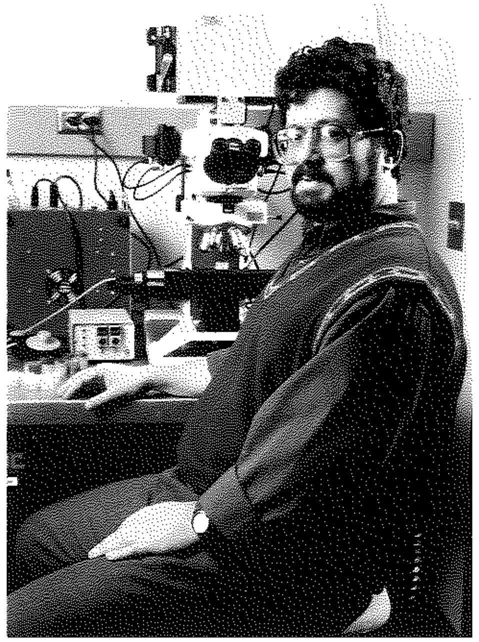

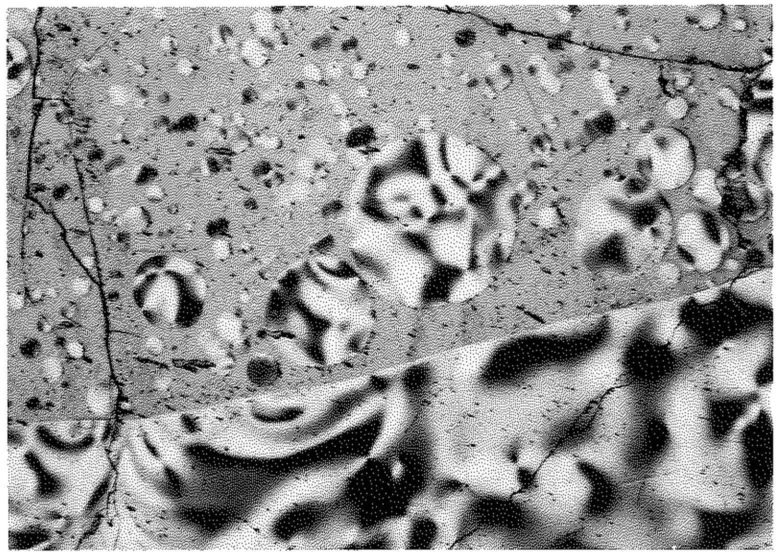

Figure 1. Polarized-light micrograph of a solid produced by carbonization of a decant oil, indicating the mesophase spheres and their coalescence to form anisotropic structures.

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Keywords

chemistry of carbonization, mesophase development

ichael Y. Frenklach

High-Temperature Chemical Kinetics, Modeling of Reaction Systems, Combustion Chemistry, Si and SiC Powder Nucleation, Diamond Film and Powder Formation, Interstellar Dust.

ormation in Hydrocarbon Combustion. tion of soot in combustion of fossil fuels s the efficiency of combustion devices uses serious environmental concerns. he last few years, detailed chemical reac- echanisms for the formation of polycy- matic hydrocarbons (PAHs)—key soot sors—have been developed in Dr. ach's laboratory. The current focus is on ablishment of the mechanisms and kinet- the oxidative destruction of PAHs, the try and physics of the evolution of PAHs ot particles and particle dynamics, and ment of kinetic models capable of pre- sooting characteristics in practical com- environments.

ic Research on Natural Gas Combus- enomena. Natural gas is one of the undant, cheap, and clean natural fuel es. The Gas Research Institute has been g the development of new technology and efficient combustion of natural gas. going research program is in support of RI efforts. The objectives are to de- reliable kinetic mechanism of methane stion, a methodology of mechanism de- ent and update, and a methodology for ient way to combine this kinetic infor- with fluid-dynamic codes used to model l natural gas combustors.

on and Silicon-Carbide Powder For- . The objective of this research program ablish reaction mechanisms and kinetics hase nucleation and growth of silicon con-carbide powders at high tempera- This knowledge is important for the al vapor deposition of silicon and sili- bide films, future technologies for cturing new materials, and formation of rstellar grains.

nation of Diamond Films and Pow- iamond is a material of choice for elec- optical, and mechanical application. In ears, vapor synthesis of diamond at low s has evolved from an issue of scientific y to a subject of technological impor- he work in our laboratory is focused on assisted chemical vapor deposition of d films and homogeneous nucleation of d powder. Particular emphasis is placed lamental aspects of diamond nucleation wth mechanisms.

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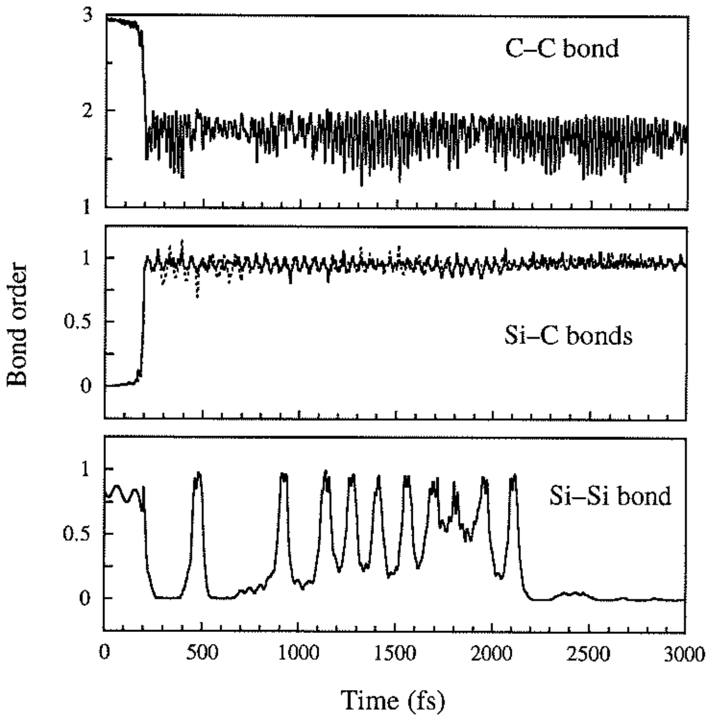
Figure 1. Time evolution of bond orders obtained in molecular dynamics simulations of acetylene reaction with a Si(100)-(2x1) surface.



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Keywords

high-temperature chemical kinetics, combustion chemistry, kinetics and mechanisms of materials synthesis.

Bernard Gordon III

Polymer Synthesis, Anionic Polymerizations, Bio-medical Materials, Degradable Polymers

Professor Gordon is interested in controlled polymer architecture to achieve specific properties. His current research program includes: controlling molecular architecture by the use of delocalized carbanion initiators for anionic polymerization, the synthesis of new bio-medical materials to control diffusion of water in the Penn State artificial heart, and the synthesis of polymers that degrade in the environment after their useful life.

Anionic initiation can be used to accurately control the molecular weight and the shape of a polymer chain. The chain can be formed in a linear, star, or cyclic form. By the use of controlled initiators we have prepared all of these structures including a new cyclic polymer that can be cleaved by treatment of mild acid. New macromonomers have also been prepared that greatly change the properties of pressure sensitive adhesives.

The Penn State Heart is made of nearly all plastic materials. One of the many crucial parts is the blood sac that pumps the blood. The sac is designed to be an elastomer and has to have a surface that is compatible with blood. Currently the best material available is a segment block copolymer that is made up of polyurethane/urea and poly ethers. This material is ideal except that water vapor easily diffuses through the material and then condenses in the mechanical heart around the motor, filling the space where the pump works. A polymer science solution is being worked on to eliminate the diffusion of the water. We have synthesized a new polymer that has similar polyurethane/urea segments to the currently used material and soft rubbery segments that are excellent barriers to water vapor transmission. The material shows greater than an order and one-half decrease in water vapor transmission.

Polymers in the environment have become a critical social issue. We have developed a new route to make polymers degradable. By making copolymers of PET, a common commercial polyester, with esters that are easily hydrolyzable, we have made a family of polyesters that have physical properties of PET, yet degrade over several years by reaction with water in the air.

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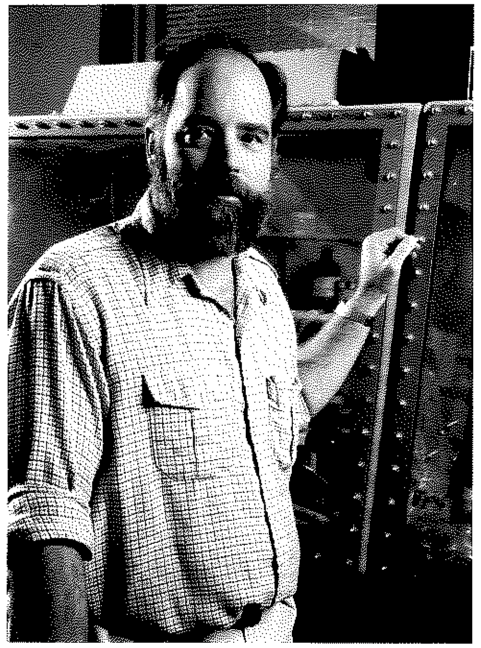
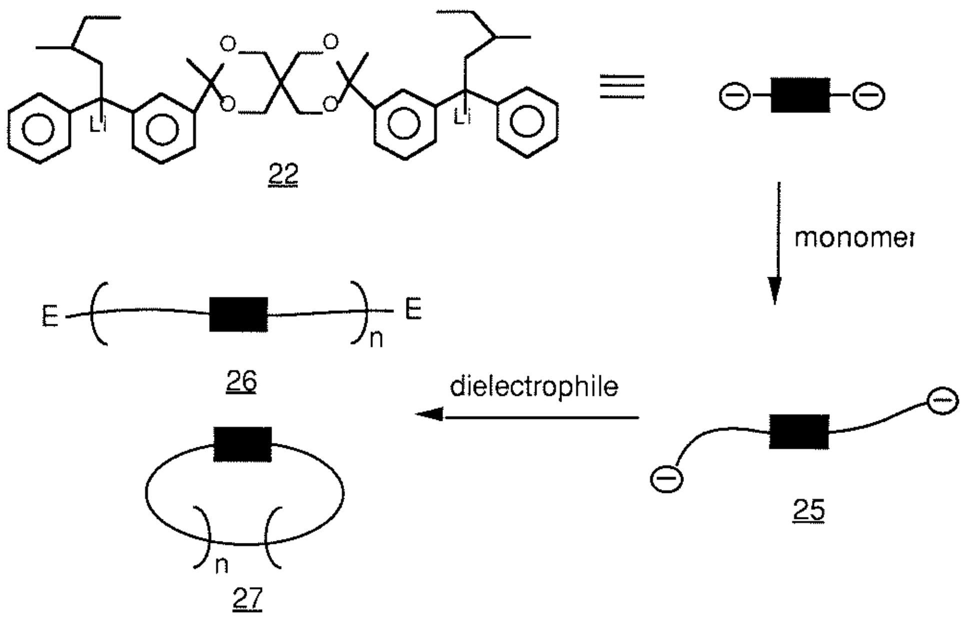


Figure 1. General scheme of reaction of a dianion with a dielectrophile.



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Keywords

polymer synthesis, controlled architecture, anionic polymerization, bio-medical polymers, hydrodegradable polymers, polymer degradation

vid J. Green *Mechanical Behavior of Brittle Materials*

materials are usually brittle, breaking
strophic manner. Indeed, this behavior
nits the use of ceramics in both struc-
nonstructural applications. The low
of energy involved in breaking these
is a result of their low toughness. In
ars, however, various mechanisms have
ntified for increasing the fracture resis-
ughness) of these brittle materials. For
improvements in fracture resistance
olved the addition of particles, plate-
kers, or fibers to a material. This type
ach has been very successful and, in
terial systems, increases in toughness
der of magnitude have been obtained.
se developments, the use of a materi-
ce approach has been a critical philoso-
aking the advances. The materials-
pproach emphasizes the relationships
processing, structure, and mechanical
as a way to understand a material, and
fy processes for improving its proper-

hysical structure of importance to a
r mechanical property may occur at
cale levels. For example, in composites
the features in the microstructure of a
that are at the key level for controlling
esistance. In laminated materials, it
he macrostructure of the material that
. The goal of this approach in materi-
e is to be able to design structures so
can obtain a targeted set of properties.
ent structures, in terms of their weight,
so be important to control the density
aterial. In some cases, this is accom-
y introducing porosity into a material.
all scientific process is akin to engi-
design but occurs at all scale levels
material.

e fracture behavior of ceramics, it has
ntly been appreciated that the fracture
e may depend on the size of the crack
s to failure. Clearly, this interest has
on situations in which this fracture
e increases with increasing crack size,
he progress of the crack more difficult
vs. Indeed, it would be of particular
o be able to control this fracture resis-
various scale levels. For example, it has
wn that residual stresses could be in-
into a material in such a way that
wth is stabilized, strength is increased,
trength variability is reduced. Such
uld be obtained from graded and lay-
erial structures. The research areas be-
tigated by Green are centered on the
behavior of ceramics. These areas in-
earch on toughening mechanisms, de-
icrostructures (for introducing crack
and crack arrest into brittle materials),
alysis, and techniques for improving
tural reliability of ceramics

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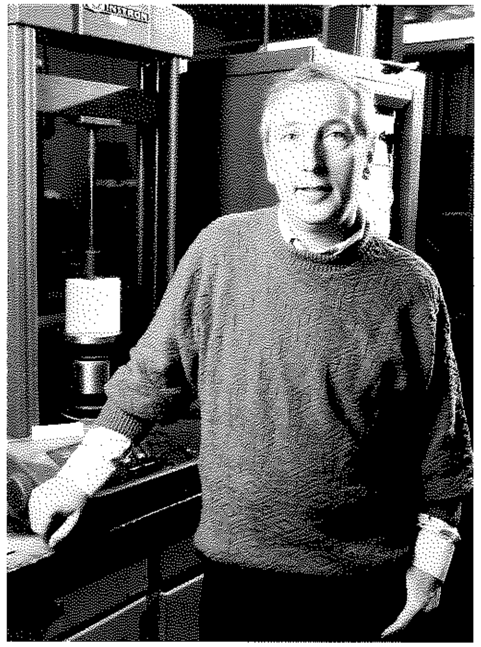
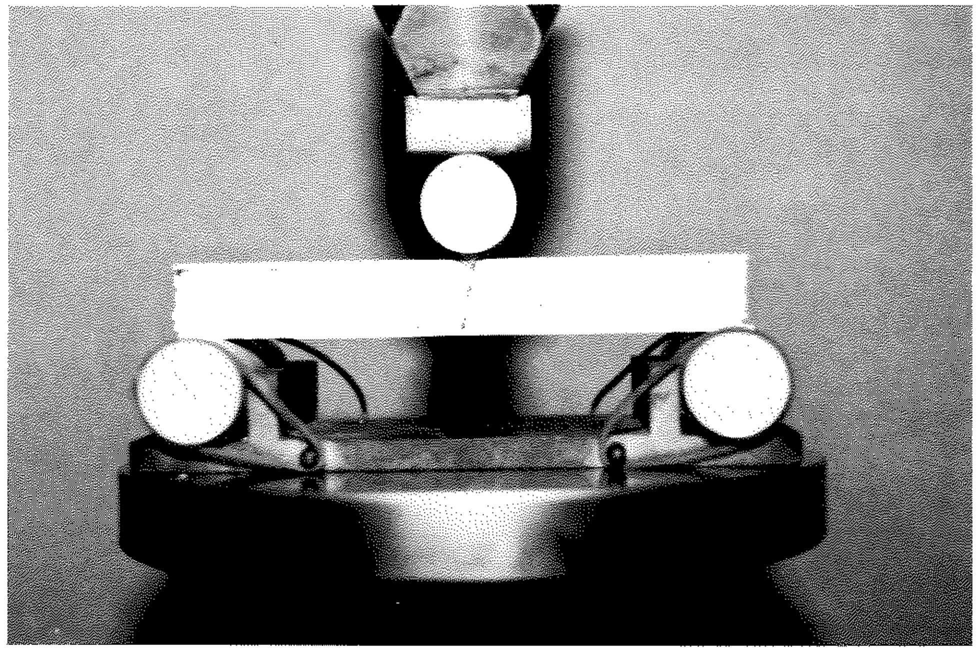


Figure 1. Three-point loading of a ceramic sandwich structure, consisting of a porous cellular core and dense faces. The failure began in the core, but was arrested by the surface layers.



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Keywords
mechanical behavior, brittle materials, failure analysis, micromechanics, fracture mechanism, structural reliability

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Ian R. Harrison *Thin Films for Long-Duration Balloon Flights*

Developing and utilizing an understanding of mechanical properties in specialty polymer films is the focus of Dr. Harrison's research, which is currently being supported by NASA. Such films are approximately the thickness of garbage bags or food wrap, yet are used to construct balloons that carry payloads of up to 7,000 pounds to altitudes of nearly 130,000 feet. When fully inflated, these balloons are many hundreds of feet in diameter, and are composed of acres of film that are assembled with approximately twenty miles of seal. The balloons are used as tools for conducting experiments in high-energy physics on atmospheric science, for instance, monitoring ozone depletion.

Harrison's contribution lies in understanding how processing and polymer structures interact to produce mechanical properties. Such an understanding is essential in trying to produce films that are tougher and more resistant to deformation. The next-generation balloon films are earmarked for the extended flight times required for future scientific payload experiments.

Current efforts are directed in three areas: (1) production of a molecular-level model that can explain film physical properties; (2) testing, evaluation, and modification of semi-commercial films; and (3) production of unique blends of existing polymers. Modeling involves integrating a large amount of characterization data into a comprehensive and consistent structural picture. This part of the study is approaching completion; the model is being "fine tuned" and key tests performed to check its validity. Incidentally, commercial film and the model studies are conducted with film formed by a blown-film process (Figure 1). There are a large number of process variables associated with this particular technique that makes the task quite difficult.

Contacts with industry have been very rewarding. A number of manufacturers have made suggestions and tested and supplied variations of their standard materials or processes in order to advance the project. Aided by understanding developed through work with the molecular model, Harrison's own study of blends falls into two areas: One approach studies fairly standard polymer mixtures, such as high- and low-density polymers, as well as polymers with unusual molecular weight distributions. Additionally, a unique combination of polyethylene (PE) and a new class of materials called *liquid crystalline polymers* are being evaluated. Appropriate processing should enable production of a fiber-reinforced PE, where the fiber is formed directly from the liquid crystal polymer phase during the film-forming operation.

Successful completion of this project will produce a new class of fiber-reinforced film systems whose properties will need to be fully will continue to benefit from interaction with this research at Penn State, yielding a more comprehensive picture of the structure-property relationships produced by controlled variations in the blown-film-processing operation.

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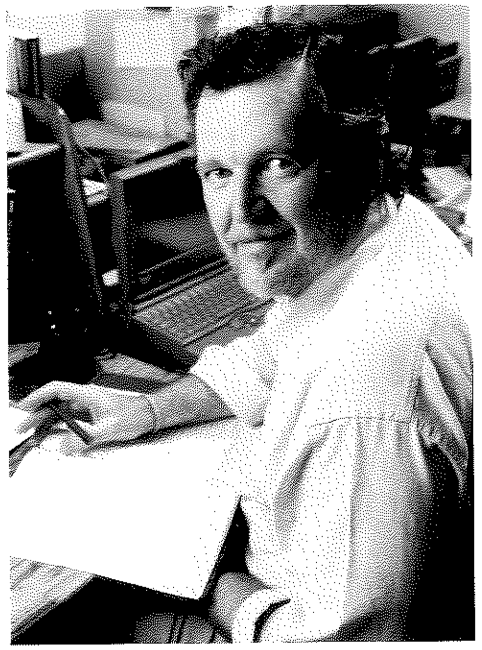
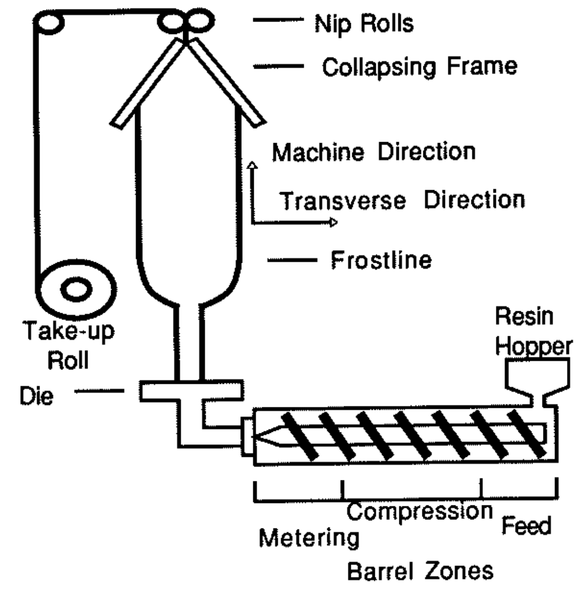


Figure 1. Schematic of the blown-film process.



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Keywords
structure–property–processing relationships in polymers, thermal properties, blown films, elongational rheology, polyolefins, TREF

atrick G. Hatcher

Organic Geochemistry of Macromolecules in Fossil Fuels and the Modern Environment

Iatcher is involved in a multitude of stud-
the field of organic geochemistry with
ic emphasis on coal, studies of humifica-
processes, and geochemistry of kerogen in
rn and ancient sediments. In addition, his
ch interests lie in applications of nuclear
etic resonance and analytical pyrolysis
iques for the study of thermal and low-
erature reactions of specific organic com-
ds in the environment.

ecific research on the organic chemistry of
nd coalified plant remains in relation to
geologic history is intended to provide a
ed understanding of the chemical struc-
nd reactivity of coal. Studies of the degra-
of plant matter in modern sediments
de information on origin of humic sub-
s and the process of humification. By
ning remnants of plant fossils in the geo-
record, Dr. Hatcher's research team can
p an understanding of the chemical
ural changes brought about by sedimen-
urial and can generate a series of struc-
nodels depicting the macromolecular
istry of the plant residues at various stages
turation or coalification. The three-di-
onal expressions of these models is gener-
nd displayed by computer. Also, the
dimensional nature of the coalified plant
nens is visualized by a newly acquired
etic resonance imaging system (Figure 1).

her studies include examination of the
stry associated with the thermal degrada-
f jet fuels, liquefaction of coal to produce
ls, and implementation of new liquefac-
echniques. Studies also include analysis of
fuels and thermal degradation products of
uels by solid-state and liquids ^{13}C NMR,
pyrolysis/gas chromatography/mass spec-
try, and gas chromatography/mass spec-
try.

vironmental chemical studies by Dr.
er's group include the determination of
nt binding sites for organic pollutants
oil organic matter by use of ^{13}C-labeled
ants and ^{13}C NMR. Using such tech-
s, one can determine whether pollutants
effectively quenched from their involve-
in the environment and, therefore, ren-
innocuous.

her environmental studies include charac-
ion of dissolved organic carbon in ocean
by solid-state ^{13}C NMR. Identifying the
and reactivity of this dissolved organic
, a major contributor to the pool of car-
the geosphere, has become a topic of
concern in efforts to understand the cy-
f carbon on Earth and its importance
espect to global warming. Solid-state ^{13}C
is one of the few methods available for
terizing the chemistry and eventually the
of this material.

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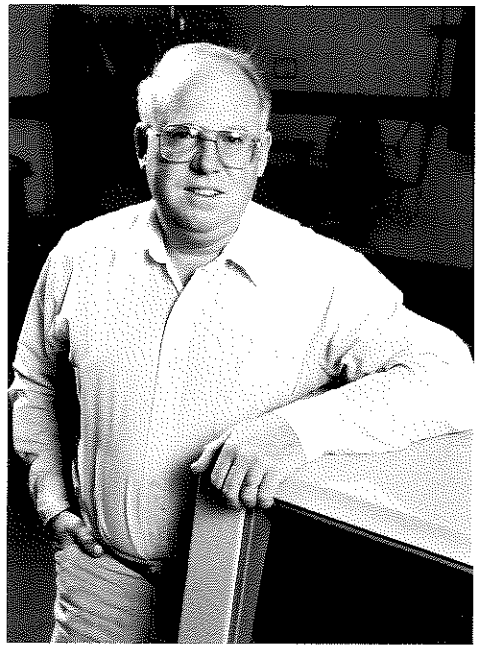

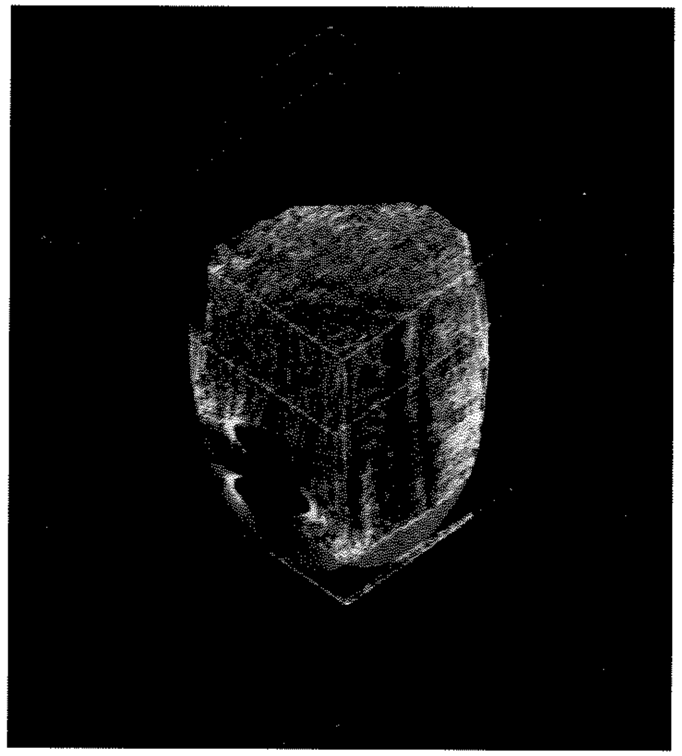

Figure 1. A three-dimensional image of coalified wood obtained by magnetic resonance imaging.

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John R. Hellmann

Development of Materials with Tailored Properties

Professor Hellmann's research interests focus on the development of new materials and complementary materials design methodologies for their application as structural and thermal members in high-performance applications. These research efforts cover the range from monolithic to composite ceramic and intermetallic materials. Effects of microstructure on thermal, mechanical, elastic, and optical properties of materials are of central interest in his studies.

Recent studies in Professor Hellmann's laboratory address tailoring of interfacial bonds in model ceramic-fiber-reinforced ceramic-, metal-, and intermetallic-matrix composites to elucidate the key mechanisms that contribute to enhanced high-temperature fracture toughness and creep resistance. His research team's development of novel fabrication methods for such materials is unique, and opens a myriad of possibilities for producing advanced ceramic-composite materials such as high-temperature structural components for the automotive, aerospace, and industrial-heating-systems manufacturing industries. Current efforts are concentrating on the selection and application of fiber coatings to achieve the levels of interfacial bonding and thermoelastic stress relief required for high fracture toughness and high-temperature strength.

A parallel activity in Professor Hellmann's laboratory focuses on establishing test and analysis methods for predicting, and experimentally verifying, physical properties such as thermal conductivity, thermal expansion, heat capacity, optical emissivity, elastic moduli, and interfacial shear strength of ceramic composite materials with tailored microstructural characteristics. His research team has combined finite-element analysis with experimental verification of interfacial shear behavior to assess the relative contributions of thermoelastic stress and applied mechanical stress to the interfacial failure in fiber-reinforced composites. Results of these efforts have been instrumental in identifying mechanisms contributing to interfacial failure, as well as in establishing criteria for properly quantifying the contribution of each to the overall interfacial failure process. Much effort has been devoted in his laboratory to developing test methods for interrogating the behavior of these important materials to temperatures as high as 1500° C in controlled environments.

Data compiled in Hellmann's lab on the temperature-dependent properties of these materials has been employed in prediction of the thermal performance and mechanical reliability of large ceramic components in industrial systems. Field evaluation of full-scale components has corroborated the applicability of the test-and-analysis methodologies developed. Resulting materials modifications and process improvements will instill systems- and component designers with confidence in advanced materials for high-temperature industrial, aerospace, and automotive applications.

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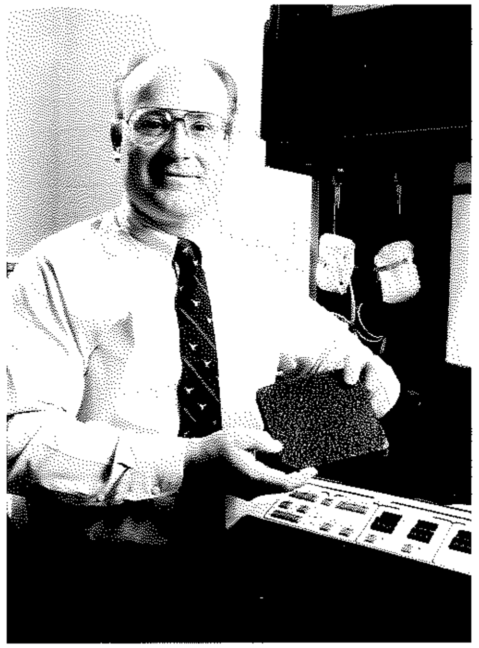
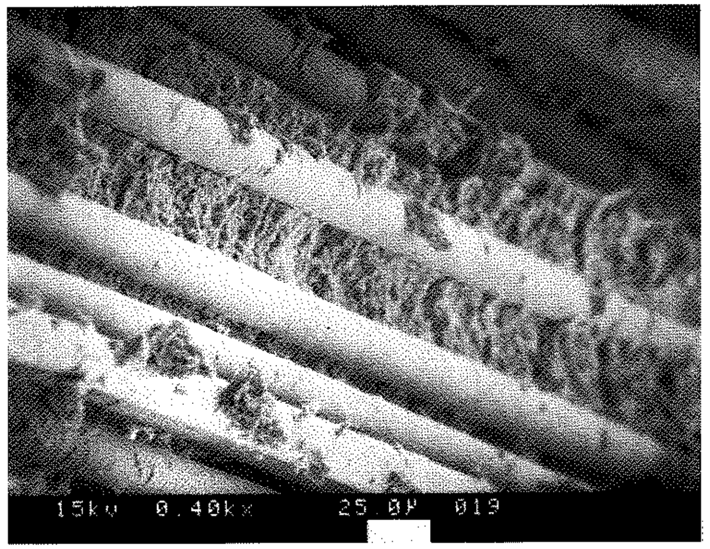


Figure 1. Longitudinal section of an alumina-fiber-reinforced polycrystalline alumina composite made by infiltration techniques developed in Hellmann's laboratory.



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Keywords

ceramics, intermetallics, composites, interfaces, coatings, mechanical properties, thermal properties, processing, microstructure, structure–properties relationships

ıl R. Howell *Phase Transformations in Bronzes*

Howell is concerned with microstruc- lopment in metals, alloys, and metal nposites. His current research inter- le the eutectoid reaction in steels and ·hase transformations in Al-Li/Silicon omposites, and laser welding of Al-Li ›nzes, and low carbon steels.

ıtectoid reaction in steels has been of · scientists for many decades. How- nagnetic nature of low-alloy steels :m difficult to examine using the on electron microscope (TEM). owell is now examining the eutectoid n a class of materials called *nickel- ı bronzed (NAB) materials.* These ma- mic steels in virtually all respects a martensitic reaction during con- ooling. Howell and his graduate stu- e shown that the proeutectoid :h phase is always responsible for initi- eutectoid reaction, by replacement of temperature, body-centered cubic h an intimate mixture of the copper- e and an aluminum-rich intermetallic mechanism for the development of the al mixture, based on a model for the ı of a phenomenologically similar dis- us reaction, has been proposed.

:ll has also devised a mechanism for the ı of solid-state dendrites of an iron- metallic phase in these bronzes.

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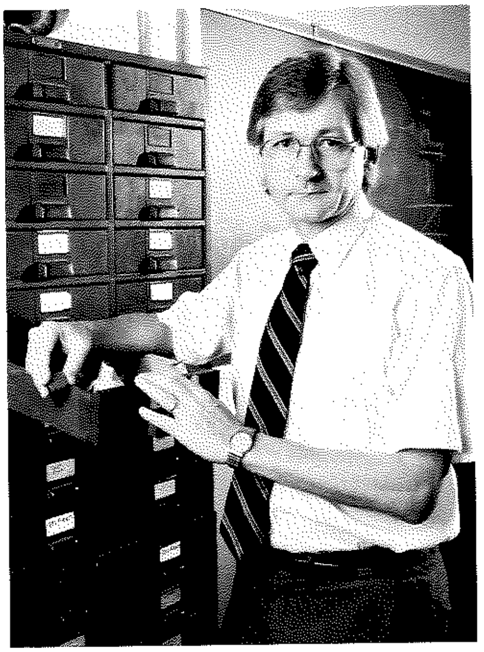
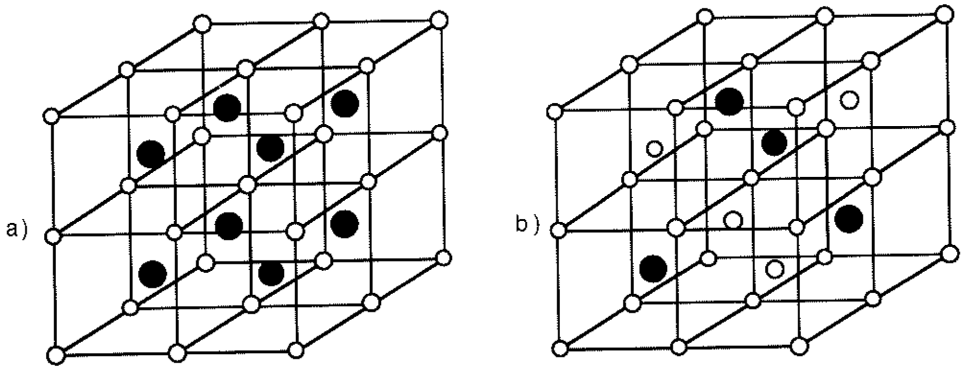


Figures 1a and b. Representation of the crystal structures of two intermediate phases in the nickel-aluminum bronze system.



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Keywords

phase transformations, transmission electron microscopy, steels, aluminum, composites, welding

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Donald A. Koss *Interfacial Shear in Metallic Matrix Composites*

A key issue in designing high-performance structural materials is optimizing both strength and fracture resistance. Metallic matrix composites provide a good example of new ways to tackle this old problem. For example, reinforcing a matrix with well-bonded, aligned, strong fibers will likely impart good strength in a composite. However, improved fracture resistance is usually obtained if the fiber/matrix interface is poorly bonded, allowing fracture energy to be consumed by crack deflection or interface shear during fiber pullout. Thus, the fiber-matrix interfacial shear behavior is an important aspect in deforming composite performance.

The importance of fiber/matrix interfacial shear behavior in controlling both the strength and the fracture behavior of fiber-reinforced composites has resulted in many studies directed at determining interfacial failure response. In metal matrix composites (MMCs), as well as intermetallic matrix composites (IMCs), the combination of chemical bonding and thermally induced clamping, due to the thermal expansion mismatch between the fiber and matrix, usually results in high interfacial shear strengths, especially at low temperatures. While this is good for strength, many of the high-performance matrix materials have intrinsically poor ductility and require some form of fiber pullout for improved toughness. Unfortunately, significant fiber pullout occurs only under conditions of low interfacial shear strengths. Thus, we are studying both the methods by which interfacial shear strengths may be controlled, and the methods of determining interfacial shear behavior. Our research focuses on high-temperature composites using sapphire-reinforced NiAl, TiAl, and Nb composites as model systems. Both experimental studies and computational modeling are being used to understand the interface behavior during loading.

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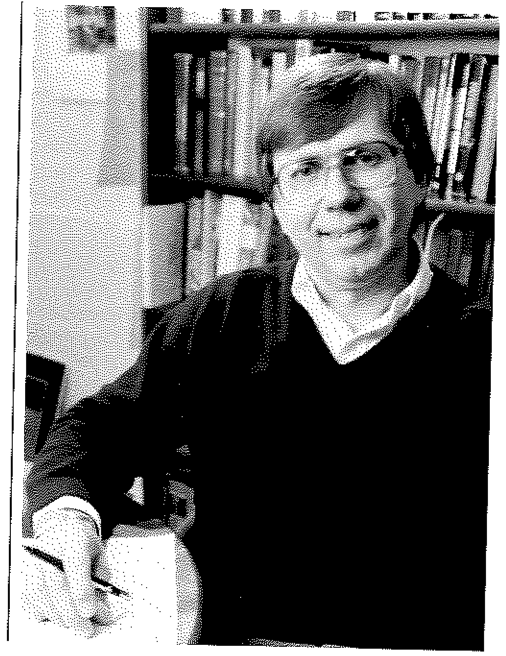
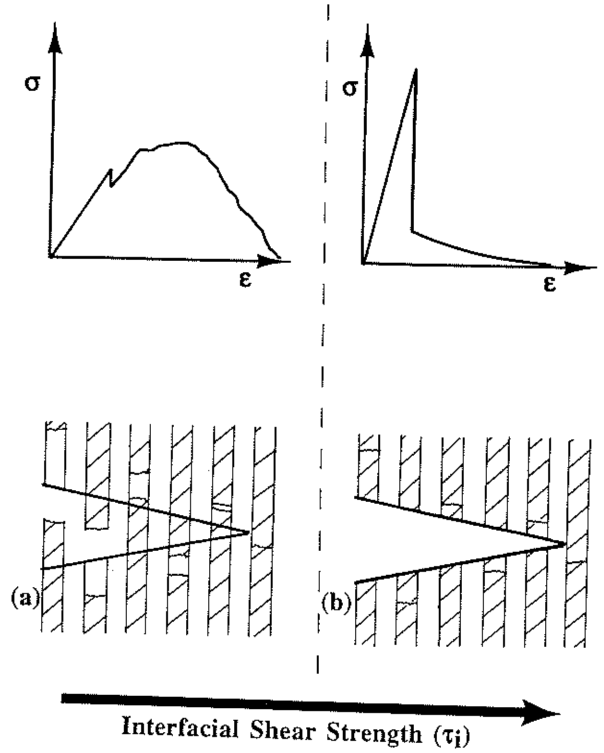


Figure 1. Influence of fiber/matrix interfacial shear strength on intermetallic matrix composite failure behavior. (a) Non-catastrophic and (b) catastrophic failure.



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Keywords

deformation and fracture, composite materials, intermetallic alloys, powder processing

Sanat K. Kumar

Theoretical and Experimental Studies of Polymer Interfaces, Semicrystalline Polymers and Blends, Thermodynamics of Polymer Solutions

he study of polymers at interfaces has ap- ications at many levels of industrial prac- :e. Our interests focus on understanding e effects of a surface on an interfacial poly- er system in the contexts of the separation mixtures of labile biomacromolecules; the hesion of thin films of homopolymers as :ll as copolymers to walls, and the dynam- of interfacial systems. The approach em- oyed in all cases is a combination of theory icluding analytical statistical-mechanics lculations and Monte Carlo simulation) d experiment (including total internal lection spectroscopy and neutron lectivity).

The characteristics of the crystal–amor- ous interphase are important in determin- the static and dynamic properties of nicrystalline polymers. Recently, it has en shown that the dynamic properties of branched, low-density polyethylene and blends can be dramatically improved ough the introduction of a small quantity out 2 percent) of relatively short branches equently butyl or hexyl). This problem is rently being explored from a theoretical d experimental viewpoint. Small angle X- and neutron-scattering studies, DSC and rmal analyses are the techniques that are d in experimentally studying this prob- 1.

The fundamental understanding of the avior of polymers, both in bulk and in ution, has important theoretical and prac- l connotations. An important example is capability to predict the solubility of ents in polymers (related to the packag- of foods in polymer containers). Re- ch is focused on this problem from a oretical perspective and new techniques, h as novel simulation and real-space ormalization or integral-equation, are d.

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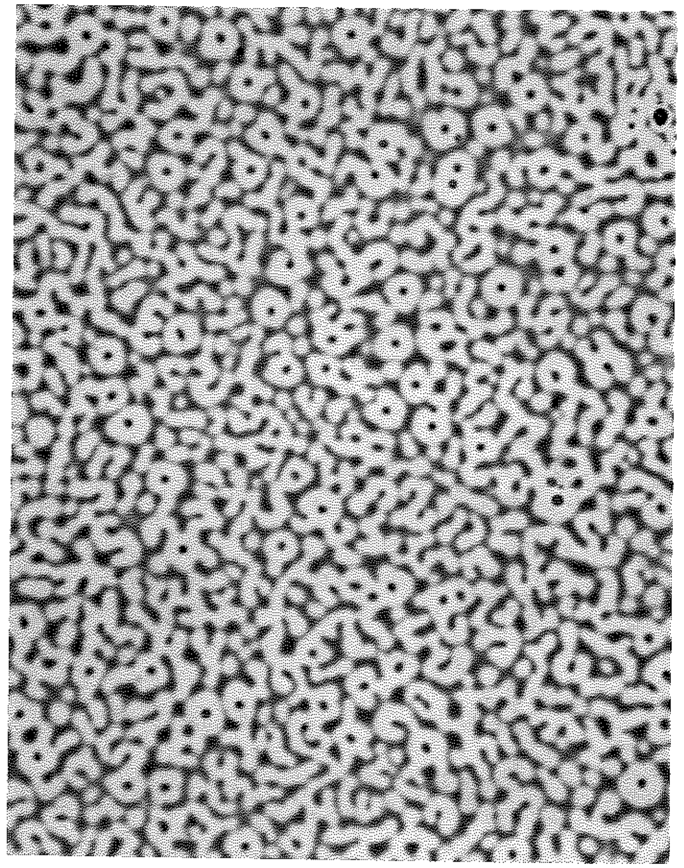
Figure 1. **An optical micrograph of a phase separation phenomenon in an ultrathin (50 nm) polymer mixture.**



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Keywords

polymers, surfaces, thermodynamics, statistical mechanics, neutron scattering and reflectivity, semicrystalline polymers

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Digby D. MacDonald

Improved Control Over the Operation of Thermal Power Plants

The development of chemistry and corrosion sensors for thermal power plants is one research project currently being conducted by Dr. Macdonald. This project, undertaken in cooperation with SRI International for a Spanish utility, aims at developing sensors to measure in situ corrosion potential, crack growth rate, general corrosion rate (via the analysis of electrochemical noise), solution conductivity, and the concentrations of hydrogen and oxygen in power plant heat transfer fluids at temperatures up to 550°C. Dr. Macdonald and his group believe that the sensors will revolutionize chemistry and corrosion control protocols in thermal and nuclear power plants because of the much tighter control that will be possible over plant operating conditions.

The first phase of the project involves the development and testing of the various sensors (for example, the fracture monitor in Figure 1). Later work will involve the installation and operation of the sensor in a Spanish power plant.

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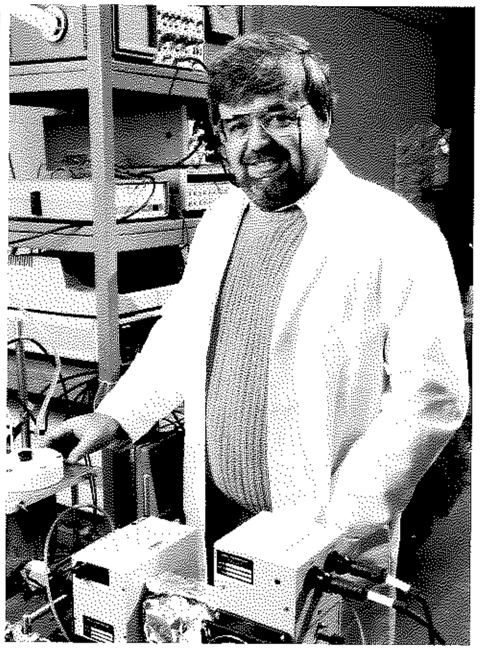
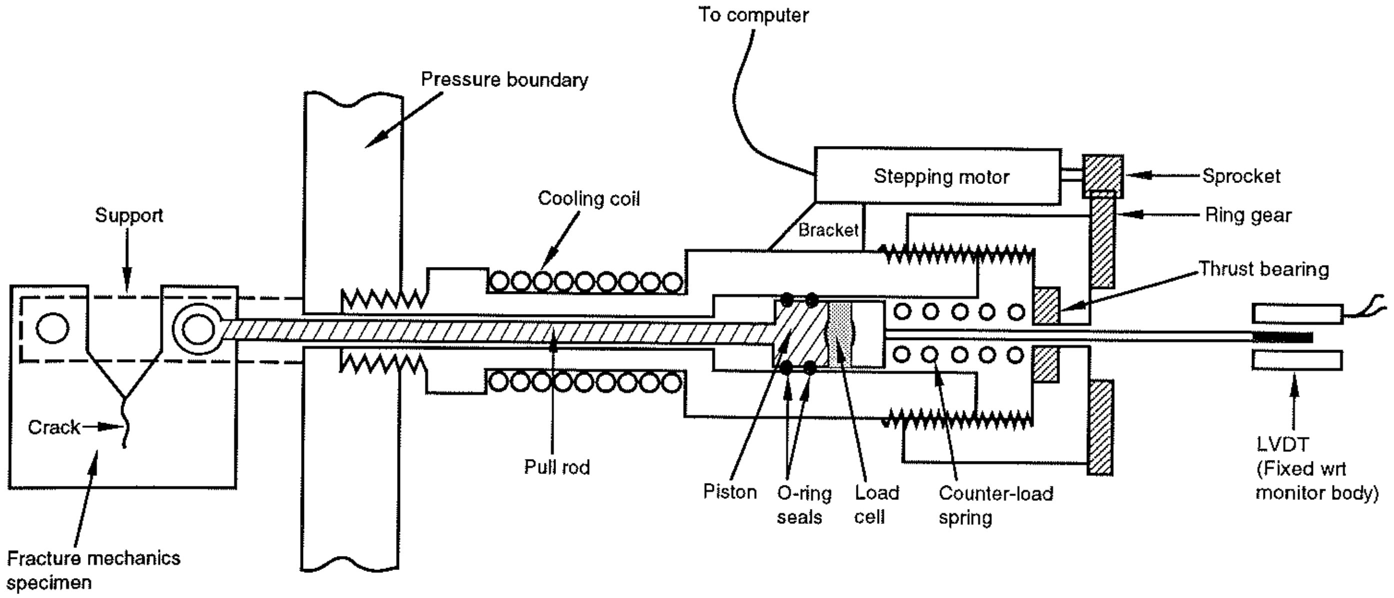


Figure 1. Schematic of an advanced fracture monitor.



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Keywords

mechanical and physical properties of ceramics, composites, electrochemistry, corrosion, high-temperature aqueous systems

errilea J. Mayo *Nanocrystalline Materials and High Temperature Deformation*

r Mayo has two main interests: stalline materials and high temperature tion. Nanocrystalline materials are ır ceramics composed of crystals smaller 0 nm—smaller than the wavelength of ight! These materials often have very properties; at one time they were seriing considered as a new form of matter. perience shows us that nanocrystalline ıre ultrahard and wear resistant, ideal for tools. Nanocrystalline ceramics, on the and, can actually be ductile at moderate atures. This allows them to be formed into parts, or to be used as a kind of r joining more conventional ceramics. scientific viewpoint, nanocrystalline ıls are fascinating, since it is the grain aries (that is, the interfaces between crysıd *not* the grains (crystals) themselves ctate the behavior of the material. In ıy nanocrystalline materials are fundally different from normal, larger-grained als.

ofessor Mayo's laboratory follows the life ınocrystalline material from start to finnthesizing ultrafine powders, processing powders into bulk form, and testing the ıanocrystalline product. Development of ssing protocols is not easy. For instance, a nary step in densifying a powder into a s to heat the powder. Unfortunately, for rystalline powders this heating causes the to grow, often to very large sizes. To aclish densification without grain growth, has explored a number of new processing iques, such as superplastic sinter-forging, ıas also attempted to understand the role res in both the densification and grain th processes. Once a viable nanocrystalline rial is made, it is tested for a number of erties of interest, such as hardness, fracture hness, ionic conductivity, diffusion bondbility, and superplasticity. Superplasticity extreme form of ductility that manifests when fine-grained materials are deformed er moderate stresses and slow strain rates. kind of ductility is currently used in aeroe applications to make extremely complex s in simple, one-step forming operations. h nonocrystalline materials, we have the ibility of further accelerating the forming s associated with superplasticity to the point re mass-market technologies (e.g., the autooile industry) can take advantage of them.

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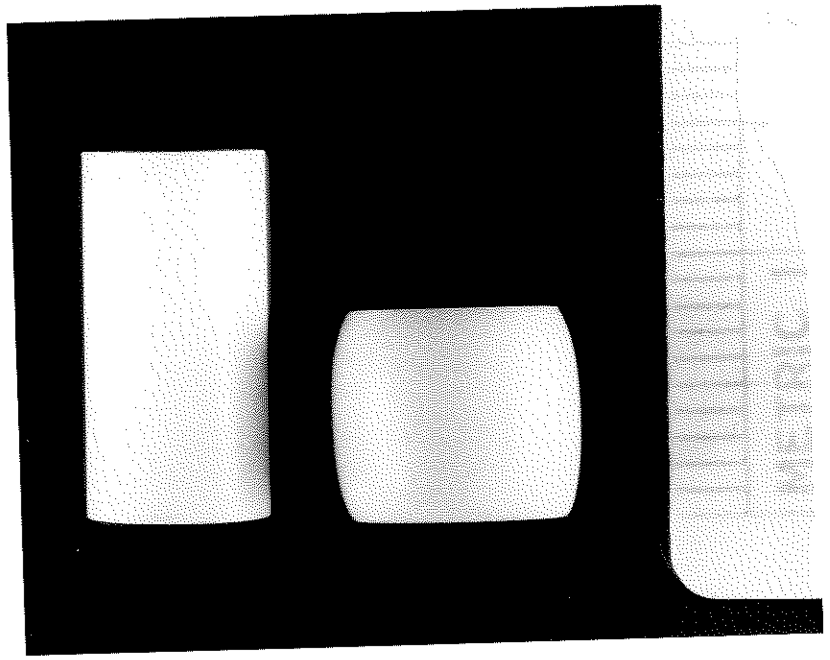

Figure 1. A superplastic ceramic. (a) before deformation, (b) after deformation.

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Keywords

nanocrystalline materials; high temperature deformation (creep), superplasticity

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Gary L. Messing *Ceramic and Particulate Materials Processing*

The fabrication of advanced ceramics with targeted properties requires control over all process stages from powder synthesis through sintering. The complex relations between the myriad processes embraced in ceramic processing is the general focus of Dr. Messing's research program. For example, he and his group have had a sustained effort for many years to understand how to regulate ceramic phase development through the application of fundamental concepts of epitaxy. By using seed crystals, or by developing self-nucleating sol-gel chemistries, they have demonstrated unique control of phase development, transformation kinetics, sintering, and microstructure development in alumina, alumina-based ceramics, and mullite.

Spray pyrolysis is a unique process for the synthesis of advanced powders and films from solution droplets. Messing's group has a comprehensive research program designed to identify how each of the processes during spray pyrolysis can be regulated to yield particles of controlled size, morphology, and chemistry. They are also developing experimental methods and in situ diagnostics for the on-line monitoring and investigation of the individual processes responsible for particle formation. By regulating the thermolysis atmosphere particulate materials and films of mixed metal oxide ceramics, nonoxide-oxide composites, and metals can be prepared.

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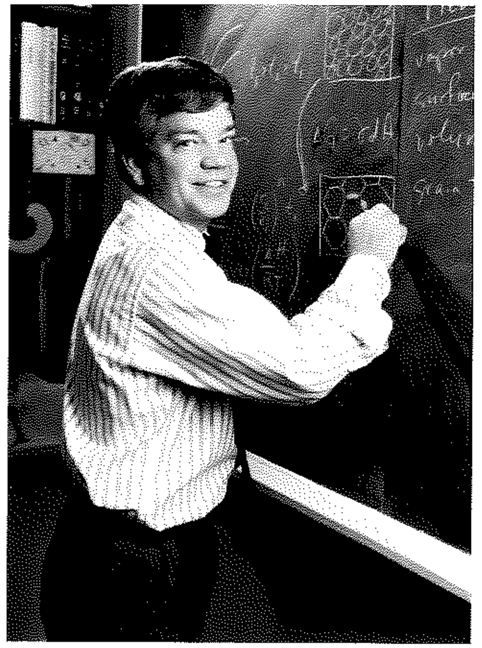
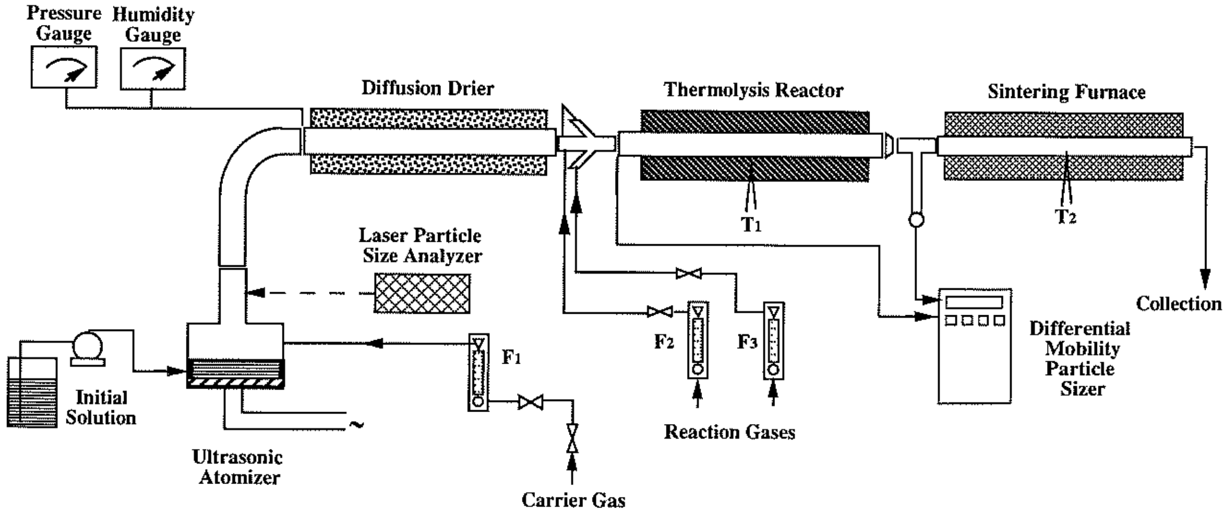


Figure 1. Schematic of spray pyrolysis system.



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Keywords

ceramic processing, powder synthesis, spray pyrolysis, solid-phase epitaxy and phase transformations, sol gels, sintering

Suzanne E. Mohney *Engineering Interfaces in Advanced Materials and Devices*

'rofessor Mohney is interested in the design of
dvanced electronic and structural materials,
ɔcusing on the study and control of metallur-
ical reactions at the interfaces between materi-
ls or between materials and their environment.
'reviously, she has studied thin-film electrical
ontacts to indium phosphide, which is an im-
ortant semiconductor for optoelectronic and
igh-speed electronic devices. The thin-film
netal contacts are an essential part of these de-
ices, and controlled metallurgical reactions
etween the contact and semiconductor are
ften required to engineer the electrical proper-
ies of the contacts. On the other hand, uncon-
rolled reactions can result in nonuniform or
reproducible contacts and poor thermal stabil-
y during processing, packaging, or extended
peration of the device. Through an examina-
ion of the thermodynamics and kinetics gov-
rning the reaction at the interface between the
ontact and semiconductor, contacts with
reatly improved thermal stability, uniformity,
nd electrical performance can be designed. For
ne study of electrical contacts to InP, phase
quilibria for the relevant metal–In–P systems
vere calculated or experimentally determined
ɔ help understand the reactions between the
netals and InP and to suggest thermally stable
ontact materials. This work also involved the
netallurgical and electrical characterization of
ne contacts, with techniques such as transmis-
ion electron microscopy, Auger depth profil-
ng, and glancing angle X-ray diffraction
roviding detailed information about the met-
llurgical reaction between the film and semi-
onductor.

Additional interests include contacts to
ther semiconductors, especially silicon carbide
nd semiconducting diamond, which are prom-
ing materials for high-temperature electronics.
lso of interest are the interfaces in high-tem-
erature structural materials. For example, it is
nportant for the fabrication of thermally stable
omposite materials to understand and control
ne reactions at the interfaces between the fiber
nd matrix as well as the composite material
nd its environment. Finally, Professor Mohney
interested in the selection, deposition, and
haracterization of thin films for electronic de-
ices, such as chemical microsensors, and coat-
ngs for structural materials.

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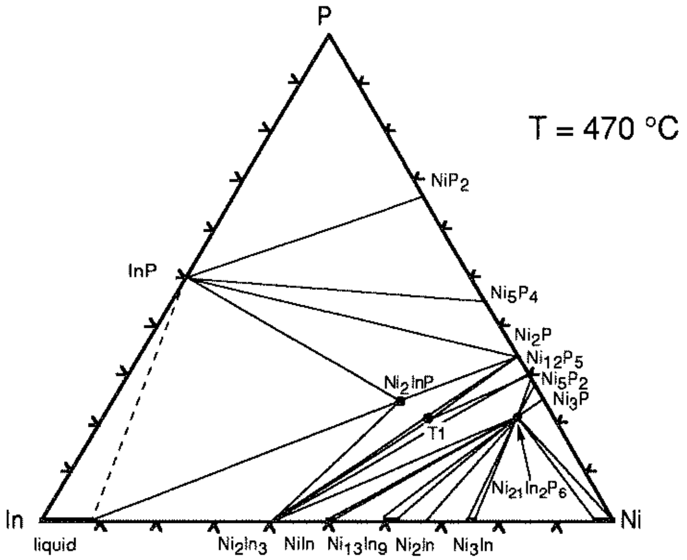
Figure 1. The experimentally determined Ni–In–P isothermal phase diagram aids in understanding the reaction between Ni contacts and the InP substrate. The diagram also shows the phases in equilibrium with the semiconductor InP. These phases may be evaluated for their potential as thermally stable (unreactive) electrical contacts to InP.



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Keywords

thermodynamics, kinetics, interfaces, electronic materials, high-temperature materials

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Robert E. Newnham *"Smart" and "Very Smart" Ceramics*

Robert E. Newnham is Alcoa Professor of Solid State Science, and Associate Director of the Materials Research Laboratory. Recently elected to the National Academy of Engineering, Newnham has written nearly 400 research papers on electroceramics and composite materials for electronic applications. During the past year, he was awarded the Centennial Prize by the Ceramic Society of Japan, the John Jeppson Medal of the American Ceramic Society, and the First International Ceramics Prize of the Academy of Ceramics for "distinguished and creative contributions to the advancement of ceramic science and culture, especially in the field of composite electroceramics." Newnham is active in several professional societies, having served as editor of the *Journal of the American Ceramic Society,* President of the American Crystallographic Association, and Distinguished Lecturer for the Institute of Electrical and Electronic Engineering.

His current research program is centered on "smart" and "very smart" ceramics. Smart ceramics are defined with reference to the sensing and actuating functions of living systems. A smart ceramic senses a change in the environment, and using a feedback system, makes a useful response. It is both a sensor and an actuator. Applications include vibration damping systems for space structures, and energy-saving windows for homes and factories. The new electronically controlled automobile suspension systems made from multilayer piezoelectric sensors and actuators are also classified as actively smart materials.

By building in a learning function, the definition can be extended to a higher level of intelligence: a very smart ceramic senses a change in its surroundings and responds by changing one or more of its property coefficients. Such a material can tune its sensing and actuating functions in time and space to optimize behavior. The distinction between smart and very smart materials is essentially one between linear and nonlinear properties. The physical properties of nonlinear materials can be adjusted by bias fields or forces to control response.

Newnham is currently developing a family of tunable transducers, which utilize the nonlinear properties of relaxor ferroelectrics interleaved with thin layers of rubber and metal end caps. The basic design is patterned after metal–ceramic composite actuators developed in his laboratory (Figure 1). Shallow cavities positioned between the metal caps and the central ceramic disk convert and amplify the radial displacements of the piezoelectric ceramic into the large axial motions of the metal end caps (Figure 2).

Five important characteristics of an electromechanical transducer are the resonant frequency *f*, the mechanical damping coefficient k, the acoustic impedance Z_A, and the electrical impedance Z_E. In the tunable transducer, the magnitudes of *f*, Z_A, and Q are controlled by stressing thin layers of rubber, while k and Z_E are manipulated by applying bias fields to tape-cast layers of relaxor ferroelectric such as magnesium niobate (PMN). As shown in Figure 2, electrostrictive PMN gives larger strains than the usual PZT transducers.

The search continues for "smarter" ceramics for use as sensors and actuators. The nonlinear properties of very smart materials are often associated with nanoscale structure and diffuse phase transformations. Under these circumstances the structure is poised on the verge of an instability, and responds readily to external influences such as electric or magnetic fields, or mechanical stress.

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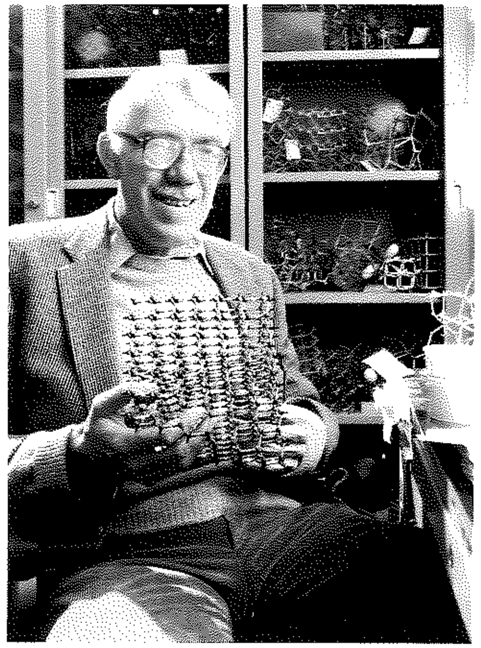


Figure 1. Flextensional actuators made from poled lead zirconate titante (PZT) ceramics and shaped metal end caps.

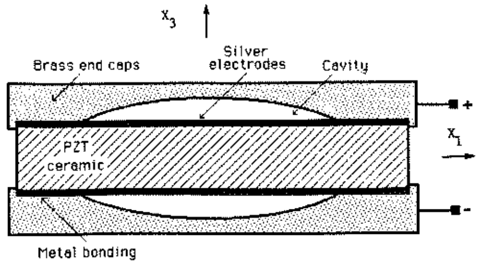
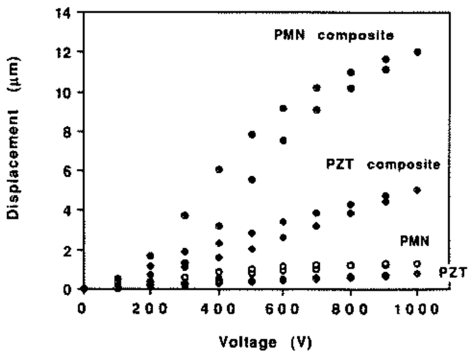


Figure 2. Capped composite actuators made with electrostrictive PMN and piezoelectric PZT amplify the strains of the uncapped ceramics. All four actuators are 1 mm thick.



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Keywords

smart ceramics, very smart ceramics, transducers, composite actuators, sensors

Kwadwo Osseo-Asare

Aqueous Systems, Materials Processing, Hydrometallurgy, Separation Science, Materials Synthesis, Dissolution Processes, Colloids and Interfaces

mpartmentalized fluids, as represented by
croemulsions, offer the attractive possibility
adapting the sol-gel and other bulk phase
cipitation methods to the synthesis of
nosize particles. Metal oxides and sulfides are
rently under investigation, with emphasis on
relationship between the properties of the
croemulsion fluid phase and particle charac-
stics.

Materials dissolution may be desired (e.g.,
drometallurgical extraction) or undesired
g., aqueous decomposition of materials in
iconductor devices). This research focuses
the electrochemical behavior of metallic and
iconductor materials in aqueous systems.
the case of the metal-based studies, the em-
asis is on the role of film formation in the
solution process. The semiconductor electro-
mical studies are concerned with the mecha-
ms of charge transfer, particularly with the
of band-gap states.

Ion separations by liquid-liquid transfer rely,
part, on the judicious manipulation of inter-
al physicochemical processes. In this re-
ch, surfactant aggregation phenomena in
anic solvents are under investigation in con-
tion with reversed micellar catalysis of liq-
-liquid extraction processes.

Transport of ionic species through mem-
nes is of central importance in a variety of
drometallurgical, chemical, biological, and
rmaceutical separation systems. Three kinds
nembranes are under investigation: liquid
factant membranes, supported liquid mem-
nes, and ion-exchange (Nafion) membranes.
emphasis is on the characterization of the
nbranes and on the relationship between
nbrane microstructure and the facilitated
nsport mechanisms of complex ionic species.

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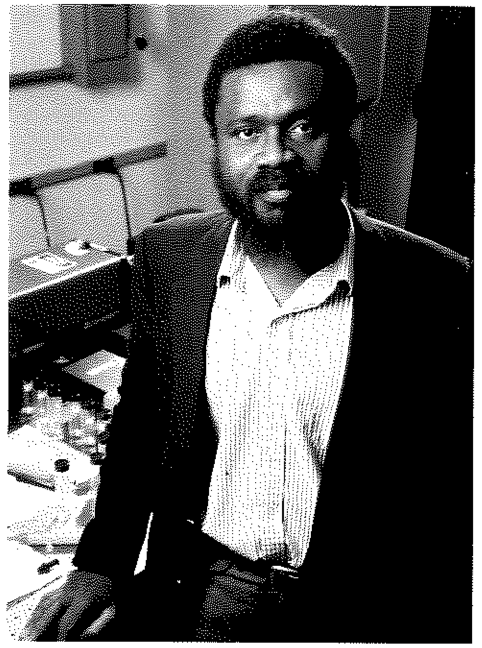
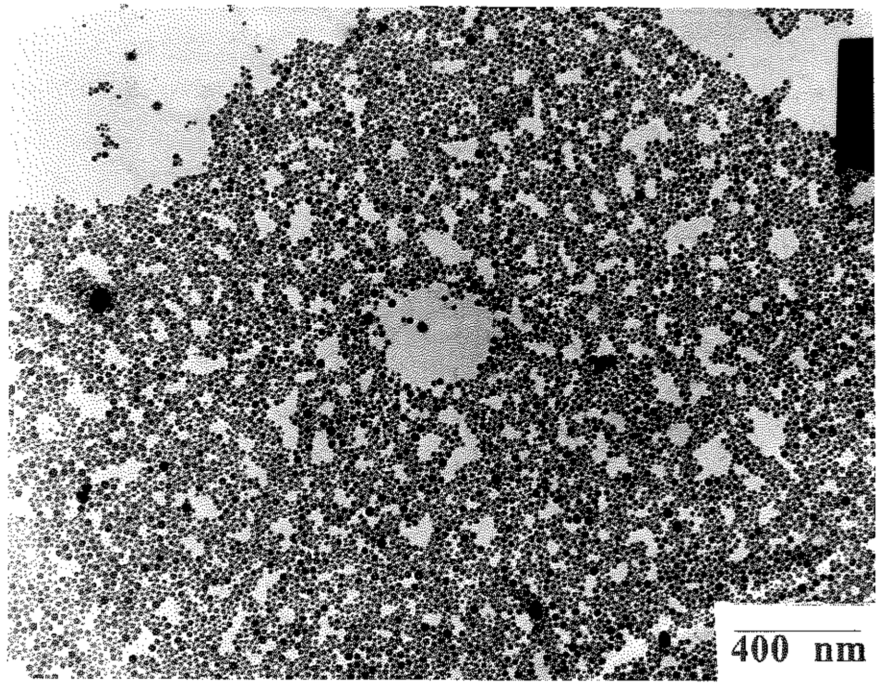


Figure 1. TEM micrograph of molybdenum sulfide particles prepared in the NP-5/cyclohexane/water microemulsion. $[MoS_4^{2-}] = 6.4\times10^{-4}$M, $[H_2SO_4] = 1.3\times10^{-3}$ M.



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Keywords

aqueous systems, materials processing, hydrometallurgy, separation science, interfaces and colloids

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Paul C. Painter

Effects of Strong Intermolecular Interactions on the Properties of Polymers

Paul Painter is interested in the effect of strong specific intermolecular interactions on the properties of polymers, particularly their ability to mix with solvents, other polymers, and liquid crystalline materials.

In describing the mixing of non-electrolytes, it has been common to distinguish between so-called "normal" and "associated" liquids. The most common examples of the latter type correspond to molecules such as water, alcohols, amines, etc., that form hydrogen bonds. At an early stage, the assumptions of simple models, such as regular solution theory, were recognized as invalid when applied to these types of mixtures, and their unusual or anomalous properties could only be accounted for by recognizing that the molecules were associated in a specific manner. Indeed, many years ago, Prigogine proposed that the formation of a complex be treated by using the assumption of a chemical equilibrium between the monomolecules of the associated species, and this approach has formed the basis for the use of so-called association models.

Association models have, until recently, been largely ignored in treating hydrogen bonding in polymer mixtures. They have most frequently been applied to mixtures of alcohols with simple hydrocarbons, where the equilibrium constants used to describe association have usually been determined by a fit to thermodynamic data (e.g., vapor pressures, heating of mixing). In collaboration with Dr. Michael Coleman, Painter has sought to do two things: first, to adapt this approach to a description of the phase behavior of polymer mixtures; and second, to develop spectroscopic methods that provide an independent measurement of the equilibrium constants. A model has been developed that provides a good description of the phase behavior of these types of mixtures.

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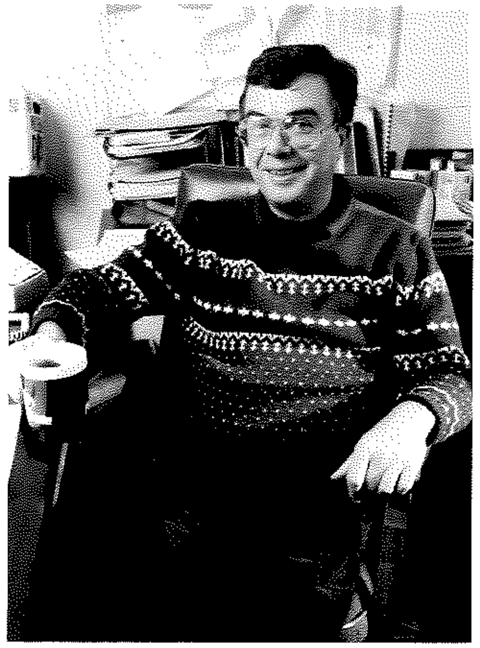
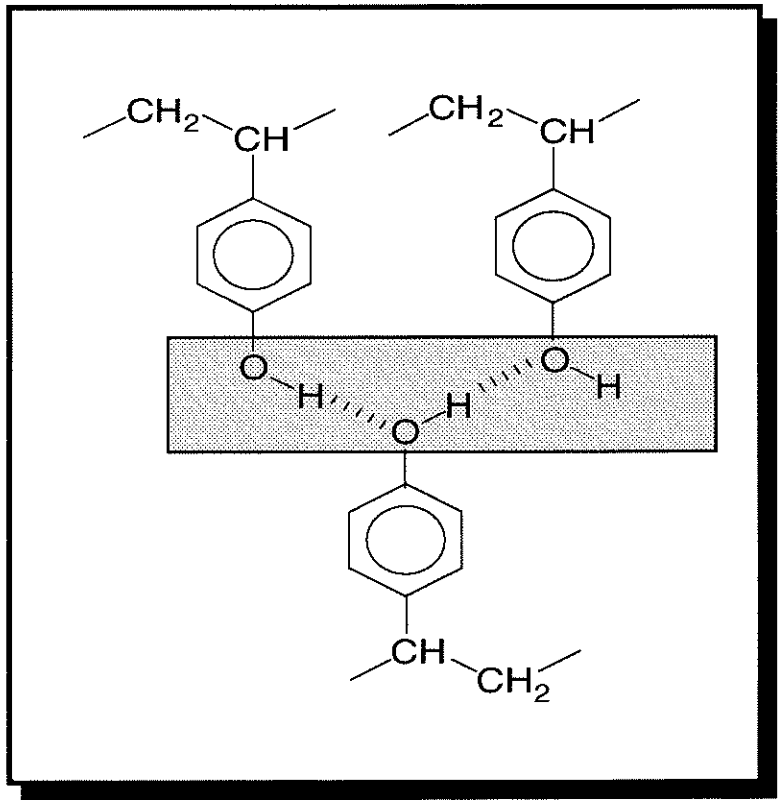


Figure 1. Hydrogen bonding in poly [vinyl phenol].



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Keywords

hydrogen bonding in macromolecular systems (synthetic polymers and coal); polymer blends; gels; liquid crystal/polymer mixtures; coal structure

arlo G. Pantano

Glass Surfaces, Interfaces, and Thin Films

ırface composition and structure of glass
nce its adsorption reactions, adhesion,
l response, and mechanical strength.
ess to say, these chemical properties of
urfaces and interfaces—which are the
on denominator in all of Professor
no's research programs—exert a profound
nce upon technological issues including
sis of thin glass films for microelectronic
ation, glass/polymer interfaces, glass-ma-
mposites, and the chemical/mechanical
lity of commercial glass products.

ıereas the fundamental understanding of
structure and chemical behavior of
and semiconductor surfaces is quite rigor-
comparable understanding has not been
ed for glass surfaces. This situation is
ıly intrinsic to the nonequilibrium, amor-
nature of the glassy state itself. In the
metals and semiconductors, the scien-
ıderstanding has come from a detailed
rison between the surface structure and
lk structure. By contrast, the bulk struc-
glass does not always provide a mean-
or convenient reference state. The very
ot of a quantifiable glass structure is still
debate. The approaches to its character-
to date are neither precise nor definitive,
e kinetics of the glass transition yield a
ude of metastable states. Thus, it is
surprising that most understanding of
ırfaces is empirical.

e empirical approach to control and tai-
of glass surface properties has been
enhanced through the use of surface-
ve measurement techniques. Due to the
at glass surfaces are most often created at
d temperatures, the surface of the glass is
an abrupt termination of the bulk com-
n and structure. Thus, the ability to
terize, directly, the surface of glasses is
ıry in research as well as in process devel-
ıt. Pantano and his group are experienced
application of these tools (including
IMS, FTIR, ISS, and TPD) to glass—
ing commercial glass products. Studies
ıown that compositional surface modifi-
due to the temperature and atmosphere
processing may extend thousands of
ıms below the surface. Moreover, expo-
the surface to humid atmospheres leads
ogressive in-depth hydration of the glass
that alters the optical reflectivity,
h, and adsorptivity of the surface. Con-
with these studies of real glass surfaces,
fundamental definition of glass surfaces
en derived through the study of model
s including clean fracture surfaces and
orous sol/gel films. These model surfaces
re suited to the understanding of adsorp-
d transport in glass surfaces, and the
nisms through which glass-surface reac-
nfluence the creation of real surfaces

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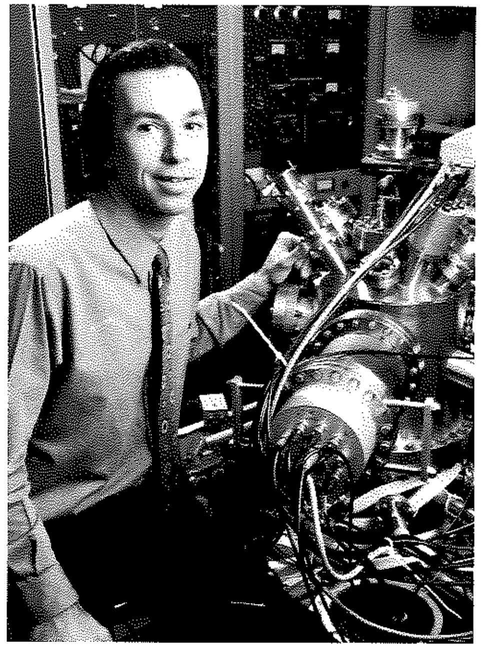

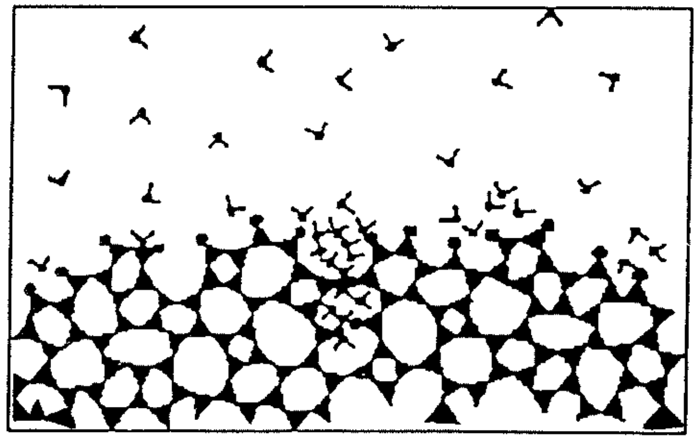

Figure 1. Model of a silica glass surface (in cross-section) showing chemisorption, physisorption, and stress-corrosion cracking in a water vapor atmosphere.

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Keywords

glass, surface chemistry, surface analysis, glass/polymer interfaces, sol/gel glasses, glass composites, glass thin films

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Sarma V. Pisupati

Emissions Control from Stationary Combustion Systems

Dr. Pisupati's research interests are primarily in studying the effects of properties fuels on combustion behavior in fixed, fluidized, and pulverized modes of combustion and capture of pollutants from the products of combustion. Specific research topics include (1) influence of weathering/oxidation/storage on the combustion behavior of bituminous coals, (2) coal-water slurry preparation and combustion in oil designed and coal-fired fluidized-bed boilers, (3) combustion behavior of blends of anthracites and bituminous coals on stokers, and (4) sorbent performance in circulating fluidized-bed combustion boilers.

Combustion of coal in any device involves bringing into contact with the fuel just enough air to completely convert all the carbon and hydrogen to CO_2 and H_2O, respectively, within the residence time available in the combustion chamber. Although this appears to be a simple process, the practical aspects are far from being simple. In stokers a variety of physical, chemical, and petrographic characteristics govern the combustion behavior. Dr. Pisupati and his group recently studied the combustion behavior of coal blends in a bench-scale stoker simulator. Caking of the bituminous coals produced clinkers on the grate and resulted in poor carbon burnout. Despite the lower reactivity of non-caking anthracite products, blending them with bituminous coals increased the carbon burnout of the blends due to a decrease in the caking properties of bituminous coals. It was noted, however, that tempering the fuel bed (with water) had an even greater effect on the combustion performance than did the particle size distribution of the fuels (over the range studied). Tempering (by addition of water) was found to change (and improve) the fuel size distribution by agglomerating the fines and this decreased the bulk density of the bed. The addition of moisture followed by good mixing enhanced the combustion efficiency. The enhancement in combustion was due primarily to the induced changes in the physical condition of the bed by agglomerating the fines into larger clusters and thereby increasing the bed voidage. An increase in carbon burnout of about 18 percent was obtained when the physical character of the tempered bed was retained but the moisture removed. The presence of moisture increased the carbon burnout by an additional 3 percent, due possibly to the induced gasification reactions. The latter increase is therefore minor compared to the former.

Emissions from circulating fluidized bed combustors CFBCs are minimized by using calcium-based sorbents to capture the SO_2 produced during the combustion of a sulfur-containing fuel. Properties that have been reported to influence sorbent performance are particle size, grain size and texture, pore size distribution and surface area. The particle size specifications of sorbents are generally governed by the cyclone efficiency and fluidization characteristics. Of particular interest are the fine particles, which are smaller than the cut point of the recycle cyclone. The residence time of such fines is equivalent to that of a single pass through the combustor, which limits the contact time for SO_2 capture and often leads to the premature removal of unreacted sorbent from the system. Dr. Pisupati and co-workers have recently completed a study on the importance of calcium carbonate content and particle size dependency of the performance of various limestones and dolostones in capturing SO_2 in fluidized bed combustors and explained in terms of the occurrence of thermally induced fractures (TIFs). Data were obtained in a bench-scale fluidized bed reactor, a pilot-scale down-fired combustor, and a 30 MW(e) circulating fluidized bed combustor (CFBC). Finer particle size fractions (100 x 400 mesh) had lower Ca/S molar ratios than coarser size fractions (plus 100 mesh) in the bed ash and recycle ash from the 30 MW (e) CFBC. Upon further sulfation of the ashes in a thermogravimetric analyzer (TGA), the minus 400 mesh fraction captured the most additional sulfur, indicating these particles did not have sufficient residence time in the CFBC to be fully sulfated. For larger particles, the slow rate of SO_2 to diffusion through the product layer limited the extent of sulfation. Hot stage scanning electron microscopy and microprobe analysis of the sulfur distribution in the particles indicated that some sorbents developed thermally induced fractures, while others with comparable $CaCO_3$ contents did not. The TIFs promoted SO_2 diffusion into the particle and, as a consequence, the sulfation behavior of such sorbents was less particle size dependent than was for sorbents that did not develop TIFs. Dr. Pisupati is currently involved in establishing a characterization methodology for sorbents for FBC applications.

Attempts to reduce NOx emissions from fossil fuel combustion sources have demonstrated a reduction in combustion efficiency and an increase in the CO and unburnt hydrocarbon emissions. In a current research program, Dr. Pisupati is studying the influence of air staging for reducing the NOx emissions on the volatile organic emissions (VOCs) from coal combustion systems.

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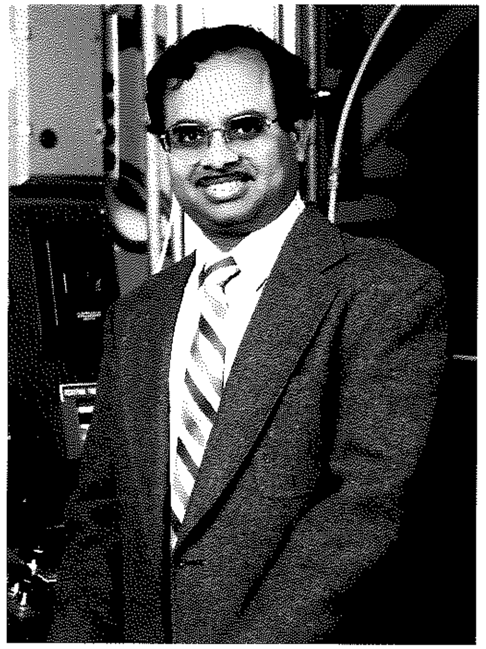

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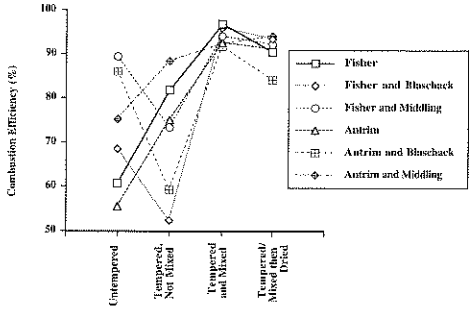

Figure 1. Combustion Efficiency Related to the Tempering Procedure for Each of the Bituminous Coals (Fisher and Antrim) and Blends with Anthracites (Blaschack and Middling)

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Keywords

Fluidized bed combustion, coal blends, SO_2 capture, sorbents

Howard W. Pickering *Corrosion of Metals*

Professor Pickering's teaching and research activities focus on the scientific and technological principles that govern the corrosion of metals and methods for its prevention. The relevant electrochemical (oxidation and reduction) and gas-phase reactions, and the changes that the metal surface undergoes during the reaction, are also of interest. More specifically, research in our corrosion laboratories includes the study of (1) selective element dissolution from alloys; (2) localized electrochemical-degradation processes such as crevice corrosion, pitting corrosion, and grain boundary corrosion; (3) reduction reactions including hydrogen evolution and its absorption and diffusion into metals; (4) precipitation, segregation, and metal–gas oxidation reactions using atom probe-field ion microscopy (AP-FIM); and (5) surface reconstruction and chemisorption in metal-gas (vacuum) systems and of metal electrodissolution in aqueous solutions using scanning tunneling microscopy (STM) and atomic force microscopy (AFM).

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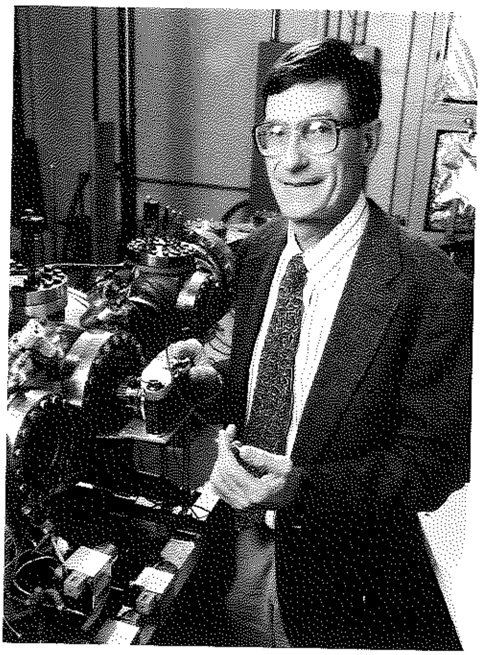
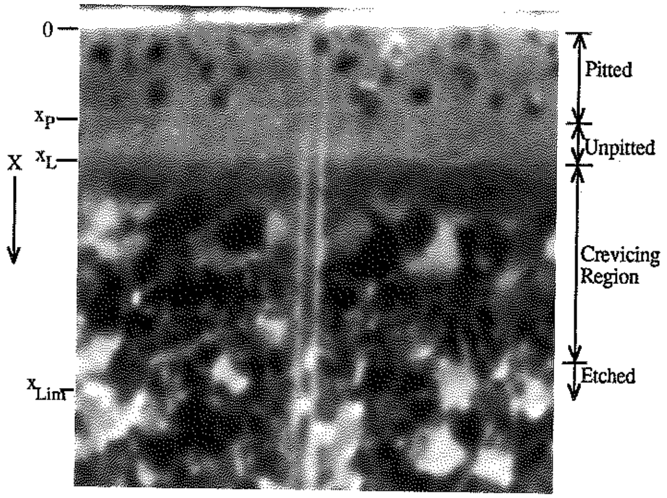
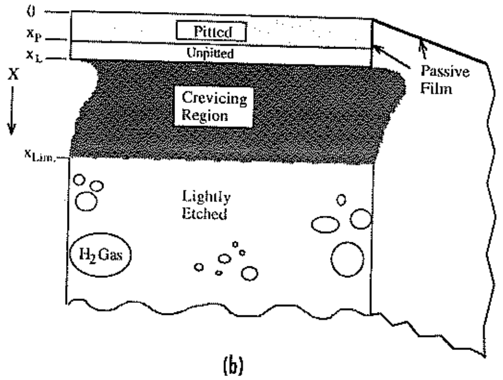




(a)



(b)

Figure 1. In situ photograph (a), and schematic (b) of the crevice wall showing the effects of the steep potential gradient that causes crevice corrosion.

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Keywords

surface properties; corrosion and oxidation of metals; electrosolidification; scanning tunneling microscopy; atom-probe FIM

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Oxidation Resistance of Carbon/Carbon Composite Materials

ındamental understanding of the oxida-
ı protection of carbon/carbon composites
ne of the most important unresolved is-
; in the quest for a new generation of ma-
als with high specific-strength properties.
)ur research, we strive to establish, in a
nitive way, the synergism, or lack thereof,
ween the fibers and the matrix in the oxi-
on behavior of composite materials.
)wledge of the concentration of oxygen
:ies on the carbon surface is the key here.
bon gasification, even though it is a
catalytic, heterogeneous gas–solid reac-
ı, is analogous in this respect to a catalytic
tion, with preferential reactive sites exist-
on the surface.

Jse of transient kinetics, coupled with
opic labeling to distinguish oxidation of
fibers from that of the matrix, will be
icularly powerful in our studies. The
nique is the only one capable of distin-
hing between the number of reactive sites
he carbon surface (under reaction condi-
s) and the reactivity of a given site, as
hasized in the following kinetic expres-
: Reactivity = [Number of reactive sites]
ıctivity per site]. All kinetic studies of
ıposite materials to date have determined
product of these two terms only (i.e., the
all reactivity of the material).

The two fundamental questions posed in
study are the following: (a) Do the fibers
ıe matrix have more reactive sites? (b) In
t way is the reactivity per site dependent
he microstructure of the fiber and matrix
erials? The answers to these questions
ıld offer clear guidelines for the oxidation
ection of these materials.

igure 1 illustrates the following impor-
point: even though the fiber material is
e graphitizable in Composite 1 (WCA-
d), its oxidation resistance is lower than
of Composite 2, whose fiber material is a
-surface-area activated carbon cloth.
d on the analysis of micrographs, we at-
ıte this result to the development of
ks in Composite 2 primarily within the
ix material, and not at the fiber/matrix
face as in Composite 1. Thus, for further
ıncement of oxidation resistance it be-
es important to distribute the inhibitor
ormly within the matrix.

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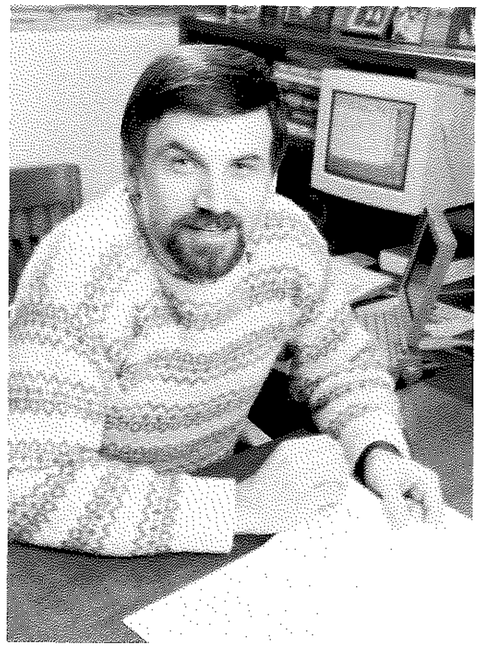
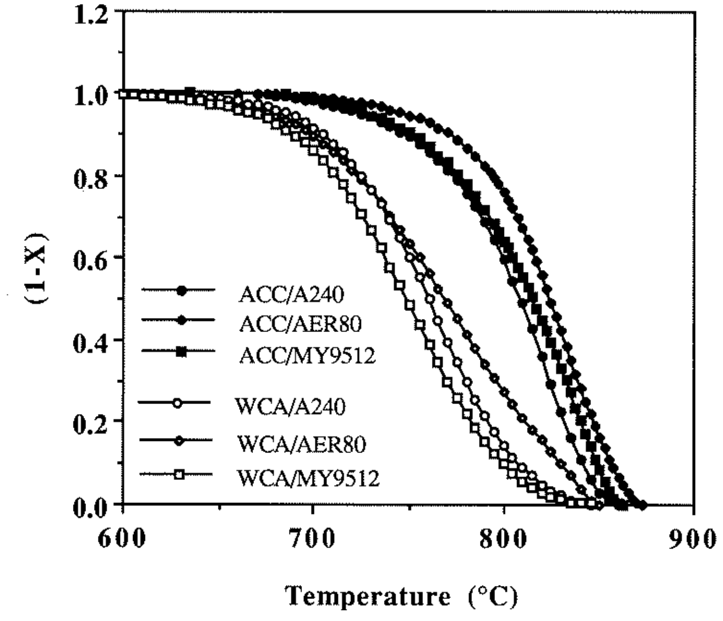


Figure 1. Weight loss vs. reaction temperature plot (5°C/min, 1 atm oxygen; X=fractional conversion) for high-temperature composites obtained using an activated carbon cloth (ACC) and a graphite cloth (WCA) as the fiber material, and two pitches (A240 and AER80) and an epoxy rein (MY9512) as the matrix material.



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Keywords

kinetics and catalysis of coal conversion and carbon gasification, surface properties of carbon materials (e.g., catalyst supports, adsorbents, fibers, composites), gas/solid reactions, and heterogeneous catalysis

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Clive A. Randall

Processing, Microstructural-Property Relations, Theoretical Implications of Microstructural Features in Advanced Electroceramic Materials

Professor Randall's research interests are in processing and microstructure-property relations in advanced electroceramic materials. Special attention is given to the problems incurred in the optimization and tailoring of elastodielectric properties as to address issues such as device miniaturization and component integration for higher volumetric efficiencies.

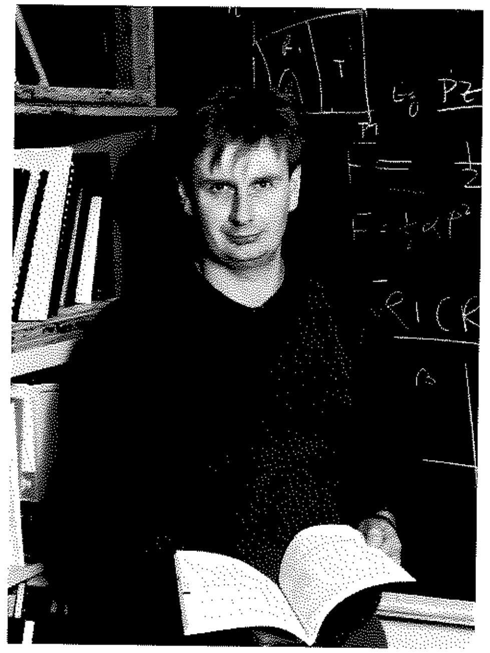
With recent advances in the fabrication of ceramic particulate materials, there exists a need to improve processing assembly techniques to create novel architectures at finer scales. We are investigating the use of electric fields to assemble particulates in composite and thick film form. In general, when an electric field is applied to a stable particle suspension the particle motion is predominantly dictated by dielectrophoretic and electrophoretic forces. Dielectrophoretic assembly involves the induction of a dipole-dipole interaction that destabilizes the system in such a way that the particles undergo uniaxial agglomeration along the electric field direction. This process has been studied in thermoset polymers that under go *in-situ* polymerization to produce unique composites with dielectric anisotropy.

Electrophoretic deposition exploits an electric surface charge on particles in suspension migrating in the presence of an appropriate electric field enabling the consolidation of particles into films onto any shaped substrate. By understanding the colloidal stability, the deposition kinetics and the constrained sintering issues we have fabricated 1–10 micron $BaTiO_3$ thick films with high dielectric constant and low losses competitive with other thick film technologies. The ongoing work is focused on establishing the scientific and engineering aspects of the deposition process. Electrophoretic deposition of electroceramic particulate materials gives potential advances in a number of applications, including piezoelectric motors, biomedical ultrasound probes, and heterojunction chemical sensors.

Ferroelectric and related materials are of interest due to their unique elastodielectric properties that are being used in piezoelectric, electrostrictive, pyroelectric, and capacitive applications. Our group has focused attention on the role of mesoscopic structures on physical properties. Recent work using detailed transmission electron microscopy studies (*in-situ* and *ex-situ*) has been on the grain size effects on domain switching mechanisms during poling and defect induced spatial modulations within domain structures, each of which shows a strong influence on the extrinsic property contributions to physical properties. With grain sizes below 1 micron, there is a change in the domain structure and reduction in the number of domain variants per grain; correspondingly there is a reduction in the dielectric and piezoelectric properties. By understanding th

dopant effects on mesoscopic structures we are developing strategies to optimized compositions to establish high-performance piezoelectric properties in sub-micron ceramics.

Similarly, in capacitor materials the kinetic control of the liquid phase sintering process permits a core shell microstructure with heterogeneous dopant distributions. These are processed as to form materials with specific temperature coefficients of capacitance. With submicron grains, the kinetics are more difficult to control, new processing and dopant selection methods are being studied in our laboratory to form specific submicron materials for next generation multilayer capacitors.



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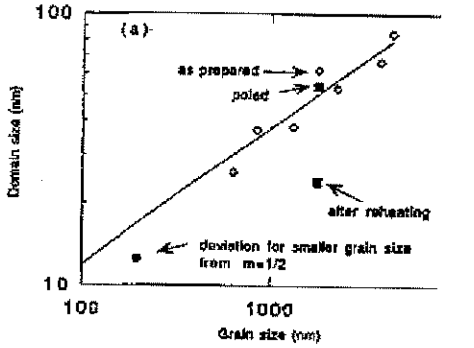

Figure 1. Piezoelectric coefficients, d_{33} and d_{31}, *vs.* logarithmic grain size in Nb-doped PZT.

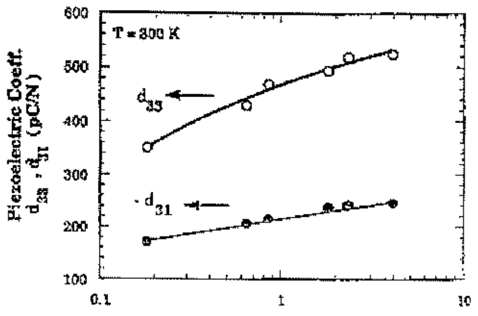

Figure 2. Log-Log plot of the grain size variations in Nb-doped PZT ceramics.

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Keywords

electroceramics, impedance measurements, transmission electron microscopy, composites, thick films

James P. Runt

Chemically Dissimilar Polymer Mixtures

Mixtures of chemically dissimilar polymers are of considerable technological importance compared to traditional single-component systems because of their potential for superior mechanical and physical properties. A particularly important class of these polymer blends are those that contain high-performance, crystallizable polymers. In general, Dr. Runt's research has focused on developing a fundamental understanding of crystallization and phase behavior in those and other multicomponent polymer systems, and their relationship to ultimate properties. Some specific research topics of current interest include: co-crystallization in homopolymer/copolymer mixtures, and the use of dielectric measurements to probe local molecular environment in multicomponent systems.

In semi-crystalline polymers, the existence of order-disorder interphases between the crystalline and isotropic amorphous phases was predicted several decades ago and subsequently confirmed experimentally. Such interphases are also of prime importance in mixtures containing crystalline polymers, but poorly understood. The focus of this part of Runt's research has been to explore the interfacial regions in semi-crystalline binary polymer blends using experimental techniques such as small-angle scattering and measurement of the relaxation behavior.

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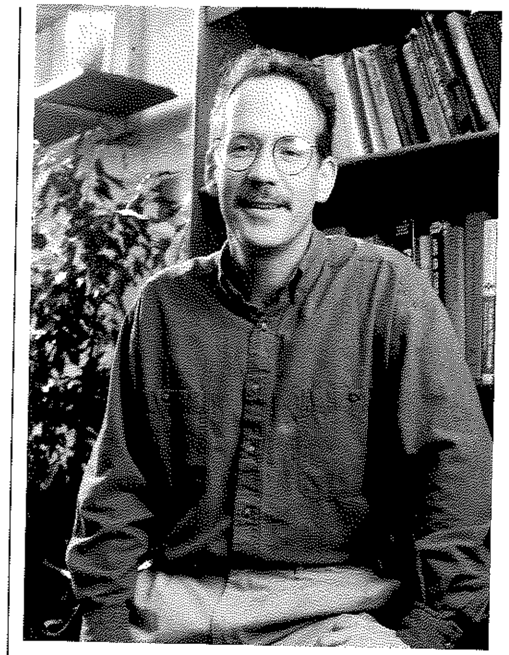

Figure 1. Schematic of three possible microstructures of a miscible binary blend of an amorphous (........) and semi-crystalline (_______) polymer. A. Amorphous polymer is Interlamellar B. Interfibrillar C. Interspherulitic.

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phase behavior and crystallization of polymer blends; interphases in crystalline polymer blends; fatigue and microstructure in crystalline polymers; quantitative fractography of polymer fracture surfaces; polymer/electroceramic composites; dielectric spectroscopy

arle R. Ryba

Determination of the Structures of Quasicrystalline Materials

icrystals are materials whose X-ray and
on-diffraction patterns exhibit non-crys-
raphic symmetries, such as five-, eight-,
and twelve-fold rotation axes. The five-
en-fold symmetries in the diffraction pat-
bely the existence of long-range bond ori-
onal order in these materials in which the
s bond along icosahedral and pentagonal
cagonal directions. While this overall pic-
of the connections between the atoms is
n, the lack of a three-dimensional struc-
repeat unit, or unit cell, has made the de-
nation of the structures of these materials
nely difficult. At Penn State, we have been
ly studying the structure of quasicrystals
the existence of these strange materials
nitially announced in 1984.

ecently, our studies have focused on the
onal phase of $Al_{65}Cu_{20}Co_{15}$. Nominally,
ructure of this compound exhibits non-
llographic symmetry in two directions,
crystallographic repetition along a third
ion. However, from a considerable
nt of X-ray and electron diffraction evi-
, we have found that its structure is even
complex. Embedded in the quasi-
lline structure are extended regions of
tially periodic atom arrangements, in
a very large three-dimensional unit cell
ts dozens to hundreds of times. Further-
, these regions of periodicity have been
l to microtwin at angles that are multiples
°. In addition, the size and shape of the
cell for the periodically arranged regions
, depending upon composition and cool-
onditions.

e have formulated a comprehensive model
e structures of this decagonal phase and
ystalline regions using electron and X-ray
ction and the results of high-resolution
on microscopy and scanning tunneling
scopy studies. This model is built from
two primary atomic clusters that are pen-
al polyhedra of differing numbers of alu-
m, copper, and cobalt atoms. These two
rs form aggregates that are easily seen in
igh-resolution electron microscopy and
ing tunneling microscopy images for this
ial. The possible structural variations,
periodic or quasiperiodic, based on these
olyhedra, are numerous. The next ques-
s how to quantitatively verify the structure
l.

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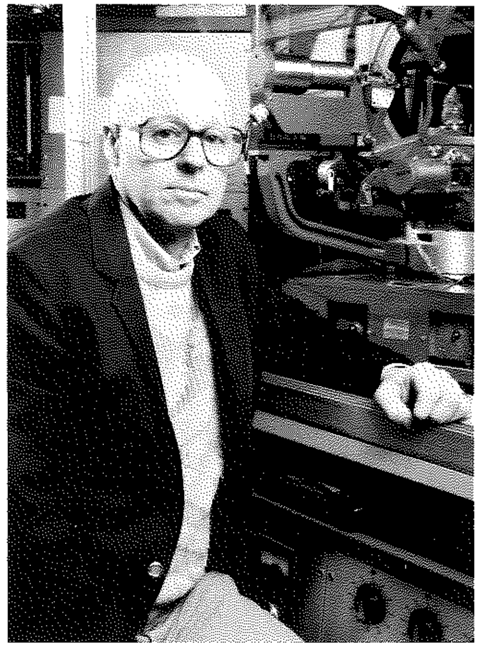

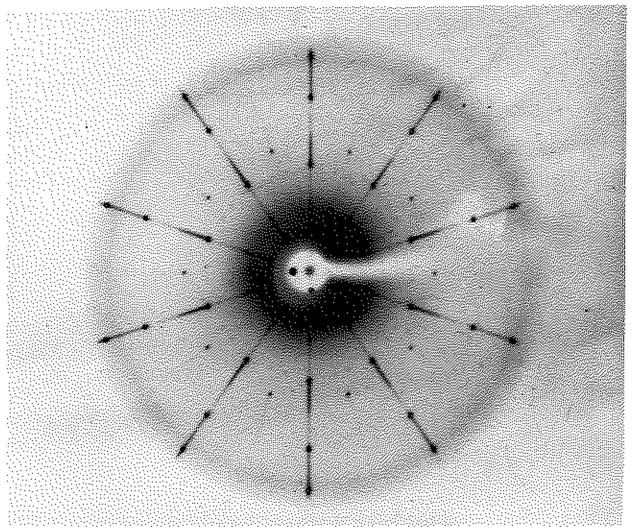

Figure 1. One of the first X-ray diffraction photographs showing non-crystallographic ten-fold symmetry. This X-ray diffraction pattern was obtained from a single fragment of quasicrystalline icosahedral Al_6CuLi_3. Precession photo. MoKα radiation.

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Keywords

X-ray diffraction, structure of thin films and interfaces in composites, grazing incidence diffraction and X-ray reflectivity, structure of intermetallic compounds

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Environmental Impact of Fossil Fuel Usage

The impact of fossil-fuel use on the global environment is dictating that efficiencies be improved and pollutant emissions reduced from combustion systems. This is especially the case for solid fuels, including coal. Advanced combustion processes involve increases in operating temperatures and pressures, which place greater demands on construction materials. In addition, it is becoming necessary to conduct hot-gas cleanup processes at the operating conditions of advanced heat engines.

A multitude of problems need to be overcome before advanced cycles can be commercialized. These include fuel-feeding problems such as erosion of nozzles and atomizer tips, and slurry stability and atomization characteristics. Advanced flue-gas cleanup systems must reduce such pollutants as acid gases, heavy metals, and ozone to extremely low levels, with zero-discharge plants being the ultimate objective.

In a recent study on removing SO_2 from the flue gas of coal-burning power plants, the performance of twenty limestones and dolomites from active quarries in Pennsylvania was determined in a laboratory-scale reactor and in a commercial power plant. The compositional specifications applied to many plants were found to be arbitrary, and the performance of the various sorbents was not related to specific chemical composition. There appears to be a rather complex relationship between the pore structures developed on calcination and subsequent sulfation performance. The results of the study have been used in the power industry to lower the cost of SO_2 emissions compliance in fluidized bed boilers.

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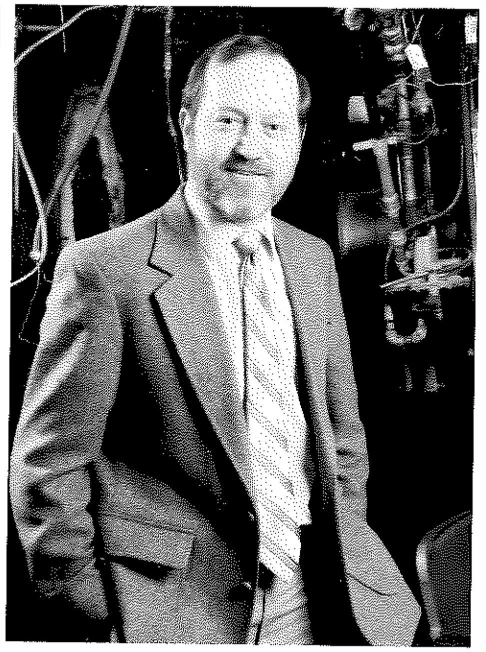

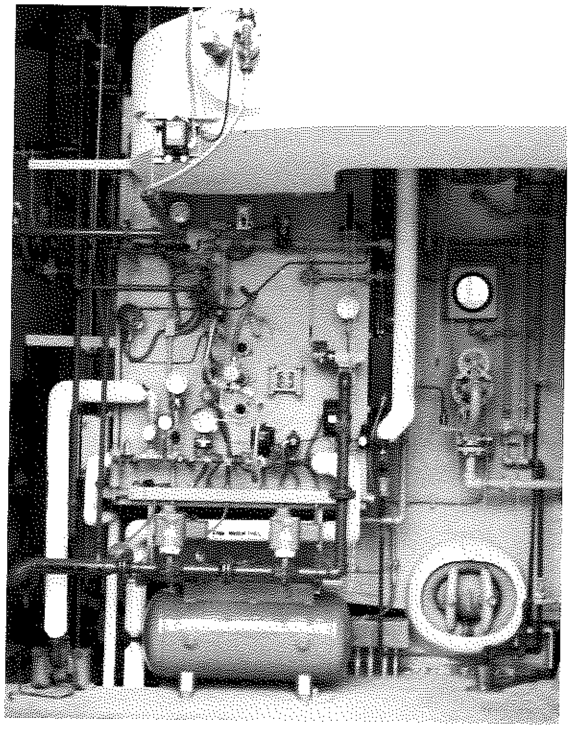

Figure 1. Details of the coal slurry demonstration boiler at the East Campus Steam Plant.

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Keywords

coal, combustion, fluidized-beds, slurry fuels, combustion-generated pollutants

arrell G. Schlom *Molecular Beam Epitaxial Growth of Oxide Thin Films*

paralleled variety of electronic properties d by oxide materials holds tremendous for electrical applications. In no other aterials is there such variety of electrical r as in oxides, which include insulators, iductors, metals, high-temperature su- luctors, ferroelectrics, piezoelectrics, and gnets. A major challenge is to prepare aterials with sufficient quality and inte- em with adequate control, so that these ies can be fully utilized in electronic Many new device concepts will likely alternately layered structures with di- is minute enough to produce quantum- cts (nanometer-scale thicknesses). The m of these materials for most electronic ions is likely to be a stack of single-crys- , each attached epitaxially to the one it and prepared in such a way that ition and structure can be controlled at l of atomic layers. Professor Schlom's is aimed at developing this capability izing it to grow novel structures to test and device concepts, as well as to study tal growth process itself.

ecular beam epitaxy (MBE) is the used by Schlom's research group to customized thin-film structures of ox- erials in an atomically controlled man- his process, which amounts to atomic inting, several beams, each of a differ- nic or molecular species, travel through high vacuum so that collisions on the he surface to be coated (the substrate) edingly rare, and chemical reactions clusively on the substrate. This allows f highly reactive or even metastable o reach the deposition surface undis- Several molecular beams may be onto the surface to be coated, either eously or sequentially as schematically n Figure 1.

om's research has concentrated on the of layered combinations of oxide super- ors and related phases. The experimen- ts of these studies demonstrate the f the shuttered MBE technique to grow lly smooth, layered, superconducting cluding ordered superlattices in situ. ized layering control with unit cell reso- as been achieved. In addition to con- the sequence of compounds in a layered e, with sufficient control this technique en capable of customizing the structure nstituent compounds themselves. De- ctures observed only locally in samples l by conventional bulk methods have pared in single-phase form and their es characterized. Even metastable struc- ve been prepared. Adapting and apply- MBE layering capability to the ed integration of oxide materials will

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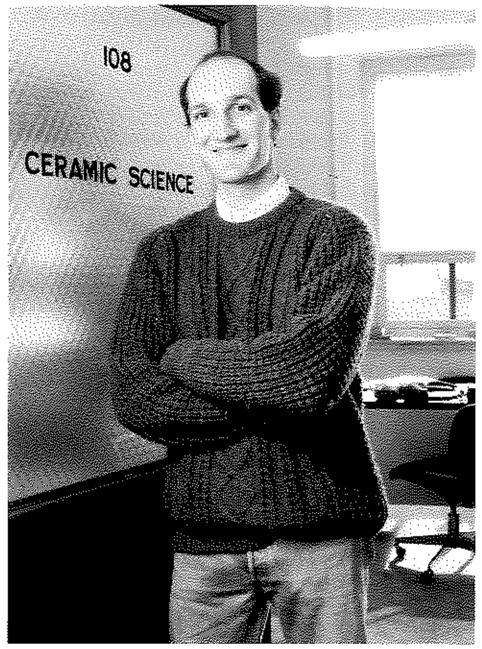

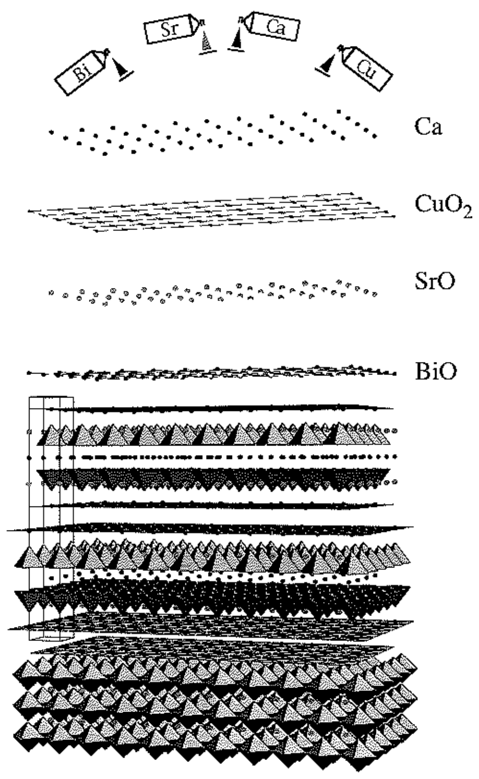

Figure 1. A highly schematic representation of the MBE process used to grow an oxide superconductor ($Bi_2Sr_2CaCu_2O_{8+\delta}$ on $SrTiO_3$). The sprayed beams are individually controlled by shutters that control the sequence and quantity of species reaching the growth surface.

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Keywords

heteroexpitaxial growth of oxide films, customized layering and metastable heterostructures, oxide superconductors, molecular beam epitaxy

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Harold H. Schobert *Fuel Formulation*

Advanced generation (high-Mach) aircraft will generate significant heat in the airframe and "skin" as a result of frictional heating. One solution to this problem is that the aircraft's fuel might serve as a heat sink to cool hydraulic fluids, sensitive electronics, and other aircraft components. The thermal stressing of the fuel in such situations can cause pyrolytic decomposition, leading to the formation of solid carbon deposits. If these deposits plug fuel lines or burner nozzles in the engine, catastrophe could result. Because thermal stresses envisioned for advanced aircraft are well above the range in which prior fuel stability studies have been conducted for conventional aviation fuels the goal is to develop a fuel formulation that will withstand temperatures of 900°F for two hours without deposition problems.

Coal-derived jet fuels are more stable in the high-temperature pyrolytic regime than are typical petroleum-derived fuels. The key compositional difference is the higher proportion of cycloalkanes, particularly polycyclic cycloalkanes, in the coal-derived fuels. For example, tests with pure compounds show that decalin possesses remarkable thermal stability. Because coals have molecular structures based mainly on polycyclic aromatics, the potential exists to produce high yields of thermally stable jet fuels from coal if the polycyclic aromatic structures can be removed chemically from the macromolecular coal structure and subsequently hydrogenated to polycyclic cycloalkanes.

Conversion of coal to jet fuels and other useful liquid products requires careful adjustment of reaction conditions and use of catalysts that can break down the coal structure, hydrogenate the high-molecular-weight, coal-derived products, or do both. Recent and current work on development of liquefaction catalysts include studies of metal-impregnated clays, thio crown-ether complexes, and organometallic cluster compounds.

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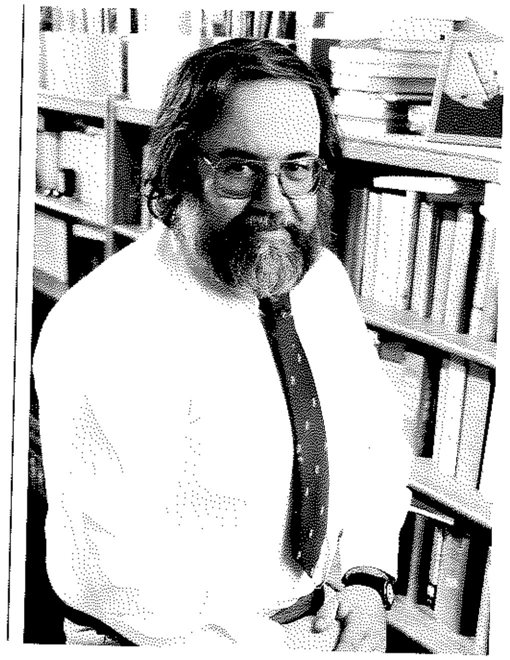
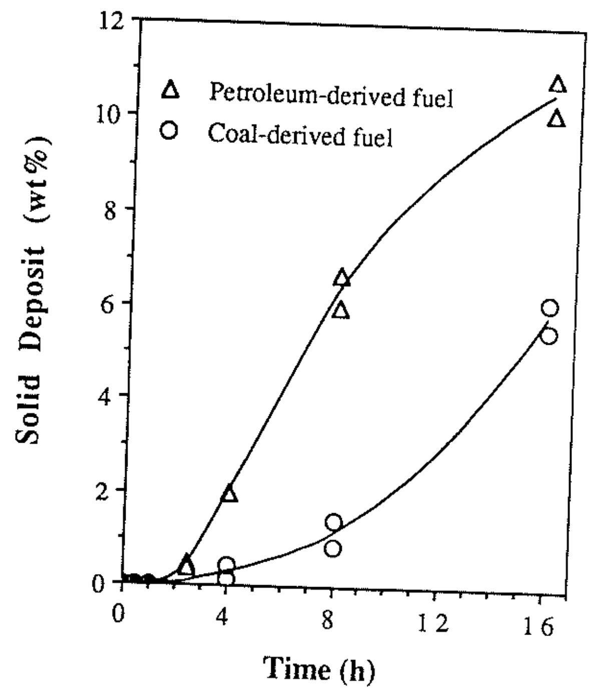


Coal-derived jet fuels are much more stable at extreme temperatures than conventional petroleum-based fuels. This graph compares the breakdown of the two fuels to undesirable solid carbon deposits at 425°C.



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Keywords

jet fuels, coal, coal liquefaction, novel catalysts, coal ash, gasification systems, combustion systems

1urray Small

Physical and Chemical Characterization of Metal Powders

ɔfessor Small is interested in the physical
l chemical behavior of metallic powders.
ɔrk has been performed in his laboratory on
ɛries of water-atomized iron powders, a
nmon material used in the domestic "press
l sinter" P/M industries to make various
all-sized automobile parts. Not only does
particle size of this variety of powder vary,
: the shapes of the particles are also very
gular; therefore, theoretical predictions
ıcerning the properties of these complex
vders are very difficult to make. Experi-
ntal studies performed at Penn State have
wn that the properties known as *flow rate*
l *apparent density* of a typical loose powder
change dramatically upon removal (indi-
ually and combined) of different fractions
ɔoth ends of the particle size spectrum. The
: of atmospheric relative humidity on the
gnitudes of these variables has been com-
tely identified. Information of this type is
ful to powder metal manufacturers in deter-
ıing such parameters as the so-called fill
o in die filling operations and the ultimate
:hanical strength of sintered parts. A fun-
nental understanding of the nature of varia-
ıs in the apparent density of powders is
ler way. Analyses of results with Small's
ɔciates have led to speculation about various
es of interesting ways in which loose metal
ticles can associate together. Some depic-
ıs of these particle interactions are shown
ɔw. Small is also involved in analyzing the
:s played by dilute solutes on the perfor-
nce of metal powders. Modern methods of
r surface analysis have been employed to
ɛrmine the composition profiles of several
ıtes—sulfur, oxygen, and carbon—along
near surface regions of typical atomized
ı particles and the relation of this informa-
ı to the stage of powder processing. Of in-
:st also is the role of dissolved nitrogen and
ɔrbed moisture on the properties of sin-
:d powder products.

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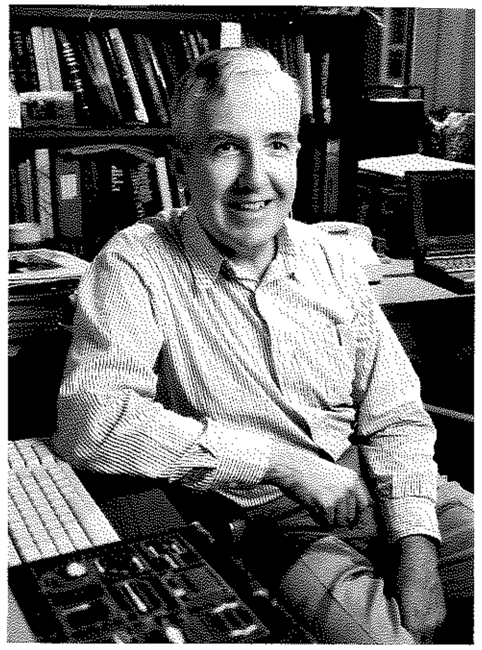
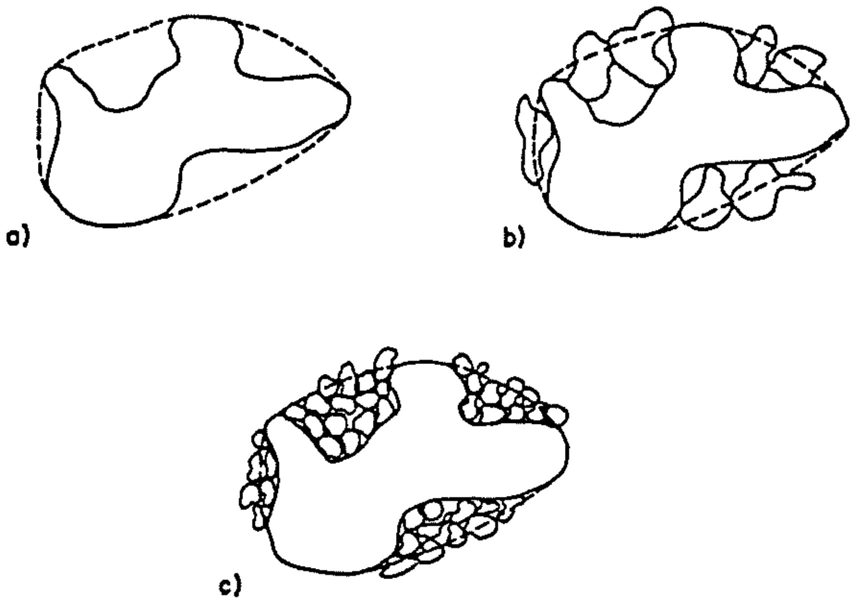


Figure 1. Schematic of an irregularly shaped +100 mesh particle: a) +100 mesh only, with b) smaller particles penetrate caverns, c) finest particles penetrate caverns in +100 mesh particle.



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Chunshan Song

Catalysis in Fuel Processing and Shape-selective Chemicals Synthesis

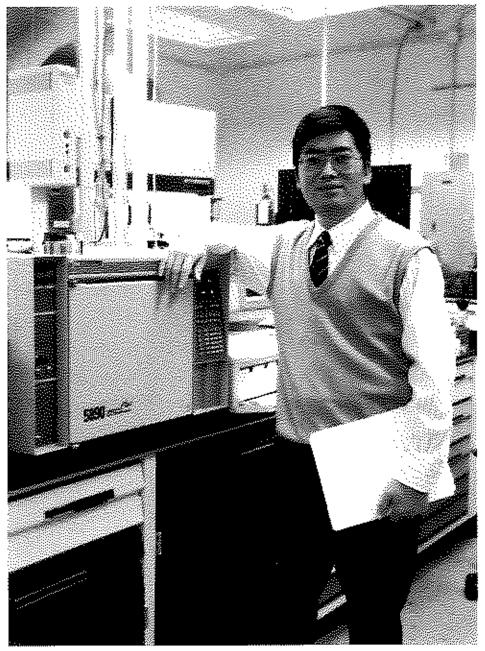
Dr. Song's research interests include catalysis in fuel processing and coal liquefaction, shape-selective synthesis of specialty chemicals, synthesis and application of novel mesoporous zeolites, and chemistry of high-pressure pyrolysis of hydrocarbons. A major challenge in coal liquefaction research is to convert coal into liquids at lower temperature. Recently Song's group has found that using water and dispersed MoS_2 catalyst together could dramatically improve coal conversion at temperatures (325–375°C) that are much lower than those used in conventional processes (400–470°C). For example, adding water to catalytic runs at 350°C can double the coal conversion, as shown in Figure 1. The promotional effect of water depends on the temperature range and water/coal ratio and catalyst type. Research is ongoing to examine whether and how H_2O affects the C-C and C-O bond cleavage and whether and how H_2O affects the activation and passivation of catalytically active phase.

Song's research on shape-selective catalysis focuses on zeolite-catalyzed conversion of polyaromatic hydrocarbons, which has great potential for new and emerging applications. Ongoing work involves catalytic tests on several types of reactions as well as analytical characterization for understanding the relationship between the pore structure and surface acidity characteristics of the catalysts and their activity and selectivity. The work on selective alkylation aims at adding two alkyl groups on naphthalene to make 2,6-dialkylnaphthalene, and on biphenyl to make 4,4'-dialkylbiphenyl, which are important building blocks for advanced aromatic polymer materials. There are many possible isomeric products from the alkylation, but only one of them is desirable. The challenge is to control the regioselectivity with zeolites possessing the desired pore structure and surface acidic characteristics. Recent work concentrated on dealuminated mordenites that exhibit high selectivity for isopropylation.

In an effort to convert phenanthrene into useful chemicals, Song's group found that some mordenite and Y zeolite catalyze the ring-shift isomerization of sym-octahydrophenanthrene to sym-octahydroanthracene. The latter can be used for producing anthracene, which is in demand in chemical industry. Recent work includes the determination of equilibrium compositions as well as catalyst screening and optimization of the conditions. The research on low-temperature selective hydrogenation of naphthalene revealed that mordenite- and Y zeolite-supported noble metal catalysts are much more active than the corresponding Al_2O_3- and TiO_2-supported catalysts. Moreover, either trans-decalin or cis-decalin can be selectively produced by tailoring the catalyst composition. A related reaction is the

trans-decalin. Song's group has found that molecular H_2 dramatically promotes such an isomerization of saturated hydrocarbon over some metal catalysts.

More recently, Song's group has initiated research on synthesis, characterization, and catalytic applications of novel mesoporous zeolites. This work revealed that certain aluminum compounds are excellent sources for incorporating Al atom into the silicate framework during hydrothermal synthesis, leading to mesoporous aluminosilicates with good acidic characteristics. Important catalytic applications of the mesoporous zeolite catalysts include low-temperature hydrogenation and hydrodesulfurization of liquid fuels, and cracking and hydrocracking of heavy oils.



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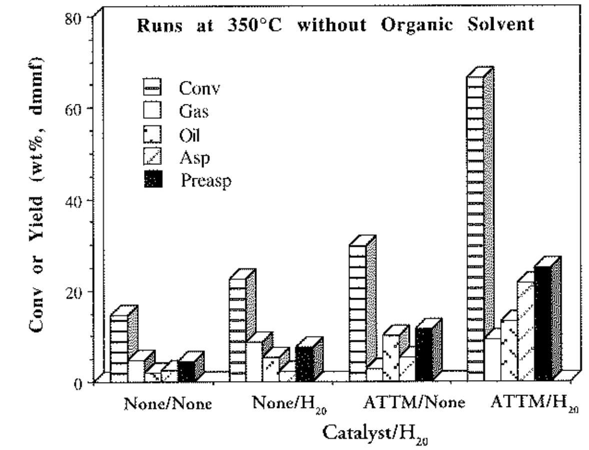

Figure 1. Water improves coal conversion in catalytic liquefaction of Wyodak coal using ammonium tetrathiomolybdate (ATTM) as catalyst precursor at 350°C for 30 min under H_2 pressure.

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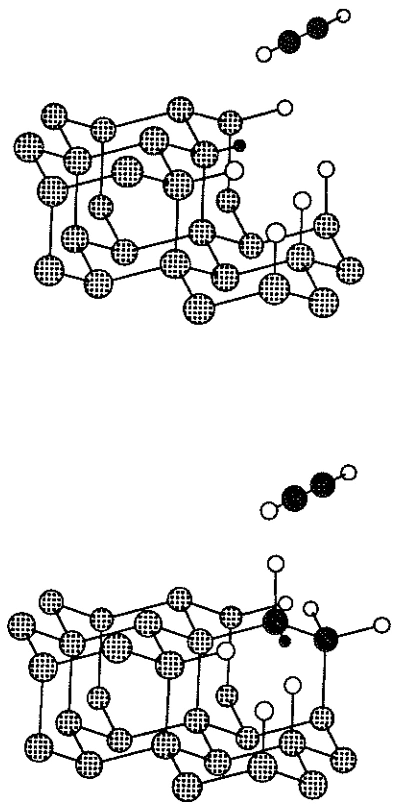
KEYWORDS
catalysis, zeolite, fuel, coal liquefaction, hydrogenation, alkylation, isomerization, shape selectivity, specialty chemicals, high-pressure pyrolysis, jet fuel, thermal stability

Karl E. Spear

Materials Chemistry of Diamond and Ceramics

The chemical mechanisms that govern the nucleation and growth of diamond from an activated gas phase, and thus the ability to manipulate and control these processes, are not established. The goal of a cooperative research project conducted with Professor Michael Frenklach is to develop detailed chemical kinetic models that accurately describe the deposition processes. The models include both gas-phase and surface reactions that produce both diamond and nondiamond carbon. The modeling studies are coordinated with experimental programs that include homogeneously nucleated and grown diamond powders from gaseous reactants, and a diamond film deposition process that systematically alternates growth and etching cycles.

Experimental and theoretical corrosion investigations of nonoxide ceramics are the focus of research conducted with Professor Richard Tressler. Base-line studies were initially performed using single crystals and dense, high-purity CVD thick films. Current studies on commercially available ceramics are being compared to the base-line data to develop predictive mechanistic models of corrosion behavior as a function of microstructure and purity of both the ceramic and gaseous environment. These current efforts have been expanded to include the oxidation behavior of ceramic–ceramic composite materials. A related project with Professor Carlo Pantano is aimed at developing a fundamental understanding of interface reactions in glass–matrix–ceramic composites through experimental studies coordinated with the development of predictive models.



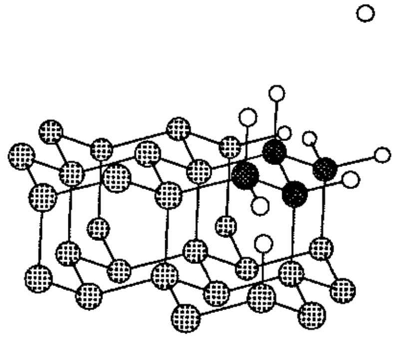


Figure 1. Schematic illustration of the addition of two acetylene molecules to a diamond {110} surface. This growth site is identical to a {111} step site. (Frenklach and Spear, 1988).

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high-temperature and solid-state chemistry; thermodynamics and phase equilibria applied to materials synthesis and behavior; vapor-deposition processes for diamond and other high-temperature materials; experimental and thermochemical modeling of CVD; corrosion; composite interfaces

ter A. Thrower

Carbon–Carbon Composites, Manufacture, Mechanical Properties, and Oxidation Resistance

: of their excellent high-temperature me-
ıl properties, carbon–carbon composites
ited in applications by their oxidation
ɔr. Inhibiting the oxidation is a major
ıt may be tackled by either a protective
; or an inherent modification of the
re of the material. The incorporation of
during processing has been explored via
routes, and later work has focused on
perties of a new material, BC_3, with the
ystal structure as graphite. Preliminary
indicated that BC_3 has superior oxida-
sistance to graphite (Figure 1), and excel-
chanical properties.

dation of carbon–carbon composites
pends on the manufacturing technique
r pitch impregnation) and the type of
ed. The existence of synergism between
nponents in the composite is quite clear
ome circumstances where the reactivity
composite cannot be determined by add-
behaviors of fibers and matrix. A sys-
: study of various fiber–matrix combin-
s currently in progress that should help
ıt the circumstances under which benefi-
ergism exists.

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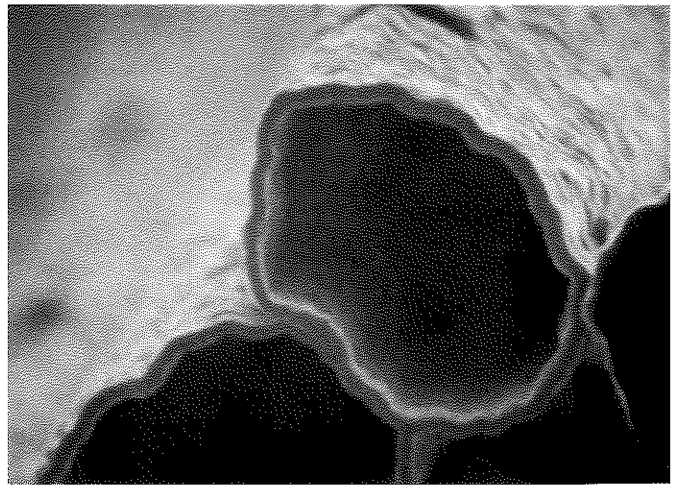

Figure 1. Carbon fiber coated with BC_3 and then oxidized to remove the fiber. The oxidation resistance of the coating is evident.

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Keywords

graphite, carbon–carbon composites, oxidation, boron-carbon compounds

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Richard E. Tressler

Degradation of Ceramics, Fibers, and Composites

In many heat-engine, heat-exchanger, and heat-generating systems, advanced ceramics with the requisite thermomechanical properties are thermodynamically unstable in the corrosive environments of the operating system. However, passive reaction products and very slow kinetics may permit adequate lifetimes for many applications. Improvements in materials and protection schemes can best be developed when the processes that control the corrosion and substrate degradation are understood in detail in terms of rate-limiting reactions and local thermodynamic equilibria.

The long-term reliability of advanced structural ceramics, ceramic fibers, and ceramic–ceramic composites under static or cyclic stresses at elevated temperatures is of major importance for most energy-usage or energy-recovery applications. The fundamental understanding of the failure processes, and the materials characteristics that control these processes, is in the very early stage of development. The design data base of reliable tensile properties of commercially available materials must be developed to assure timely application of these materials.

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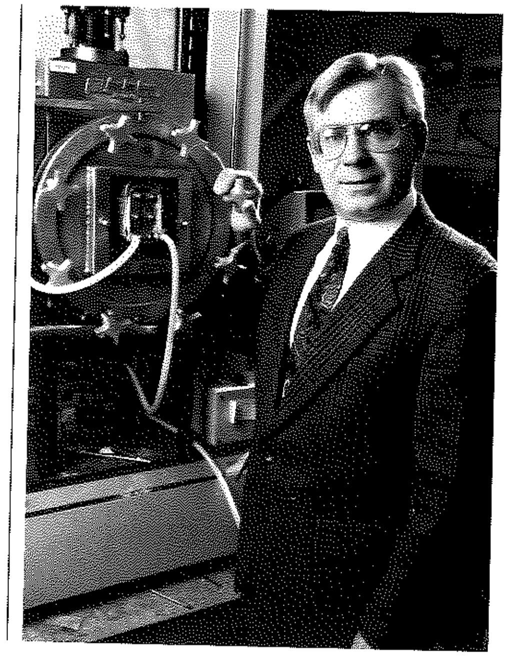
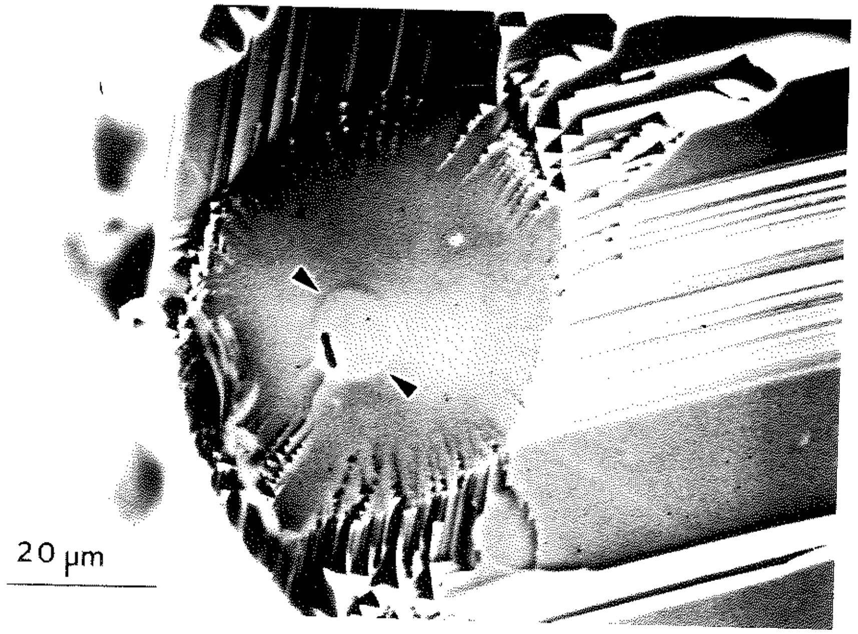


Figure 1. Fracture mirror on the fracture surface of a sapphire fiber tensile tested at 1400°C. There is a region of slow crack growth around the failure origin, a pore.



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point defect and impurity diffusion in silicon and silicon carbide; properties of oxide films on silicon or silicon carbide; processing of fibers, composites, and in situ reinforced ceramics; oxidation, corrosion, creep rupture, crack growth

san Trolier-McKinstry

Structure–Microstructure Property Relations in Ferroelectric Films

›lier-McKinstry is interested in the de- ent of electronic ceramics as active ma- or sensors and actuators. Her current ı program is focused on understanding ors influencing ferroelectric surface and m properties. This has also led to the f intrinsic and extrinsic (processing-re- caling effects in ferroelectric materials.

oelectric thin films are attractive for a of electronic applications, including y elements for information storage, optic switches, and miniature electro- ical transducers. However, due to the xity of the deposition processes in- preparation of films that are both dense crostructurally homogeneous is difficult. ult, there is considerable variability in erved properties of films and consider- viations from the properties expected ılk materials of the same composition. ı turn, has limited the implementation based devices.

ier-McKinstry has demonstrated that scopic ellipsometry can be utilized to erize the inhomogeneities present in ctric films on both conducting and in- ; substrates. Spectroscopic ellipsometry ıdestructive technique capable of depth g the dielectric function of insulating ls over scales ranging from angstroms to s. As a result, it bridges the gap between ; tools designed to characterize either the the surface of ceramic materials. Both ınd ex-situ spectroscopic ellipsometry ently being utilized to examine the role sition and annealing processes on the eneity of thin films. An example of the on in the physical structure of an ini- omogenous, amorphous $Pb(Zr_{0.5}Ti_{0.5})O_3$ ring crystallization is shown in Figure 1. pe of measurement has permitted -McKinstry to model the effect of geneities on the observed electrical ies of ferroelectric films. Studies of this able the critical factors in controlling rostructure of ferroelectric films to be ned so that higher quality devices can ared.

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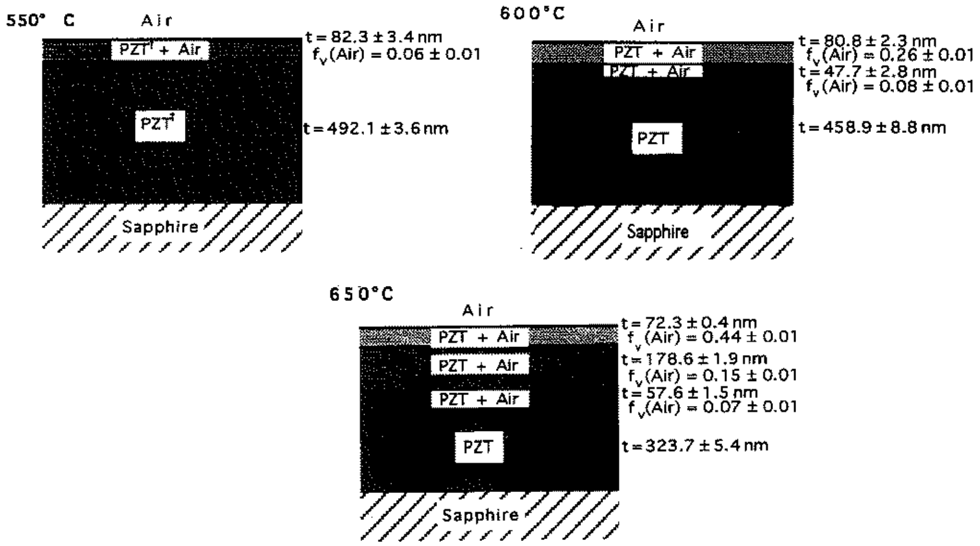
Figure 1. Evolution of microstructure during annealing of a $Pb(Zr_{0.5}Ti_{0.5})O_3$ film deposited by multi-ion-beam reactive sputtering. A Sellmeier oscillator was used to model the optical properties of the film. For this sample, generation of surface roughness appears to be tied to the crystallization process. It has also been shown that the final degree of inhomogeneity present in such films is a strong function of the annealing profile utilized.



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Keywords

ferroelectricity, spectroscopic ellipsometry, thin films, electroceramics

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Peter M. Walsh

Fuel Specification and Combustion Adjustment for Power Plant Optimization

The properties of solid particles formed during combustion of coal and oil in electric power boilers determine heat-exchanger life, emissions of pollutants from the stack, and ease of disposal of solid waste from the plant. When the unit design, fuel, and combustion processes have been optimized, there are few unexpected failures of superheater tubes, particulate emissions are consistently within regulatory limits, and ash can be utilized as a building material. The specification of fuels and adjustment of operating conditions to satisfy these conditions are the subjects of Professor Walsh's research.

In a recent study with Mr. Jianyang Xie, working jointly with Professor Alan Scaroni of the Penn State Combustion Laboratory, Walsh has found that a layer of small ash particles deposited on a superheater tube can provide protection from erosion by more aggressive particles, such as quartz, which are a significant component of the ash in many coals. Because excessive deposit formation is also undesirable, optimum heat-exchanger performance may be achieved only over a rather limited range of conditions of flue-gas velocity, temperature, ash concentration, and particle size distribution. These conditions depend upon the source of coal and its preparation.

In a recent experiment, a high-velocity jet of air was directed at the surface of a test coupon mounted near the exit of an industrial boiler firing coal-water slurry in place of oil. The air jet accelerated particles suspended in the flue gas toward the surface of the specimen. Figure 1 shows an electron micrograph looking down on the surface of the specimen after exposure to the jet and particles for two hours. The pattern of rings resulted from the competition between erosion and deposit formation by ash and unburned carbon. In this case, erosion was observed at the center of the pattern, deposition of ash occurred in the first ring, and erosion was observed in the region farthest from the center of the jet. This shows how the balance between erosion and deposition can be tipped one way or the other by small changes in temperature, velocity, and particle concentration. The interpretation of such patterns provides the information needed to determine conditions under which coal can be substituted for oil in industrial boilers. Walsh's work is supported by the Commonwealth of Pennsylvania and the U. S. Department of Energy/Pittsburgh Energy Technology Center.

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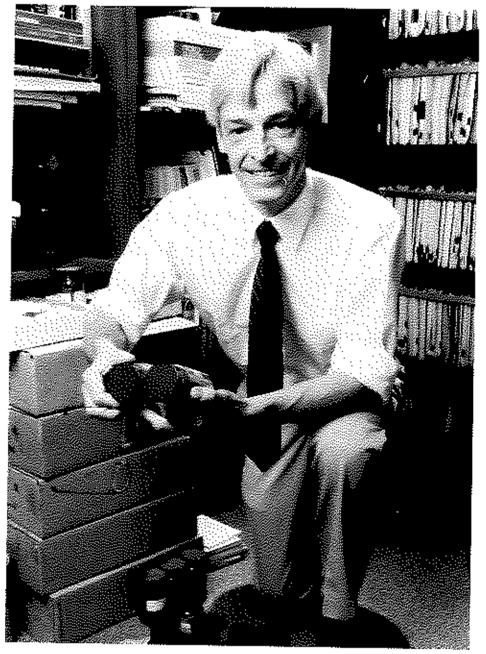
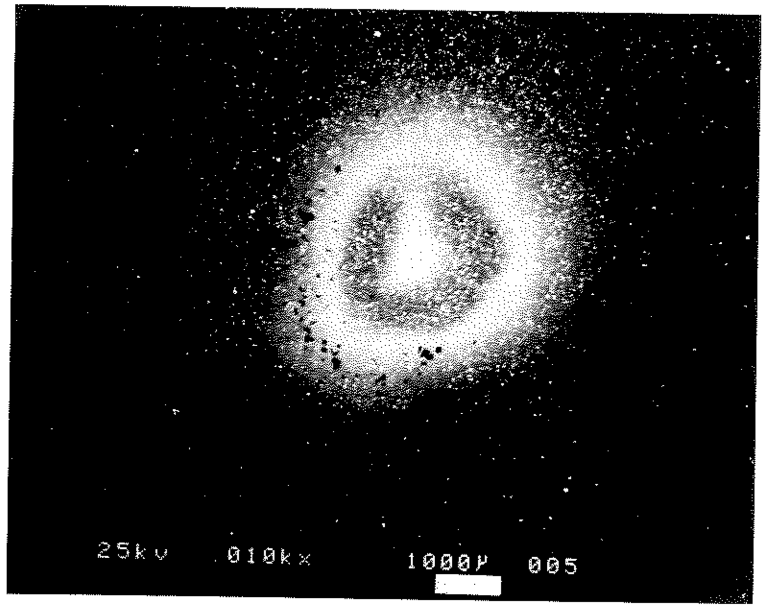


Figure 1. Scanning electron micrograph of the pattern of erosion and ash deposition produced by a small jet of gas directed at the surface of a steel tube. The jet entrains ash and unburned carbon particles suspended in the combustion products and accelerates the particles toward the surface. In this case, erosion was observed at the center of the pattern, an ash deposit was formed in the dark ring, and erosion again appeared in the region farthest from the center.



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Keywords

coal combustion, particulate-matter emissions, fouling and erosion of heat exchangers

alter A. Yarbrough

Synthesis and Preparation of Materials

or Yarbrough's major research inter-
in the synthesis and preparation of
ls. A major focus continues to be how
tructural development and phase-
ion processes in the fabrication of ma-
re influenced by the presence of sur-
d interfaces. These interests include
leation and growth of both stable and
ble phases. He and his students have
concentrated on the synthesis of
ble phases, principally diamond and
oron nitride, through the use of
al vapor deposition (CVD). Although
ports from Russia and elsewhere that
stallized diamond could be synthe-
sing CVD met with considerable
ism, by 1984 it became apparent that
ports were accurate. Much of the
epticism in the scientific community
from the well-known phase diagram
d carbon, which suggests that the for-
of diamond from graphite should be
ible at pressures less than approxi-
15 kbar. Thus, Yarbrough and his
s are focusing on two major issues.

first of these issues is the question of
ll-crystallized diamond should be
during CVD and not during one of
y other possible carbon phases. What
itical factor that dictates the structure
stalline perfection of the solid dia-
ormed in CVD? Closely related to
he second issue: Can other similarly
but metastable crystalline phases be
ized using CVD and related methods?
ue has practical importance in that
ver would help in selecting poten-
uitful approaches for novel materials'
is and fabrication. Paramount among
r materials of interest is the ultra-
igh-band, gap refractory semiconduc-
c boron nitride. Like diamond, cubic
itride is extremely valuable techno-
and is also a high-pressure phase,
ble at atmospheric pressure. Unlike
d it is not available naturally and can
reproducibly prepared at very high
s.

e effort to provide answers to these
s, Yarbrough and his students have
theoretical and experimental work
ynthesis of metastable phases by
arbrough has shown that a well-crys-
metastable phase (e.g., diamond),
leed be thermodynamically preferred
conventionally accepted stable
his is because, in most processes,
rowth occurs by the addition of ma-
the solid surface. If bulk recrystalliza-
transformation is sufficiently
d, then phase control can be estab-
the solid surface (i.e., the interface
the crystal and the reactants contrib-

of the bulk phase may at best be irrelevant, and at worst misleading, to the researchers interested in novel approaches to materials synthesis. Yarbrough has shown that the relevant thermodynamics rationalizing the formation of diamond use thermodynamic potentials appropriate for the solid surface in local equilibrium with vapor or liquid phase in contact with the solid. These thermodynamic potentials differ from those appropriate for the bulk solid. With this approach, Yarbrough has shown that many diamond-growth methods can be understood since at high atomic hydrogen concentrations, the diamond surface structure is more stable than that of graphite. For example, the dominantly observed surface of graphite, the (0001) or basal plane surface, is thermodynamically preferred relative to the commonly observed (111) surface on diamond at low atomic hydrogen concentration. However, when the atomic hydrogen concentration is higher than that expected at true thermostatic equilibrium, the diamond surface is indeed preferred to the graphite surface.

The successful use of this formalism as a guide to understanding the growth of diamond implies a useful paradigm in materials synthesis: If reconstruction or transformation in the bulk solid can be ignored, as is true with many refractory phases, control of the solid structure can be achieved by adjusting synthetic parameters to control the surface structure during the crystal growth process. Thus the challenge with cubic boron nitride synthesis may well lie with the question of what conditions stabilize the solid surface to the desired cubic structure during nucleation and growth. Research exploring this and other similar possibilities is continuing.

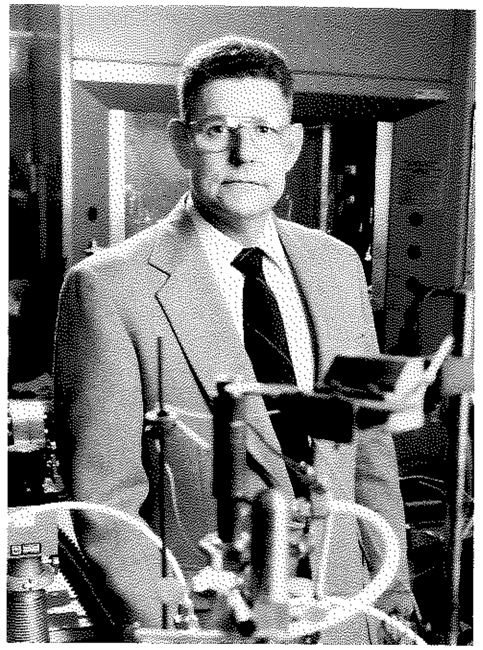

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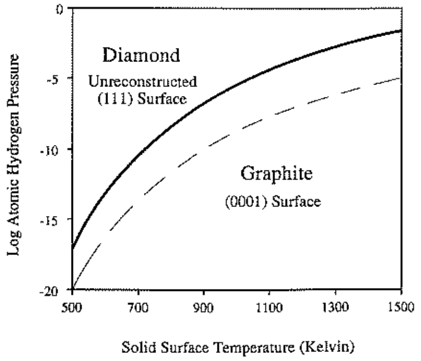
Figure 1. Results of calculations comparing commonly observed surfaces of diamond and graphite. It is generally recognized that the unreconstructed octahedral or (111) surface of a diamond crystal is most often terminated by chemisorbed hydrogen. This surface consists of a "puckered" hexagonal array of carbon atoms, and as such is quite similar to the hexagonal array or "sheet" of carbon atoms that form the (0001) basal plane surface of graphite. At low atomic hydrogen partial pressures for a given temperature, including those expected at global equilibrium (the dashed line), the preferred surface structure is that of graphite. At high atomic-hydrogen partial pressures, such as might be expected if a nearby continuous source of atomic hydrogen is present, the expected surface structure switches to that of the diamond surface. The dark continuous line represents the boundary between the conditions where the diamond and graphite surfaces are preferred.



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Keywords

synthesis, diamond, cubic boron nitride, surface chemistry, chemical vapor deposition, solution-sol-gel synthesis, non-equilibrium thermodynamics

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DR. ROBERT N. PANGBORN, IN CHARGE OF GRADUATE PROGRAM
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